FATIGUE CRACK PROPAGATION IN Al-Li ALLOY 8090
- ENVIRONMENTAL EFFECTS

by

XIÀNDE CHEN

B.Sc., Zhengzhou University, China, 1982
M.Sc., Research Institute of Solid State Physics, Academia Sinica, China, 1985

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES
(Department of Metals and Materials Engineering)

We accept this thesis as confirming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

December 1994
© Xiande Chen, 1994
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the head of my department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

(Signature)

Department of Metals and Materials Engineering
The University of British Columbia
Vancouver, Canada

Date March 24, 1995
Abstract

Fatigue crack propagation behaviour in Al-Li alloy 8090 plate were studied in four main testing environments: a relatively inert environment - desiccated air; and three freely corroding aqueous environments consisting of distilled water, 0.6 M NaCl and 1 M AlCl₃. It was found that the major role of the aqueous environments in the T-L orientation crack growth behaviour of the Al-Li alloy plate was to promote S-L splitting (delamination) at grain boundaries, with a subsequent effect on the stress state at the crack tip. The splitting preceded the main crack advance, and helped to keep the crack in the same macroscopic crack plane and restricted the fracture surface roughness, and consequently reduced crack closure effects. In contrast, the absence of the splitting effects in desiccated air, combined with the planar deformation features and the strong crystallographic texture of the Al-Li alloy plate, led to out-of-plane cracking and ridge formation in the mid-thickness of the specimen. This resulted in severe crack growth retardation and a crack growth rate plateau at $\Delta K$ values above $\sim 3 \text{ MPa.m}^{1/2}$. Analyses of the observations led to the conclusion that the S-L splitting phenomenon is associated with both localized anodic dissolution processes and hydrogen embrittlement effects. The effect of changing the loading frequency was not obvious, except in the dry air environment where decreasing the frequency from $\sim 80$ to $\sim 0.5$ Hz led to the disappearance of the crack growth rate plateau. The fatigue cracking resistance of the Al-Li alloy plate is superior in the dry air environment and slightly better or equivalent in the aqueous environments when compared to a conventional crack-tolerant Al-alloy plate, 2024-T351.

The effects of a re-aging treatment on fatigue cracking in the S-L orientation of the Al-Li plate were also studied. The presence of aqueous environments also accelerated crack propagation in the S-L orientation, and crack propagation is faster in the S-L orientation than in the T-L orientation. The re-aging treatment was effective in increasing the short-transverse
fracture toughness and also improved the intergranular corrosion resistance of the material. However, the re-aging treatment did not improve the corrosion fatigue crack propagation resistance.
# Table of Contents

Abstract .......................................................................................................................... ii
Table of Contents ........................................................................................................... iv
List of Tables ................................................................................................................... ix
List of Figures ................................................................................................................ x
List of Symbols and Abbreviations .............................................................................. xv
Acknowledgements ....................................................................................................... xix
1 Introduction ................................................................................................................ 1
2 Literature Review ....................................................................................................... 3
  2.1 The corrosion fatigue failure .................................................................................. 3
    2.1.1 Crack initiation ............................................................................................... 3
    2.1.2 Crack propagation ......................................................................................... 5
    2.1.3 Types of corrosion fatigue crack growth ...................................................... 10
    2.1.4 Models for corrosion fatigue ........................................................................ 12
        2.1.4.1 Superposition model ........................................................................... 12
        2.1.4.2 Competition model ............................................................................. 12
        2.1.4.3 Interaction model ................................................................................ 13
    2.1.5 Mechanisms for corrosion fatigue ................................................................. 13
        2.1.5.1 Oxidation-related mechanisms .............................................................. 13
        2.1.5.2 Hydrogen assisted cracking mechanisms ............................................ 14
        2.1.5.3 Surface-related mechanisms ............................................................... 15
    2.1.6 Crack closure effects ...................................................................................... 15
        2.1.6.1 Plasticity induced closure ................................................................... 16
        2.1.6.2 Oxide induced closure ....................................................................... 17
4.4 Test setup and procedures ......................................................... 51
  4.4.1 Potentiodynamic polarization tests ..................................... 51
  4.4.2 Corrosion fatigue crack propagation tests ............................ 53
    4.4.2.1 High frequency ....................................................... 53
      4.4.2.1.1 Precracking ..................................................... 53
      4.4.2.1.2 Fatigue tests ................................................... 54
    4.4.2.2 Low frequency ....................................................... 55
      4.4.2.2.1 Precracking ..................................................... 57
      4.4.2.2.2 Fatigue tests ................................................... 57
    4.4.2.3 Intermediate frequency ............................................ 59
      4.4.2.3.1 Precracking ..................................................... 59
      4.4.2.3.2 Hardness and fracture toughness tests ...................... 60
      4.4.2.3.3 Fatigue tests ................................................... 60
  4.4.3 Fractographic study ........................................................ 61
  4.4.4 Crack profile study ........................................................ 61
  4.4.5 Microstructural and compositional study .............................. 63
    4.4.5.1 TEM ................................................................. 63
    4.4.5.2 STEM + EDX .......................................................... 63
    4.4.5.3 EELS ................................................................. 63
5 Results .................................................................................. 64
  5.1 Electrochemical behaviour ................................................... 64
    5.1.1 Al-Li alloy ............................................................... 64
    5.1.2 Al-Cu alloy ............................................................... 73
5.2 Crack growth behaviour ................................................................. 75
5.2.1 Al-Li alloy ................................................................................. 75
   5.2.1.1 T-L crack plane orientation, 80 Hz loading frequency .......... 75
   5.2.1.2 T-L crack plane orientation, 0.5 Hz loading frequency .......... 78
   5.2.1.3 S-L crack plane orientation, 30 Hz loading frequency .......... 84
5.2.2 Al-Cu alloy ................................................................................. 86
   5.2.2.1 T-L crack plane orientation, 80 Hz loading frequency .......... 86
   5.2.2.2 T-L crack plane orientation, 0.5 Hz loading frequency .......... 86
5.3 Fractography .................................................................................. 93
   5.3.1 Al-Li alloy ................................................................................. 93
      5.3.1.1 T-L crack plane orientation, 80 Hz loading frequency ........ 93
      5.3.1.2 T-L crack plane orientation, 0.5 Hz loading frequency ........ 108
      5.3.1.3 S-L crack plane orientation, 30 Hz loading frequency ........ 108
   5.3.2 Al-Cu alloy ................................................................................. 112
      5.3.2.1 T-L crack plane orientation, 80 Hz loading frequency ........ 112
      5.3.2.2 T-L crack plane orientation, 0.5 Hz loading frequency ........ 113
5.4 Macroscopic fracture surface appearance, roughness and crack profile .... 117
   5.4.1 Al-Li alloy ................................................................................. 117
      5.4.1.1 T-L crack plane orientation, 80 Hz loading frequency ........ 117
      5.4.1.2 T-L crack plane orientation, 0.5 Hz loading frequency ........ 122
      5.4.1.3 S-L crack plane orientation, 30 Hz loading frequency ........ 122
   5.4.2 Al-Cu alloy ................................................................................. 123
5.5 Microstructure and compositional distribution ..................................... 126
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 Discussion</td>
<td>132</td>
</tr>
<tr>
<td>6.1 Corrosion fatigue crack propagation in the Al-Li alloy in the T-L</td>
<td>132</td>
</tr>
<tr>
<td>orientation and comparison with the Al-Cu alloy</td>
<td></td>
</tr>
<tr>
<td>6.1.1 Role of splitting</td>
<td>132</td>
</tr>
<tr>
<td>6.1.2 Role of environment</td>
<td>146</td>
</tr>
<tr>
<td>6.1.3 Effects of loading frequency</td>
<td>152</td>
</tr>
<tr>
<td>6.1.4 Effects of microstructure and deformation behaviour</td>
<td>154</td>
</tr>
<tr>
<td>6.2 Corrosion fatigue crack growth in the Al-Li alloy in the S-L</td>
<td>157</td>
</tr>
<tr>
<td>orientation and effects of the re-aging treatment</td>
<td></td>
</tr>
<tr>
<td>6.2.1 Possible changes in the material caused by the re-aging treatment</td>
<td>157</td>
</tr>
<tr>
<td>6.2.2 Effects of re-aging on the S-L crack growth rates</td>
<td>160</td>
</tr>
<tr>
<td>6.2.3 Effects of environments on the S-L crack growth rates</td>
<td>161</td>
</tr>
<tr>
<td>7 Summary and Conclusions</td>
<td>164</td>
</tr>
<tr>
<td>8 References</td>
<td>166</td>
</tr>
<tr>
<td>9 Appendix</td>
<td>181</td>
</tr>
<tr>
<td>9.1 Appendix I. Increased stiffness of Al-Li alloys</td>
<td>181</td>
</tr>
<tr>
<td>9.2 Appendix II. Identification of grain boundary precipitate by</td>
<td>182</td>
</tr>
<tr>
<td>selected area electron diffraction</td>
<td></td>
</tr>
<tr>
<td>9.3 Appendix III. EELS analyses</td>
<td>186</td>
</tr>
<tr>
<td>9.4 Appendix IV. Threshold stress state</td>
<td>189</td>
</tr>
<tr>
<td>9.5 Suggestions for further work</td>
<td>190</td>
</tr>
</tbody>
</table>
List of Tables

Table 4.1 Chemical Compositions (Nominal wt.%) ......................................................... 37
Table 4.2 Physical and Mechanical Properties .............................................................. 38
Table 5.1 Values of Microhardness ($H_V$) and Short Transverse (S-L) Orientation Fracture Toughness ($K_{IC}$) ................................................................. 84
Table 5.2 Threshold Cyclic Stress Intensities ($\Delta K_{th}$) of S-L Fatigue Cracking in the Two Tempers of the Al-Li Alloy in Different Environments ....................... 85
Table 6.1 Boundary Conditions, $\Delta K_{th}$, above Which Plane Stress Conditions Become Important in the Presence of $N_b$ Splits .................................................. 139
Table 6.2 The Operative \{111\} <110> Slip Systems and Schmid Factors Under Uniaxial Loading ([111] Direction) ................................................................. 142
Table A1 Comparison of Calculated Spacing and Angle Values of a Possible Phase ......................................................................................................... 184
List of Figures

Figure 2.1 The three modes of loading [32]. ................................................................. 5

Figure 2.2 Schematic variation of fatigue crack growth rate as function of stress intensity rang [36]. ................................................................. 7

Figure 2.3 Schematic diagram illustrating the model for fatigue crack propagation based on restricted slip reversal at the crack tip [41]. .................... 9

Figure 2.4 The plastic blunting process of fatigue crack propagation in the Stage II mode [43]. ................................................................. 10

Figure 2.5 Three types of corrosion fatigue crack growth behaviour [44]. .......... 11

Figure 2.6 Schematic illustration of the principal mechanisms of fatigue crack closure [56]. ................................................................. 16

Figure 2.7 Terminology used to describe the various orientations for crack extension in an isotropic material containing specific planes of weakness in one direction [107]. ................................................................. 24

Figure 4.1 Grain structures of (a) Al-Li 8090-T8771 and (b) Al-Cu 2024-T351. .... 40

Figure 4.2 Crack plane orientation identification code for plate [188]. .............. 42

Figure 4.3 Geometry of the electrochemical test specimen. ............................... 43

Figure 4.4 Geometry of the single edge notched (SEN) specimen. ..................... 46

Figure 4.5 Geometry of the compact tension (CT) specimen. ............................ 47

Figure 4.6 Geometry of the double cantilever beam (DCB) specimen. .......... 50

Figure 4.7 Schematic experimental set-up of the potentiodynamic polarization test. ................................................................. 52

Figure 4.8 Schematic environmental cell set-up for the high frequency fatigue test. ......................................................................................... 56

Figure 4.9 Schematic environmental cell set-up for the low frequency fatigue test. ......................................................................................... 58

Figure 4.10 Schematic environmental cell set-up for the intermediate frequency fatigue test. ........................................................................ 62

Figure 5.1 Potentiodynamic polarization behavior of Al-Li alloy 8090-T8771 in 0.6 M NaCl and 1 M AlCl₃. ......................................................... 66
Figure 5.2 Appearance of polished surfaces (T orientation) of Al-Li 8090 after freely corroding in 1 M AlCl₃ for ~20 hours. .................................................. 68

Figure 5.3 Appearance of polished surfaces (T orientation) of Al-Li 8090 after freely corroding in 1 M AlCl₃ for ~170 hours. .................................................. 69

Figure 5.4 Sectioning parallel to the L plane showing depths of intergranular corrosion after corroding in 1 M AlCl₃ for ~170 hours. ........................................ 70

Figure 5.5 SEM + EDX analysis of the intergranularly corroded slots in the re-aged Al-Li alloy, showing uncorroded Cu-containing particle. .......................... 71

Figure 5.6 SEM micrographs showing location of Cu-rich particle containing intergranular surface of the re-aged Al-Li alloy before and after corroding in 1 M AlCl₃ for ~12 hours. .................................................. 72

Figure 5.7 Potentiodynamic polarization behavior of Al-Cu alloy 2024-T351 in 0.6 M NaCl and 1 M AlCl₃ .................................................. 74

Figure 5.8 Effect of environment and ΔK on the growth of fatigue cracks in Al-Li alloy 8090-T8771 at ~80 Hz. .................................................. 76

Figure 5.9 Consecutive fatigue crack growth behaviour in Al-Li alloy 8090-T8771 when the testing environment is changed from distilled water to desiccated air. .................................................. 79

Figure 5.10 Fatigue crack growth behaviour in Al-Li alloy 8090-T8771 at ~80 Hz in desiccated air, starting from ΔK = 5 MPa.m¹⁄₂. .......................... 80

Figure 5.11 Fatigue crack growth behaviour in Al-Li alloy 8090-T8771 at ~80 Hz in desiccated air after hydrogen precharge. .......................... 81

Figure 5.12 Fatigue crack growth in Al-Li alloy 8090-T8771 at 80 Hz in 1 M HCl solution under controlled potential of -2.1 V SCE. In this potential and pH condition, Al is in the immunity region and the rate of hydrogen evolution is high. .................................................. 82

Figure 5.13 Effect of environment and ΔK on the growth of fatigue cracks in Al-Li alloy 8090-T8771 at ~0.5 Hz. .................................................. 83

Figure 5.14 Fatigue crack growth in the S-L orientation of the Al-Li alloy plate in desiccated air at ~30 Hz. .................................................. 88

Figure 5.15 Fatigue crack growth in the S-L orientation of the Al-Li alloy plate in 1 M AlCl₃ at ~30 Hz. .................................................. 89

Figure 5.16 Fatigue crack growth in the S-L orientation of the Al-Li alloy plate in distilled water at ~30 Hz. .................................................. 90
Figure 5.17 Effect of environment and $\Delta K$ on the growth of fatigue cracks in Al-Cu alloy 2024-T351 at ~80 Hz. ................................................................. 91

Figure 5.18 Effect of environment and $\Delta K$ on the growth of fatigue cracks in Al-Cu alloy 2024-T351 at ~0.5 Hz. ................................................................. 92

Figure 5.19 (a) SEM fractograph showing transgranular fracture surface of Al-Li alloy specimen fatigued at ~80 Hz in distilled water near $\Delta K_a$. Macroscopic direction of crack propagation is from the right to the left of the page. (b) Schematic diagram of the transgranular crack front in the primary crack plane showing tongues extending into uncracked material, with uncracked ligaments between the tongues. ....................... 94

Figure 5.20 SEM fractograph of Al-Li alloy specimen fatigued at ~80 Hz in 1 M AlCl$_3$ near $\Delta K_a$, showing transgranular cracking on the primary crack plane and S-L splitting of grain boundaries normal to the primary plane. Macroscopic direction of crack propagation is from the right to the left of the page. ......................................................... 96

Figure 5.21 Effect of environment and $\Delta K$ on the number of splits ($N_h$) across the thickness of the T-L orientation Al-Li 8090-T8771 specimen fatigued at ~80 Hz. ................................................................. 99

Figure 5.22 SEM micrograph of Al-Li alloy 8090-T8771 specimen precracked surface exposed to 1 M AlCl$_3$ during ~80 Hz test. Area shows localized dissolution of grain boundaries. .............................................. 100

Figure 5.23 Optical micrograph of sectioned and etched Al-Li alloy 8090-T8771 specimen fatigued at ~80 Hz in 0.6 M NaCl. Sectioned normal to the primary crack plane in Stage II at $\Delta K = 5$ MPa.m$^{1/2}$. ......................................................... 101

Figure 5.24 Optical micrograph of sectioned and etched Al-Li alloy 8090-T8771 specimen fatigued at ~80 Hz in 0.6 M NaCl. Test terminated in Stage II and sectioned normal to the primary crack plane very close to the main crack front. ............................................................. 102

Figure 5.25 SEM fractograph of Stage II cracking ($\Delta K = 6$ MPa.m$^{1/2}$) of Al-Li 8090-T8771 in 0.6 M NaCl at ~80 Hz, showing river patterns running away from the S-L split. Note very faint striations normal to the river lines. Macroscopic cracking direction is from the right to the left of the page. ......................................................... 103

Figure 5.26 SEM fractograph showing change of fatigue fracture surface of Al-Li 8090-T8771 produced at ~80 Hz in distilled water and desiccated air consecutively. Macroscopic cracking direction is from the right to the left of the page. ................................................................. 104

Figure 5.27 Change of the number of splits ($N_h$) across the thickness of the T-L orientation Al-Li 8090-T8771 specimen with $\Delta K$, when fatigued at ~80 Hz under continuous hydrogen charging at -2.1 $V_{SCB}$. ......................................................... 105
Figure 5.28 SEM fractographs of near $\Delta K_a$ cracking of Al-Li alloy 8090-T8771 in distilled water at $\sim$80 Hz. The opposing fracture surfaces indicating a "peak to valley" match of small details. Macroscopic cracking direction is from the top to the bottom of the page. ............................................. 106

Figure 5.29 SEM fractographs of matching fatigue fracture surfaces of Al-Li alloy 8090-T8771 produced by Stage II cracking ($\Delta K = 6$ MPa.m$^{1/2}$) in distilled water at $\sim$80 Hz. Macroscopic cracking direction is from the top to the bottom of the page. ................................................................. 107

Figure 5.30 SEM fractograph showing transgranular fracture surface of Al-Li 8090-T8771 specimen fatigued at $\sim$0.5 Hz in desiccated air. $\Delta K = -6$ MPa.m$^{1/2}$, location near the mid-thickness of the specimen. Macroscopic direction of crack propagation is from the right to the left of the page. Micrograph (b) shows the central region of Micrograph (a) in higher magnification. ..................................................... 109

Figure 5.31 Effect of environment and $\Delta K$ on the number of splits ($N_a$) across the thickness of the T-L orientation Al-Li 8090-T8771 specimen fatigued at $\sim$0.5 Hz. ................................................................. 110

Figure 5.32 SEM fractographs showing transition from fatigue precracking to monotonic overload fracture in the S-L orientation fracture toughness test specimens of Al-Li alloy 8090. Macroscopic cracking direction is from the right to the left of the page. .............................................. 111

Figure 5.33 SEM micrographs showing fatigue fracture surfaces of Al-Li alloy 8090 in the S-L orientation in the re-aged temper near $\Delta K_a$. Macroscopic cracking direction is from the right to the left of the page. ..................................................... 114

Figure 5.34 SEM fractographs of near $\Delta K_a$ cracking of Al-Cu alloy 2024-T351 in the T-L orientation at $\sim$80 Hz. ................................................................. 115

Figure 5.35 SEM fractograph of Stage II cracking ($\Delta K = 8$ MPa.m$^{1/2}$) in Al-Cu alloy 2024-T351 in the T-L orientation in distilled water at $\sim$80 Hz. ..... 116

Figure 5.36 Macroscopic appearance of opposing fracture surfaces of Al-Li alloy 8090-T8771 tested in the T-L orientation at $\sim$80 Hz. Scale shows crack length. ................................................................. 118

Figure 5.37 (a) Schematic diagram of ridge formation in mid-thickness of specimens fatigued in the T-L orientation in desiccated air at $\sim$80 Hz. Arrow shows direction of macroscopic crack propagation. (b) The angle of the central ridge with respect to the original macroscopic crack plane. ..................................................... 120

Figure 5.38 Optical micrographs of sectioned and etched Al-Li 8090-T8771 specimen fatigued at $\sim$80 Hz in the T-L orientation in desiccated air. Sectioned normal to the primary crack plane. ................................................................. 121
Figure 5.39 Macroscopic appearance of opposing fracture surfaces of Al-Cu alloy 2024-T351 fatigued in the T-L orientation in 0.6 M NaCl at ~80 Hz. Scale shows crack length. .......................................................... 124

Figure 5.40 Optical micrographs showing crack front profiles of specimens fatigued in the T-L orientation in 0.6 M NaCl at ~80 Hz. Sectioned normal to the primary crack plane at ΔK = 5 MPa.m^{1/2}. ........................................ 125

Figure 5.41 TEM micrograph showing 8' phase in Al-Li alloy 8090. Centered dark field image. .......................................................... 127

Figure 5.42 TEM micrograph showing precipitates containing grain boundaries in Al-Li alloy 8090-T8771. Bright field image. ........................................ 128

Figure 5.43 STEM + EDX analyses showing Cu content profiles across a grain boundary containing precipitates. .......................................................... 129

Figure 6.1 Schematic diagram showing the triaxial stress state near the tip of a crack. .......................................................... 133

Figure 6.2 Schematic diagram showing effect of S-L splitting on linkage of uncracked ligaments near the crack front. Arrow shows direction of macroscopic crack propagation. .......................................................... 136

Figure 6.3 Deformation patterns [32]. .......................................................... 137

Figure 6.4 (a) Schematic diagram showing the relation of the initial T-L macroscopic crack plane with the texture in the mid thickness of the Al-Li 8090-T8771 plate. (b) Standard (111) projection for a face-centred cubic crystal. .......................................................... 143

Figure 6.5 Relative orientations of the operative slip systems in the overall (111)[1211] cracking. .......................................................... 144

Figure 6.6 Schematic theoretical polarization diagram showing possible cathodic protection on the other part of the grains by the active dissolution of the grain boundary regions. I_p < I_u due to enhanced corrosion at the grain boundaries (I_GB) .......................................................... 156

Figure A1 Selected area diffraction pattern obtained from a grain boundary precipitate. .......................................................... 183

Figure A2 Selected area diffraction pattern obtained from a grain boundary precipitate, showing five-fold symmetry. .......................................................... 185

Figure A3 Schematic diagram of an electron energy loss spectrum. .......................................................... 187
## List of Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>crack length</td>
</tr>
<tr>
<td>$b$</td>
<td>beam thickness</td>
</tr>
<tr>
<td>$B$</td>
<td>specimen thickness</td>
</tr>
<tr>
<td>$C$</td>
<td>scaling constant</td>
</tr>
<tr>
<td>$C_{Cu}, C_{Li}, C_{Mg}$</td>
<td>atomic concentration of Cu, Li, and Mg</td>
</tr>
<tr>
<td>$C_h$</td>
<td>hydrogen concentration at crack tip surface</td>
</tr>
<tr>
<td>$C_x$</td>
<td>hydrogen concentration at a distance of $x$ ahead of crack tip</td>
</tr>
<tr>
<td>$d$</td>
<td>plane spacing</td>
</tr>
<tr>
<td>$da/dN$</td>
<td>crack propagation rate</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion constant</td>
</tr>
<tr>
<td>$E$</td>
<td>elastic modulus</td>
</tr>
<tr>
<td>$E_{corr}$</td>
<td>free corrosion potential</td>
</tr>
<tr>
<td>$E_{oc}$</td>
<td>open circuit potential</td>
</tr>
<tr>
<td>$E_{pit}$</td>
<td>pitting potential</td>
</tr>
<tr>
<td>$E_p$</td>
<td>plasmon energy loss</td>
</tr>
<tr>
<td>$h$</td>
<td>beam height</td>
</tr>
<tr>
<td>$H$</td>
<td>specimen height</td>
</tr>
<tr>
<td>$H_V$</td>
<td>Vickers hardness</td>
</tr>
<tr>
<td>$i$</td>
<td>current density</td>
</tr>
<tr>
<td>$I$</td>
<td>current</td>
</tr>
<tr>
<td>$K$</td>
<td>crack tip stress intensity</td>
</tr>
<tr>
<td>$K_{I}$</td>
<td>opening mode stress intensity</td>
</tr>
<tr>
<td>$K_{IC}$</td>
<td>fracture toughness</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$K_{\text{ISCC}}$</td>
<td>threshold stress intensity for stress corrosion cracking</td>
</tr>
<tr>
<td>$K_{\text{max}}, K_{\text{min}}$</td>
<td>maximum stress intensity, minimum stress intensity</td>
</tr>
<tr>
<td>$K_{\text{clo}}$</td>
<td>stress intensity for crack closure</td>
</tr>
<tr>
<td>$\Delta K$</td>
<td>stress intensity range</td>
</tr>
<tr>
<td>$\Delta K_b$</td>
<td>boundary cyclic stress intensity</td>
</tr>
<tr>
<td>$\Delta K_{\text{eff}}$</td>
<td>effective stress intensity range</td>
</tr>
<tr>
<td>$\Delta K_{\text{th}}$</td>
<td>threshold stress intensity range</td>
</tr>
<tr>
<td>$l$</td>
<td>support distance of beam</td>
</tr>
<tr>
<td>$L$</td>
<td>camera length</td>
</tr>
<tr>
<td>$m$</td>
<td>scaling exponent in Paris law</td>
</tr>
<tr>
<td>$n$</td>
<td>scaling exponent in Forman equation</td>
</tr>
<tr>
<td>$N$</td>
<td>load cycle number</td>
</tr>
<tr>
<td>$N_B$</td>
<td>split number</td>
</tr>
<tr>
<td>$P$</td>
<td>load</td>
</tr>
<tr>
<td>$P_{\text{max}}, P_{\text{min}}$</td>
<td>maximum load, minimum load</td>
</tr>
<tr>
<td>$r_Y$</td>
<td>crack tip plastic zone size</td>
</tr>
<tr>
<td>$\Delta r_Y$</td>
<td>crack tip cyclic plastic zone size</td>
</tr>
<tr>
<td>$R$</td>
<td>load ratio, $R = P_{\text{min}}/P_{\text{max}} = K_{\text{min}}/K_{\text{max}}$</td>
</tr>
<tr>
<td>$R_1, R_2, R_3$</td>
<td>distance between diffraction spots</td>
</tr>
<tr>
<td>$S$</td>
<td>beam stiffness</td>
</tr>
<tr>
<td>$t$</td>
<td>time variable</td>
</tr>
<tr>
<td>$t_B$</td>
<td>specimen thickness required for plane strain conditions</td>
</tr>
<tr>
<td>$W$</td>
<td>specimen width</td>
</tr>
<tr>
<td>$W_p, W_{\text{ii}}$</td>
<td>beam weight</td>
</tr>
<tr>
<td>$x$</td>
<td>distance</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>elongation</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>angle between the loading direction and the normal of the slip plane</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>angle between the loading direction and the slip direction</td>
</tr>
<tr>
<td>$\lambda_e$</td>
<td>electron wavelength</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson’s ratio</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
</tr>
<tr>
<td>$\sigma_S, \sigma_T, \sigma_L$</td>
<td>principal tensile stresses in S, T, L directions</td>
</tr>
<tr>
<td>$\sigma_y$</td>
<td>yield strength</td>
</tr>
<tr>
<td>$\sigma_{UTS}$</td>
<td>ultimate tensile strength</td>
</tr>
<tr>
<td>$\theta$</td>
<td>angle coordinate in front of a crack tip</td>
</tr>
<tr>
<td>CF</td>
<td>corrosion fatigue</td>
</tr>
<tr>
<td>COD</td>
<td>crack opening displacement</td>
</tr>
<tr>
<td>CT</td>
<td>compact tension</td>
</tr>
<tr>
<td>CTOD</td>
<td>crack tip opening displacement</td>
</tr>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>DCB</td>
<td>double cantilever beam</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray analysis</td>
</tr>
<tr>
<td>EELS</td>
<td>electron energy loss spectroscopy</td>
</tr>
<tr>
<td>FCC</td>
<td>face centred cubic</td>
</tr>
<tr>
<td>LT</td>
<td>long transverse</td>
</tr>
<tr>
<td>M</td>
<td>molarity</td>
</tr>
<tr>
<td>PFZ</td>
<td>precipitate-free zone</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>RSR</td>
<td>restricted slip reversibility</td>
</tr>
<tr>
<td>S, T, L</td>
<td>directions with respect to rolling plane: S - short transverse, T - transverse, L - longitudinal</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>SCC</td>
<td>stress corrosion cracking</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SEN</td>
<td>single edge notched</td>
</tr>
<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>SSRT</td>
<td>slow strain rate technique</td>
</tr>
<tr>
<td>ST</td>
<td>short transverse</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>V_{SCB}</td>
<td>potential with respect to saturated calomel electrode</td>
</tr>
<tr>
<td>V_{SHB}</td>
<td>potential with respect to standard hydrogen electrode</td>
</tr>
<tr>
<td>WDX</td>
<td>wavelength dispersive X-ray analysis</td>
</tr>
<tr>
<td>β' phase</td>
<td>Al$_2$Zr</td>
</tr>
<tr>
<td>δ phase</td>
<td>AlLi</td>
</tr>
<tr>
<td>δ' phase</td>
<td>Al$_3$Li</td>
</tr>
<tr>
<td>S' phase</td>
<td>Al$_2$CuMg</td>
</tr>
<tr>
<td>T$_1$ phase</td>
<td>Al$_2$CuLi</td>
</tr>
<tr>
<td>T$_2$ phase</td>
<td>Al$_5$CuLi$_3$</td>
</tr>
<tr>
<td>θ' phase</td>
<td>Al$_2$Cu</td>
</tr>
</tbody>
</table>
Acknowledgements

I would like to express my sincere gratitude to Professor Desmond Tromans for his guidance and encouragement throughout this project. My thanks are also extended to other faculty and staff members, and fellow graduate students for their help, particularly to Mr. Ru-hong Sun for his assistance in the initial stages of the project.

Special thanks go to my wife for her patience, understanding and support during the course of this work.

The author is grateful for the financial support provided via Research Assistantship by the Canadian Department of Defence and the Natural Sciences and Engineering Council of Canada, and via Teaching Assistantship by the Department of Metals and Materials Engineering.
1 Introduction

Aged Li-containing aluminium alloys are candidate materials for airframe applications because their reduced density and increased elastic modulus combine to give a class of alloys that have a higher specific stiffness than the more widely used, and more conventional, high strength 2000 and 7000 series Al-alloys [1-3]. The early problems of poor ductility and toughness that were associated with Li-addition have now been largely overcome [2-4]. This has increased the opportunity for their use in high stiffness, crack tolerant situations. The problem of crack tolerance is a critical consideration in airframe structures where the fluctuating loading conditions can lead to time-dependent sub-critical crack propagation (fatigue). Furthermore, it is well established that conventional Al-alloys are susceptible to increased fatigue crack propagation rates in the presence of water vapor, water, and saline solutions [5], leading to the phenomenon of corrosion fatigue (CF). Consequently, it is essential to study the CF behaviour of the new Al-Li alloys, and compare such behaviour with that of the more conventional Al-alloys, in order to confirm that the new alloys are a suitable replacement material for airframe structures.

Extensive studies have been conducted on the fatigue and corrosion fatigue behaviour of Li-containing aluminium alloys and comparisons have been made to the more conventional Al-alloys. In particular, these studies have found that the commercial Al-Li alloys have better resistance to fatigue propagation in air environment than the conventional Al-alloys when tested in specific plate orientations such as L-T [6]. This improved resistance is attributed mainly to the "extrinsic toughening" effects of crack deflection, crack branching and roughness induced crack closure [6-11], which are associated with the planar slip characteristics inherent in Al-Li alloys. Several studies have been conducted to determine the effects of the environment on
Introduction

Fatigue crack propagation in Al-Li alloys, especially the presence of water and saline solutions, and deleterious effects have been explained by different mechanisms based on anodic dissolution [12], hydrogen embrittlement [13-16], change of crack closure level [15,17-19] and slip reversibility effects [15,20]. However, definitive studies on the mechanism of environment-related fatigue cracking behaviour are still relatively scarce.

The present research is concerned with the corrosion fatigue crack propagation behaviour of an Al-Li alloy, 8090-T8771, particularly in the near threshold low cracking rate region, where environmental effects are more likely and the cracking behaviour plays an important role in determining the overall service lifetime of a structure or component. Corrosion experiments are conducted in controlled environments, with different loading frequencies, crack orientations and heat treatments. Comparisons are also made to the corrosion fatigue crack propagation behaviour of a conventional crack tolerant Al-Cu alloy, 2024-T351.
2 Literature Review

Since the recognition of the influence of different environments on fatigue of metals about seventy years ago [21,22], corrosion fatigue has been extensively studied because it is frequently cited as the cause of engineering failures in a broad range of material-environment systems [23]. Although a generalized framework describing corrosion fatigue has emerged [24], a thorough understanding of this complex problem is still far from complete. No single theory has reached the point of fully predicting or even explaining all the problems encountered in load bearing structures. New challenges for higher efficiency and reliability continue to arise, and new materials, environments and loading situations have been continuously extending the domain of corrosion fatigue research.

2.1 The corrosion fatigue failure

The corrosion fatigue process leading to failure is usually divided into two steps or stages: (i) crack initiation and (ii) crack propagation. However, the transition between the two stages is not sharply defined.

2.1.1 Crack initiation

The fatigue crack initiation stage under cyclic (repeated) loading conditions is generally defined as the period required for the formation of microcracks of sufficient length that they begin to affect the local slip behaviour. Crack initiation typically occurs on (i) external surfaces (or subsurface interfaces) at stress concentrating defects and flaws or (ii) smooth surfaces where
slip reversal has produced persistent slip bands containing intrusions/extrusions which then act as local stress concentrators, or flaws [25]. The presence of an environment may accelerate this initiation process.

Several mechanisms have been proposed to explain the effects of environments on crack initiation, depending on the nature of the environment:

Gaseous environments:
1. Obstruction of reversible slip [26].
2. Inhibition of crack re-welding in slip bands [27].
3. Reduction of surface energy at highly stressed locations [28].
4. Formation of bulk oxide [29].

Aqueous environments [30]:
1. Pitting, where nucleation of cracks occurs at pits formed through corrosive attack.
2. Preferential dissolution, where highly deformed material acts as a local anode with the surrounding undeformed material acting as a local cathode. The anodically dissolved regions then serve as crack nucleation sites.
3. Rupture of protective oxide films, where localized corrosion occurs on the exposed metal at the sites of deformation-induced rupture of the protective oxide. Fatigue then starts at the regions of localized attack.
4. Surface energy reduction, where adsorption of environmental species promotes crack formation by reducing the surface energy.
2.1.2 Crack propagation

Crack propagation refers to the sub-critical, time-dependent crack growth that occurs after initiation. Based on the realistic assumption that cracks and flaws are always present in a structure due to its processing history before service [31], the crack propagation stage is considered to be the governing factor on the total service life of an engineering structure. In recent years, there have been many studies where precracked fracture mechanics specimens were used to investigate fatigue crack propagation behaviour. These studies avoided the problems associated with using smooth specimens, where both initiation and propagation stages are present and a clear separation between them is difficult.

For a solid containing a crack, three modes of loading can be classified, as schematically shown in Figure 2.1 [32],

![Diagram](image)

*Figure 2.1 The three modes of loading [32].*

Normal stresses give rise to the "opening mode" or Mode I loading; the displacements of the crack surfaces are perpendicular to the plane of the crack. In-plane shear results in "sliding
mode" or Mode II loading; the displacements of the crack surfaces are in the plane of the crack and perpendicular to the leading edge of the crack. The "tearing mode" or Mode III loading is caused by out-of-plane shear; the crack surface displacements are in the plane of the crack and parallel to the leading edge of the crack. Superposition of the three modes describes the general case of loading. Mode I loading is technically the most important one. In experimental studies, this is also the most commonly applied loading condition.

Fatigue crack propagation behaviour is further refined to include short crack and long crack behaviour; as studies have revealed differences between the two situations [33,34]. Generally, cracks defined as microstructurally short, mechanically short, physically short and chemically short cracks [35] all propagate faster than long cracks under the same nominal mechanical driving force, and can even propagate below the apparent crack propagation threshold for long cracks. To a certain extent, short fatigue crack propagation can be considered as covering the transition region between crack initiation and (long) crack propagation.

For long cracks, the fatigue behaviour can be well described with the application of a fracture mechanics factor (stress intensity, $K$). The curve in Figure 2.2 shows the typical variation of fatigue crack propagation rate per cycle, $da/dN$, with the alternating stress intensity range $\Delta K (= K_{\text{max}} - K_{\text{min}})$ [36]. Crack growth behaviour is usually divided into three regimes or stages in terms of their different sensitivities to various microstructural, mechanical and environmental variables. In detail, the three stages of crack propagation for long cracks have been defined as follows:

1. **Stage I, near threshold propagation:** Crack growth rate is very low, usually $<10^{-6}$ mm/cycle, and can be even less than the lattice parameter, indicating crack growth is not occurring uniformly over the entire crack front or propagating on every cycle. The threshold $\Delta K_{th}$ is the stress...
intensity range value below which no crack growth occurs or can be detected within a specified number of load cycles or time. Some researchers [37,38] suggested that the crack growth rate corresponding to the defined $\Delta K_{th}$ should be lower than $10^{-7}$ mm/cycle. The value of $\Delta K_{th}$ and the crack growth rates are strongly sensitive to microstructure, mean stress and environment [39]. From the engineering point of view, Stage I crack growth is important to the high cycle, low amplitude resistance of the materials.
Stage II, often called the Paris power law region: Crack growth rates are usually between $10^{-6}$ and $10^{-3}$ mm/cycle. In this region, the relationship between the crack growth rate per cycle, $da/dN$, and $\Delta K$ follows the empirical Paris power law:

$$\frac{da}{dN} = C\Delta K^m$$  \hspace{1cm} (2.1)

where $C$ and $m$ are scaling constants [40]. Although there is no strict theoretical foundation for the Paris law, it is the best description for fatigue crack growth behaviour and has been widely accepted. In this region, the crack growth rates are generally insensitive to microstructure and mean stress relative to the effect of $\Delta K$. While certain combinations of environment, mean stress and frequency may have a large influence on the crack growth.

Stage III: As $K_{\text{max}}$ approaches $K_{\text{IC}}$ for unstable cracking, the crack growth rate is much faster than that predicted by the Paris law and $da/dN$ is usually $>10^{-3}$. It is better described by the Forman equation [32]:

$$\frac{da}{dN} = \frac{C\Delta K^n}{(1-R)(K_{\text{IC}}-K_{\text{max}})}$$  \hspace{1cm} (2.2)

Equation (2.2) is based on a modification of the Paris law and takes into account the increasing value of the maximum stress intensity factor, where $R (= K_{\text{min}}/K_{\text{max}})$ is the load ratio and $K_{\text{IC}}$ is the fracture toughness value for unstable cracking. Crack growth in this stage is influenced by microstructure and mean stress, but is not significantly affected by the test environment.

The Stage I fatigue cracking normally produces a crystallographically dependent fracture surface without well defined striations. It is generally accepted that the crack advances through a process of restricted slip reversals on relatively few slip systems. The model depicting the event at a propagating crack tip is shown schematically in Figure 2.3 [41,42], which assumes
alternative slip systems operating at the crack tip. The amount of slip reversal is affected by (i) work hardening in the forward slip and (ii) the degree of oxidation of the bare slip step created during the forward slip.

Figure 2.3 Schematic diagram illustrating the model for fatigue crack propagation based on restricted slip reversal at the crack tip [41].

The Stage II fatigue crack normally proceeds by transgranular fracture with ductile striation formation on the fracture surface. The crack growth rate $da/dN$ corresponds closely to the striation spacing [43]. It is widely accepted that the crack advances through a process of crack tip blunting and re-sharpening. The model for crack advance and striation is shown in Figure 2.4, which assumes multiple slip systems operating simultaneously at the crack tip.
Figure 2.4 The plastic blunting process of fatigue crack propagation in the Stage II mode [43].

In the Stage III fatigue cracking, static fracture modes, such as cleavage, intergranular and fibrous fracture, occur in addition to striation growth.

2.1.3 Types of corrosion fatigue crack growth

In the presence of an environment, the general shape of the $da/dN - \Delta K$ curve described in Figure 2.2 may be changed. Three general types of changes are shown schematically in Figure 2.5 [44]. They illustrate the corrosion fatigue crack growth resulting from different mechanical-environmental interactions.
Type A is termed "true corrosion fatigue". The combined action of cyclic loading and corrosion enhances crack growth under all conditions of loading, except when ΔK is very high and mechanical crack growth becomes so rapid that the effect of chemical corrosion is overshadowed.

Type B is termed as "stress corrosion fatigue". Environmental contributions to cyclic crack growth only occur at ΔK levels with $K_{\text{max}} > K_{\text{ISCC}}$, where $K_{\text{ISCC}}$ is the threshold for stress corrosion cracking (SCC). The waveform of loading has a strong effect on cracking rate in addition to cyclic frequency, stress intensity level, and stress ratio.

Type C is the combination of A and B types.
2.1.4 Models for corrosion fatigue

Based on the types of crack growth, three major models have been proposed for corrosion fatigue.

2.1.4.1 Superposition model [45,46]

Initially, the superposition model assumed that the rate of crack growth in any environment can be predicted by summing the crack growth rate for pure mechanical fatigue and the rate for stress corrosion cracking in the same environment [45], analogous to the type B situation. Later, a third term was added to include the synergistic interaction between mechanical fatigue and environmental actions [46]. Therefore the crack growth rate in any aggressive environment is of the form:

\[
\frac{da}{dN}_e = \frac{da}{dN}_r + \frac{da}{dN}_{scc} + \frac{da}{dN}_{cf}
\]  

(2.3)

where \( \frac{da}{dN}_r \), \( \frac{da}{dN}_{scc} \) and \( \frac{da}{dN}_{cf} \) are the cracking rates for pure mechanical fatigue, SCC and mechanical fatigue - environment interactions, respectively.

2.1.4.2 Competition model [47]

The competition model is based on the assumption that the fatigue crack growth rate involves competition among various processes. It suggests that the processes of fatigue and stress corrosion cracking are mutually competitive and a crack will grow at the fastest available rate pertinent to the prevailing stress intensity factor.
2.1.4.3 Interaction model [48]

The interaction model was developed to allow interactions between mechanical fatigue and stress corrosion cracking to occur, particularly in alloy systems which exhibit a high degree of susceptibility to stress corrosion cracking. In this model, the effects of predominantly mechanical and predominantly electrochemical crack propagation processes are added, but each is modified to account for the presence of the other. Owing to interactions, one process may be inhibited or enhanced by the action of the other.

2.1.5 Mechanisms for corrosion fatigue

The main mechanisms by which the environment may affect the crack growth can be put into three categories as oxidation-related mechanisms, hydrogen assisted cracking mechanisms, and surface-related mechanisms.

2.1.5.1 Oxidation-related mechanisms

The main mechanisms include:

1. Anodic or strain enhanced dissolution [49,50]. Preferential anodic dissolution of the strained material at the crack tip increases the extent of crack growth during each cycle. The anodic dissolution can also help by dissolving the cyclically strain hardened material or other barriers to slip processes (e.g. a hard precipitate) at the crack tip and thereby sustaining the deformation related cracking process.

2. Film rupture and dissolution [51]. The protective film is ruptured at the crack tip by the cyclic strain from the alternating stress. The bare surface exposed acts as anode and the rest of the film covered metal serves as cathode. This results in localized
corrosion at the crack tip and crack growth.

3. Restricted slip reversibility [41,42]. The bare metal formed in the forward slip part of a fatigue cycle is covered with oxide patches. These oxide patches restrict slip reversibility on the same slip plane during the reverse part of the cycle, in addition to the work hardening effects on the slip system. The amount of restricted slip is equal to the crack growth per cycle.

2.1.5.2 Hydrogen assisted cracking mechanisms

In these mechanisms, hydrogen (either generated by corrosion processes during fatigue or pre-existing in the metal) accumulates in the region ahead of the crack tip and contributes to hydrogen assisted cracking via one or a combination of the following processes [35,52,53]:

1. Pressure buildup. Molecular hydrogen precipitates at internal interfaces or defects and generates a pressure that is in equilibrium with the local activity of the atomic hydrogen dissolved in the metal lattice. The pressure augments the applied tensile stress and assists crack propagation.

2. Decohesion. Presence of hydrogen at the crack tip region causes a reduction of metal-metal bond strength and allows mechanical separation to occur more easily.

3. Hydride formation. Hydrides are well known to exhibit brittle behaviour. The formation and cracking of brittle metal hydrides will facilitate advance of the fatigue crack.

2.1.5.3 Surface-related mechanisms

The mechanisms include:

1. Surface energy reduction. Reactions at the crack tip that produce adsorbed species may
lower the surface energy and increase the ease of crack growth [49,50,54], because of the lower energy required to create new surfaces.

2. Adsorption-induced localized slip. Chemisorption of species facilitates the injection of dislocations from crack tips and thereby promotes the coalescence of cracks with voids ahead of cracks [25,55].

Processes 1 and 2 constitute another form of hydrogen embrittlement when hydrogen is the adsorbing species.

2.1.6 Crack closure effects

It has been found that a fatigue crack can be in the closed state, with opposing crack tip surfaces in contact, even during part of the tensile load cycle. Therefore, based on the concept that the load is effective in propagating the crack only when the crack is open, this leads to the definition of the effective stress intensity range,

\[ \Delta K_{\text{eff}} = K_{\text{max}} - K_{\text{clo}} \]  \hspace{1cm} (2.4)

where \( K_{\text{clo}} \) is the stress intensity value at which the crack begins to close. Many crack closure mechanisms have been identified, the principal ones are shown schematically in Figure 2.6 [56]. The phenomenon of crack closure is now widely acknowledged to exert a strong influence on near threshold fatigue crack growth. Closure ideas have helped to explain, at least in a qualitative manner, many crack propagation effects, especially concerning the near threshold region. However, the crack tip sharpening effect and changes to the plastic zone during the compressive part of the loading cycle, or after the crack is closed, is not well accounted for in these mechanisms.
Figure 2.6 Schematic illustration of the principal mechanisms of fatigue crack closure [56].

2.1.6.1 Plasticity induced closure

Plasticity induced closure arises from the fact that the propagating crack generates a plastic zone (enclave) in the crack tip region that is contained in an elastically strained matrix. Due to elastic constraint from the uncracked material, the crack tip region is placed under compressive stress on the closing portion of the load cycle. The resulting effect is to press the sides of the crack together near the crack tip before the gross applied load reaches zero. This compressive
stress effectively imposes a constant stress on top of the applied cyclic stress, shifting the mean stress of the cycle to a lower value. Therefore, if the applied load cycle is at a sufficiently low $R$ ratio the residual stress will bring part of the load cycle into the compressive region, creating closure effect, even when $R$ is positive ($R = K_{\text{min}}/K_{\text{max}} = P_{\text{min}}/P_{\text{max}}$).

This fundamental source of closure was first conjectured and later established experimentally by Elber [57]. After Elber’s pioneering work, other sources of crack closure have also been identified.

### 2.1.6.2 Oxide induced closure

When oxide deposits or corrosion products build up on the fracture surfaces to the extent that their thickness is of the same order of magnitude as the calculated crack tip opening displacement, crack closure may result.

Ritchie, Suresh and coworkers [58,59] reported the first quantitative experimental study of this kind of closure, in which they noticed that oxide deposits on the fracture surfaces of a steel tended to be more pronounced near threshold and at low $R$ values, causing black bands on a fracture surface which delineate the position of the crack front under near threshold loading.

### 2.1.6.3 Roughness induced closure

Roughness induced closure arises from the scenario that the relative motion of the opposing fracture surfaces at the crack tip may contain some Mode II and III displacements, even though fatigue may be occurring under nominally Mode I displacements. In particular it has been established that significant Mode II stresses operate at the crack tip even under far field Mode
I loading. When any such relative motion occurs, the two opposing faces of the crack will not fit together perfectly on the closing part of the cycle. Opposing asperities will come into contact at some point and, since these can transmit stresses across the crack faces, some degree of closure will occur.

This kind of closure was first suggested by Purushothaman and Tien [60], and Walker and Beevers [61].

2.1.6.4 Viscous fluid induced closure [56]

Fluid induced closure relies on the fact that a viscous fluid is capable of transmitting stress. Therefore a crack filled with, say, oil, may demonstrate some closure effects at all stress levels, depending on the loading frequency. This mechanism is confined to fluids which are viscous enough to exert an effect but also capable of flowing into the narrow openings afforded by near threshold cracks.

2.1.6.5 Phase transformation induced closure [56]

In materials which undergo stress or strain induced phase transformations under cyclic loading, a further mechanism of fatigue crack closure can result. This phase transformation induced closure arises also from the constraint effect of the surrounding elastic material on the transformed region, analogous to the plasticity induced closure mechanism. When the phase formed is more voluminous than the original phase, a compressive residual stress results, leading to crack closure.
Literature Review

2.1.7 Rate controlling process in corrosion fatigue

Corrosion fatigue involves many processes, any of which can act independently or synergistically to control the cracking rate. A list of such processes includes [35,49-63]:

1. Transport of reactants to the crack tip region.
2. Rupture of a protective film by straining.
3. Dissolution of freshly exposed metal.
4. Passivation of freshly exposed metal.
5. Production of hydrogen atoms.
6. Adsorption of deleterious species (hydrogen atoms).
7. Diffusion of hydrogen atoms into the matrix and ahead of the crack tip.
8. Promotion of fracture by the deleterious species (e.g. surface energy reduction, hydrogen embrittlement).
9. Build up of corrosion products which influence crack closure and the effective stress intensity range.
10. Transport of corrosion products from the crack tip region.

2.2 Corrosion Fatigue of Li-Containing Aluminium Alloys

Corrosion fatigue is related to both the mechanical and corrosion properties of the material and the interaction between them. Therefore, the mechanical properties, fracture toughness, corrosion and stress corrosion cracking behaviour of Li-containing alloys will also be included in the review. Adequate knowledge of these properties is necessary for the understanding of the fatigue and corrosion fatigue behaviour of Li-containing aluminium alloys.
2.2.1 Brief historical development of Li-containing aluminium alloys

The development of Al-based alloys containing lithium began in Germany in the 1920's [64] and was primarily concerned with additions of small amounts of lithium to age-hardening alloys to increase their strength. In the 1950's, metallurgists at ALCOA recognized that lithium increases the elastic modulus of aluminium and developed the high strength Al-Cu-Li alloy 2020 [65]. In the mid-1960's Al-Mg-Li alloy 1420 was introduced in the former Soviet Union [66]. However, there were only limited applications because these early generation Li-containing alloys exhibited major problems relating to poor ductility and low fracture toughness.

Major development of Al-Li alloys began in the 1970's [2,3,67]. The stimulus was the consistent pursuit of materials with high strength/weight ratio, which is a critical requirement of the airplane and aerospace industries. Moreover, to meet demands for increased fuel efficiency, one of the most feasible methods is to replace conventional construction materials with new materials which have similar structural characteristics but lower specific weight. Unlike other alloying elements in aluminium alloys, lithium increases the elastic modulus and strength while reducing the density of the alloys. Each weight percent lithium added to an aluminium alloy reduces the density approximately 3% and increases the elastic modulus approximately 6% for lithium additions up to 4% (which is the maximum solid solubility of Li in Al at 610 °C) [1,3]. Therefore the specific stiffness can be increased significantly (see Appendix I). As such, the development of Li-containing alloys makes aluminium alloys more resistant to replacement by composite materials, with the added advantage that Li-containing aluminium alloys can be produced and processed by existing equipment with only slight modifications [1,2,4,68].
Alloy development has led to the introduction of two of the most promising Li-containing alloys, Al-Li-Cu-Zr alloy 2090 by ALCOA and Al-Li-Cu-Mg-Zr alloy 8090 by ALCAN in the mid-1980's. Generally, the 2090 alloys are planned primarily as a replacement for the conventional high strength 7000 series Al-alloy, and the 8090 alloys are intended to substitute for conventional 2000 series Al-alloys in medium strength and damage tolerant applications [67,69,70].

Several conferences have been held in the past decade [71-76] that relate specifically to the development, characterization, and properties of Li-containing Al-alloys.

2.2.2 Mechanical properties and fracture toughness of Li-containing aluminium alloys

The major strengthening phase in Li-containing aluminium alloys is the metastable δ' (Al₃Li) phase which is coherent with the Al matrix, although a study by Noble et al. [77] found that the main increase in modulus of Li-containing aluminium alloys comes from lithium in solid solution, and to a lesser degree from the δ' phase. The major strengthening increment in all Al-Li based alloys comes from the formation of this phase upon age-hardening. In addition, Li and other alloying elements also contribute to strength by solid solution strengthening and other precipitation hardening processes (e.g., formation of T₁ (Al₂CuLi), θ' (Al₂Cu) and β' (Al₂Zr) in Al-Li-Cu-Zr alloys, and T₁ (Al₂CuLi), S (Al₂CuMg) and β' (Al₂Zr) in Al-Li-Cu-Mg-Zr alloys) [1,3,78,79].

The fatal problem with the early generation Al-Li alloys was poor ductility and toughness, which was the cause for the withdrawal of the early 2020 Al-Li alloy from commercial production.
in the late 1960's. Extensive studies attributed the poor ductility and toughness to several causes. These include grain boundary segregation of impurity alkaline elements (e.g. sodium and potassium) introduced with the lithium addition [3,80-84], strain localization at grain boundaries associated with the shearing of $S'$ phase by dislocations and resultant planar slip [1,3,85,86], strain localization favoured by the highly textured structure [85], formation of a precipitate-free zone (PFZ) at grain boundaries and large grain boundary precipitates [3,86-92]. Considerable effort has been made to combat these problems by (i) increasing the purity of the alloying Li or adding impurity bonding elements, like bismuth, silicon or iron [93-95], (ii) addition of dispersoid forming elements like Mn and Zr to promote more homogeneous deformation [79], (iii) addition of solid solution and precipitate hardening elements (Mg and Cu) [79,96], (iv) thermomechanical processing [87], (v) mechanical alloying and powder metallurgy [97,98].

While slip planarity is generally considered to have a harmful effect on fracture toughness, studies by Suresh et al. [92,99,100] showed that it can also lead to a concomitant beneficial geometric effect on toughness by causing crack bifurcation. Crack bifurcation occurs in the under-aged Al-Li-Cu-Zr alloys when the amount of grain boundary precipitates is insufficient to cause intergranular fracture, leading to enhancement in crack growth resistance.

For the newly developed Al-Li alloys like 2090 and 8090, the goal of improving ductility and toughness without significant loss in other mechanical properties has been reached with great success. Moreover, excellent cryogenic properties have been found with Al-Li alloys, as shown by increasing strength, ductility and toughness with decreasing temperature [81-83,101-110]. The increased fracture toughness values of Al-Li alloy plates in the L-T and T-L orientation at low temperature have been attributed primarily to the effects of crack-divider delamination toughening [107,108]. Modern Al-Li alloy plates usually have the pan-cake shaped
Literature Review

grain structures, analogous to laminates. These structures lead to anisotropic mechanical properties. For cracks in laminate material, three distinct orientations exist, as shown in Figure 2.7 [107]. According to the delamination toughening mechanism, the enhanced splitting (delamination) along the weak interfaces not only consumes energy but also changes the stress state at the crack tip from plane strain to plane stress, resulting in increased toughness. On the other hand, some studies attributed the increased toughness at low temperature to the solidification of embrittling liquid impurity phases of alkaline metals [82] and the greater homogeneity of plastic deformation with increased strain hardening [103-105].

![Crack division diagram](image)

Crack divider
(L-T,T-L)

Crack arrester
(T-S,L-S)

Crack delamination
(S-L,S-T)

Figure 2.7 Terminology used to describe the various orientations for crack extension in an anisotropic material containing specific planes of weakness in one direction [107].
Associated with the anisotropic grain structure of Al-Li alloy plates, fracture toughness values are low when the crack plane is parallel to the plane of the pancake-shaped grain (i.e. in the S-L or S-T orientation). In order to improve the low fracture toughness of Al-Li alloy 8090-T8771 in these orientations, a re-aging heat treatment has been proposed [111-114]. This re-aging treatment has been shown to increase the S-L fracture toughness by 2 to 3 times with only slight sacrifice in strength (~7%). However, different mechanisms [112-114] have been reported to explain the effects of the heat treatment. These include grain boundary Li desegregation by Lynch [112] and reduced slip planarity by Blankenship et al. [113] and Slavik et al. [114].

2.2.3 Corrosion and stress corrosion cracking of Al-Li alloys

It is expected that Li-containing aluminium alloys will be more susceptible to corrosion than other aluminium alloys, because of the reactive nature of lithium. Studies have found that corrosion is generally associated with the precipitates in the material [115]. In addition to the well known deleterious effect on corrosion by the δ (AlLi) phase, which is anodic to the aluminium matrix [116,117], corrosion has also been attributed to other precipitates, like T₁ (Al₂CuLi) and S' (Al₂CuMg) [118-120] and T₂ (Al₆CuLi₃) [121], to the formation of PFZs [122] associated with precipitation, and to the increasing size distribution of δ' precipitates with aging [123]. These precipitates cause the formation of galvanic cells, leading to corrosion. Whether a heat treatment improves or degrades the corrosion behaviour depends on its effect on the formation of the precipitates and PFZs and the resultant driving force for the corrosion process.

There are some "indirect" studies suggesting that the Li content in the Al alloys is beneficial for their corrosion resistance. The result obtained by Gui et al. [124] from a corrosion study of
6061 Al-alloy in aqueous solutions with and without Li ions suggested that Li in solution has a beneficial effect on corrosion resistance. Instead of increasing corrosion, they found that Li in an alkaline solution decreases the corrosion rate by incorporating Li in the formation of a protective film that results in anodic passivation behaviour. When Li\(^+\) is not present in the alkaline solution, passivation behaviour is not observed. The result of Fernandes and Ferreira [125], based on electrochemical polarization measurement of pure Al in mixed solutions of Na\(_2\)CO\(_3\) and Li\(_2\)CO\(_3\), also showed that the presence of Li\(^+\) in solution improves the passivation of aluminium above a critical concentration of carbonates. The presence of chlorides above a certain level in these solutions is deleterious to the passivating films, causing film breakdown and pitting. Generally, the corrosion resistance of Al-Li alloys is equivalent to or better than the conventional alloys that they are intended to replace.

Similar to the conventional high strength aluminium alloys [126,127], the stress corrosion cracking susceptibility of Li-containing alloys is of great concern. Studies of SCC behaviour of Al-Li alloys in sodium chloride test solutions have shown that SCC susceptibility changes with material orientation, heat treatment, electrochemical potential, loading and environment exposure conditions [128-145].

A study by Braun et al.[128] on peak-aged 8090 alloy showed that it is susceptible to SCC in the short transverse (ST) direction but not in the long transverse (LT) direction. Lumsden et al. [129] also found much higher SCC severity in the ST than in the longitudinal direction in their study on 8090 alloy and that SCC behaviour is insensitive to aging treatment. A study by Dorward et al. [130] showed that the under-aged 2090 alloys are susceptible to SCC in both LT and ST directions, but the near peak-aged alloy is immune to SCC.
Although it is established that over-aging improves SCC resistance for conventional high strength aluminium alloys [126,127], many studies on Al-Li alloys [130-140] have shown that heat treatment produces different effects. Studies by Christodoulou et al. [131] on binary Al-Li alloys and Lane et al. [132] on Al-Li-Cu-Mg alloys showed that the peak-aged tempers are most susceptible to SCC and over-aging improves SCC resistance, similar to conventional Al alloys. Gray [133] showed that under-aged tempers of Al-Li-Cu-Mg alloys exhibit greater SCC susceptibility than either peak-aged or overaged tempers. Rinker et al. [134] reported that the SCC resistance of Al-Li alloy 2020 is excellent in both peak-aged and under-aged tempers. Meletis [135] reported that the peak-aged temper of an Al-2.9Cu-2.2Li-0.12Zr alloy is most resistant to SCC, over-aging induces susceptibility to SCC owing to the development of strain at the grain boundaries resulting from preferential T1 precipitation. Vasudévan et al. [136] and Balasubramaniam et al. [137,138], reported a decreasing SCC resistance with increasing aging time. A recent study by Hu et al. [121] showed that over-aging increases SCC resistance of Al-Li alloy 8090 with simultaneous significant reduction in tensile strength, while a retrogression and re-aging process is able to improve the optimum combination of tensile strength and the SCC resistance, i.e., achieving the high SCC resistance of the overaged temper without losing the high ultimate tensile strength and yield strength of the peak-aged temper.

Lumsden et al. [129] studied the effect of electrochemical potential on SCC behaviour of 8090 alloy in 3.5% NaCl. They found that susceptibility to SCC depends on electrochemical potential. There is a critical potential below which SCC does not occur. The critical potential is near the pitting potential (only about 70 mV below $E_{pit}$). Strain-to-failure decreases rapidly as the potential approaches the pitting potential.
While most workers [128-138,141-145] have studied SCC of Al-Li alloys using a variety of testing methods (e.g. alternate immersion, drip feed or constant immersion together with constant strain, constant load, slow strain rate technique (SSRT) on smooth specimens and bolt loaded precracked double cantilever beam (DCB) specimens), Holroyd et al. [146] and Craig et al. [147,148] have drawn attention to the influence of the environment exposure conditions on SCC of Al-Li alloys. They found that SCC does not occur in 3.5% NaCl under constant immersion conditions with either smooth or precracked specimens under constant load (or strain), but occurs under alternate immersion or pre-exposure testing conditions. They proposed that the local chemistry at the crack tip, or within other limited geometries, in Li-containing alloys is alkaline after the specimen is removed from the bulk solution. This alkaline chemistry is opposite to the acidic local chemistry that forms inside long cracks under total immersion in Al-Li alloys (as proven by artificial crevice corrosion tests [119,147,148]) and in conventional Al-alloys [149]. They explained that under alternate immersion, drip feed or pre-exposure testing condition, a critical balance between activity and passivation necessary for SCC can develop, due to the absorption of CO₂ from the atmosphere. They supported their explanation with further test results that showed exposure of the test solutions to CO₂ determines whether SCC occurs, and that SCC occurs in Li₂CO₃/LiHCO₃ buffered NaCl solution under constant immersion condition. The need for CO₂ in the SCC was attributed by Moran et al. [150,151] and Buchheit et al. [152] to an increase in carbonate concentrations which eventually leads to the passivation of blunted fissures by precipitation of Li₂CO₃. These studies also attributed the local alkaline chemistry to the reduction of protons (H⁺) that occurred within the crack or crevice upon removal of the bulk solution. However, several researchers [141,142,145] have reported results of SCC susceptibilities obtained with DCB specimens under constant immersion conditions, which are contrary to the above assertion on environment exposure conditions.
The proposed mechanisms of SCC of Al-Li alloys are similar to those for conventional aluminium alloys. Both anodic dissolution and hydrogen embrittlement have been proposed. Anodic dissolution mechanisms are based on the potential difference between grain boundary precipitates (such as \( \delta \), \( T_1 \) and \( T_2 \)), PFZs and the interior of grains (and possibly the solute depleted zone) \([121,130-134,140,144,150-153]\). Hydrogen embrittlement mechanisms are based on pre-exposure embrittlement \([146]\), the discontinuous nature of crack growth, hydrogen-generating corrosion reactions behind the crack tip \([131,141]\), hydride formation \([137,138]\), and facilitated hydrogen entry by \( T_1 \) phase \([154,155]\). Hydrogen has been shown to dramatically decrease tensile properties of 2090 alloy \([156,157]\). The recent work of Lee et al. \([145]\) on an Al-Li-Zr alloy proposed a transition in the SCC mechanism from anodic dissolution in stage I to hydrogen embrittlement in stage II by considering the temperature dependence of SCC susceptibility based on the anodic dissolution and hydrogen embrittlement models.

It is probable that anodic dissolution and hydrogen embrittlement both play a role in SCC of Al-Li alloys. In comparison with the conventional Al-alloys, the SCC resistance of Al-Li alloys is graded as equivalent or superior.

2.2.4 Fatigue and corrosion fatigue of Al-Li alloys

Low resistance to fatigue crack initiation was observed for the early generation Al-Li alloys such as 2020. This was attributed to strain localization caused by the shearing of the coherent \( \delta' \) phase by dislocations and resultant planar slip \([158,159]\). In similar manners to the fracture toughness, fatigue crack initiation resistance can be improved by dispersing the planar slip and increasing the strain hardening ability, e.g., by adding dispersoid forming elements and
producing semi-coherent/incoherent precipitates [90] or by mechanical alloying to incorporate finely distributed oxide and carbide particles [98]. The recently developed Al-Li alloys, like 2090 and 8090, have equivalent or better fatigue crack initiation resistance than the conventional Al-alloys [6].

The fatigue crack growth resistance of Al-Li alloys is generally superior to the conventional aluminium alloys [6]. Coyne et al. [158] attributed the improved resistance of two Al-Li-Mn and Al-Cu-Li alloys to sub-critical crack growth at low cyclic stress intensities (about 4 to 10 MPa.m$^{1/2}$) to the increase in elastic modulus by addition of Li, which leads to decreased crack opening displacement (COD) and hence decreased fatigue crack growth rate [160].

Besides changes in elastic modulus, Bretz et al. [159] and Vasudévan et al. [161] attributed the much slower crack propagation rates of alloy 2020 relative to those of alloy 7075 to the coarse, recrystallized grain structure and highly non-linear and deflected crack profiles resulting from planar slip of the Al-Li alloy. The cracking rates in alloy 2020 are an order of magnitude lower at intermediate $\Delta K$ levels and up to 2 orders of magnitude lower in the near-threshold region than the cracking rates in alloy 7075. Non-linear and deflected crack surfaces can significantly reduce the effective crack propagation driving force, $\Delta K$ [162-164].

In studies with three high purity Al-alloys containing different amount of lithium and copper, Vasudévan et al. [7] and Petit et al. [11] found that increasing the Li/Cu ratio in aluminium alloys leads to an improved resistance to cyclic crack growth at room temperature in moist air and vacuum environments. They explained that differences in elastic moduli of the materials are not the cause of their different resistances to cyclic crack growth, as considerable differences still exist between the materials when propagation rate $da/dN$ is plotted against $\Delta K/E$. 
The beneficial fatigue properties appear to arise from the crystallographic crack growth mechanism and a crack deflection process induced by the $\delta'$ precipitates in the alloys of higher Li content.

Harris et al. [8] studied the effect of grain size and shape on mechanical properties and fatigue resistance with 8090 alloys. In addition to the reduced fatigue crack growth rate of 8090 at $\Delta K$ values close to threshold and up to 20 MPa.m$^{1/2}$, relative to the 2000 series Al-alloys, they found that for the Li-containing alloy the fatigue crack growth rate is slower when the grain size is large and when subgrain boundaries contain the precipitated S ($Al_2CuMg$) phase. The improvement in fatigue properties with increasing grain size is largely due to the highly faceted crack path (on $\{111\}$ slip planes), the resulting surface roughness causing early crack closure and hence reducing the effective $\Delta K$ range at the crack tip [162]. High slip reversibility in Li-containing alloys also contributes to the improved fatigue properties. The improvement of fatigue crack propagation resistance with increase in grain size was also indicated by Ruch et al. [165] in their study on fatigue propagation in mechanically alloyed Al-Li-Mg alloys. They elucidated that increased grain size allows an increase in slip length, resulting in more reversible slip, and that sharp texture increases the effective grain size by making slip transfer across grain boundaries easier, because of small misorientation angles between neighboring grains.

Rao et al. [9,10,166-168] studied fatigue crack propagation of long and short cracks in different Li-containing aluminium alloys. They found that fatigue crack growth is highly anisotropic for long cracks [9,166]. In a commercial 2090 alloy, L-T, T-L and T-S orientations show the best crack growth resistance, and S-L, S-T and L+45° show the worst [9]. Different grain orientations cause different magnitudes of crack tip shielding (reduction in local crack driving force) arising from crack deflection and roughness induced crack closure. Short cracks
Literature Review

propagated much faster than long cracks at equivalent nominal $\Delta K$, and propagated below the long crack threshold stress intensity $[10,167,168]$. The major reason for this behaviour was attributed to the lack of crack deflection and roughness induced closure for short cracks. The absence of an intrinsic threshold, together with crack growth below the closure-corrected $\Delta K_{\text{ct}}$ threshold for long cracks, was explained by factors such as enhanced cyclic plastic strain at the tip of small cracks and the differing statistical sampling effect of large and small cracks with microstructural features $[33,34]$.

Studies by Yoder et al. $[169]$ related the extraordinary fatigue fracture surface roughness and crack closure level of the Al-Li alloy 2090-T8E41, which are responsible for its uncommonly good fatigue crack growth resistance, to the microstructure of the material. They concluded that the slip band facets and the unusual height of asperities in the fatigue fracture surface of the Al-Li alloy plate are the consequence of (i) the propensity for a planar slip mode, and (ii) the alloy's unusually intense crystallographic texture ($\{110\} <112>$ and $\{123\} <634>$).

Oxide induced closure was also investigated in some of the above studies $[7,9,98]$, but was found to have only a relatively minor effect when compared with the crack tip opening displacement (CTOD).

Al-Li alloys exhibit strong tensile overload retardation effects on crack growth $[11,159,170,171]$, but they are also very sensitive to periodic compression overload cycles $[9,13,172]$. In the latter case, the compressive loads act to reduce closure effects by crushing the asperities, which decreases roughness induced closure stresses, causing accelerated crack propagation rates and crack growth at the threshold.
Besides the increased toughness with decreasing temperature for Al-Li alloys [81-83,101-110], fatigue resistance was also found to increase with decreasing temperature [104,173] and attributed to deeper and larger delamination that occurred on the fracture surface [173]. Also, it has been noticed that factors which improve resistance to fatigue crack propagation tend to have a detrimental influence on fatigue initiation [17], such as grain size, and planarity of slip.

While structure related effects play an important role in fatigue resistance of Li-containing aluminium alloys, the influence of environment is another key factor that needs to be included in corrosion fatigue of Al-Li alloys. Vasudévan et al. [161] found with an Al-Li-Cu alloy that only a small difference in fatigue crack growth rates can be detected between moist air (90% relative humidity (RH)) and dehumidified helium (< 3 ppm moisture). It was suggested that due to the highly reactive nature of lithium with moisture, a moisture content of even less than 3 ppm can cause embrittlement. Many studies conducted in air and vacuum or dry argon have shown that the crack propagation rate can be accelerated and the threshold value decreased when tested in air [11-17,20]. The presence of water vapor, liquid water and sodium chloride solution can further accelerate fatigue crack propagation rate and decrease the threshold [13,15-19,142,174], although sometimes the opposite effects have been observed [17,18]. With smooth specimens, environmental effects lead to reduced fatigue lifetime and fatigue limit [175-180].

Many mechanisms have been proposed to explain the influence of environment on fatigue cracking resistance. These are primarily anodic dissolution [12,176,178,180], hydrogen embrittlement [13-16,176,179,180], environmental effects on crack closure level [15,17-19,179] and on slip reversibility [15,20], or a combination of any of them. For example,
anodic dissolution is assumed to accelerate crack initiation and crack propagation in a corrosive solution through pitting [178,180], intergranular corrosion [12,176], and slip-enhanced dissolution [12,180]. On the other hand, the studies of Piascik et al. [16] suggest that a hydrogen embrittlement mechanism may be operative. They reported the following results as supportive to the hydrogen embrittlement mechanism: (i) the fatigue crack growth is accelerated by the presence of only ppm levels of water vapour where condensation is not possible; (ii) the dependence of $da/dN$ on water pressure agrees with the predictions of an impeded molecular flow model; (iii) the fatigue crack growth is not affected by the presence of film-forming O$_2$, and is the same as those in purified helium and vacuum; (iv) the crack paths in the ppm level water vapour and the aqueous NaCl environments have identical brittle morphologies and process zone volume dependence [181]. Pao et al. [19] concluded that the presence of an aggressive environment may enhance or retard fatigue crack growth depending upon whether the crack closure level is reduced or elevated during corrosion fatigue, based on their study of 2090 and 7075 in air and 3.5% NaCl solution. Fatigue crack growth rates of alloy 2090 in 3.5% NaCl were increased approximately six fold relative to those in air, due to the conjoint action of salt water corrosion and mechanical fretting which largely removed the fracture surface tortuosity and reduced roughness induced closure. Tests on alloy 7075 showed that in the low $\Delta K$ region, corrosion product induced crack closure in salt water and led to lower fatigue crack growth rates than those in air. Peters et al. [17,18] also attributed the higher threshold value of Al-Li alloys in aqueous NaCl, relative to air, to corrosion product induced crack closure. Studies by Jata et al. [20] and Shin et al. [15] found that although crack path tortuosity, and hence crack deflection and fracture surface roughness, were increased in vacuum relative to those in air, the crack closure level was lower in vacuum. They proposed that in vacuum the slip reversibility increases due to the lack of a significant surface oxide. Thus although fractography
of vacuum tested samples indicated extensive faceting, it did not result in increased crack closure caused by the mode II displacements behind the crack tip. The extent of slip reversibility plays an important role in the fatigue crack growth rates of planar slip material. The lower fatigue crack growth rate in vacuum is due to increased slip reversibility rather than an increase in the roughness induced crack closure.

Overall, the corrosion fatigue resistance of Al-Li alloys is superior or equivalent to the conventional aluminium alloys. The addition of reactive lithium element does not appear to cause severe environmental sensitivity problems, while the increase of elastic modulus, strength and slip reversibility, and especially the "extrinsic toughening" effects from crack deflection, roughness and branching, all contribute to improve the fatigue crack growth resistance. Ideally, we would like to have new materials with both improved fatigue crack propagation resistance and increased fracture toughness. Therefore, when comparing to the materials to be substituted, the new materials will not only exhibit lower crack growth rates at comparable ΔK but also can sustain longer critical crack lengths before unstable fracture occurs (i.e. when $K_{\text{max}}$ in the fatigue cycle reaches $K_{\text{fc}}$). Consequently, much longer service lifetime will be obtained for the engineering structures or components made from the new materials.
3 Objective

The main objectives of the present study are as follows:

1. To evaluate the corrosion fatigue crack propagation behaviour of the Al-Li alloy 8090 in the T8771 temper in the T-L orientation, covering a broad range of fatigue crack growth rates from the near threshold (Stage I) to the Stage II region, and to investigate the effects of controlled environments and cyclic load frequency on the fatigue behaviour.

2. To compare the fatigue crack propagation behaviour of the Al-Li alloy in the T-L orientation with that of the conventional aluminium alloy 2024 in the T351 temper.

3. To study the corrosion fatigue crack propagation behaviour of the Al-Li alloy in the short-transverse orientation (S-L) and to determine the effects of a toughness-enhancing re-aging treatment on the fatigue and corrosion fatigue crack growth resistance in the S-L orientation.

4. To gain further understanding of the mechanisms related to the generally reported superior fatigue crack growth resistance of Li-containing aluminium alloys, by assessing the influence of alloy composition, microstructure, deformation behaviour, environmental sensitivity and electrochemical corrosion behaviour on fatigue cracking resistance.
Objective

5. To clarify the relative importance of anodic oxidation processes, hydrogen evolution and surface-related processes in the mechanism of corrosion fatigue crack growth, and the possible roles they play in affecting corrosion fatigue crack propagation in Al-Li alloys through effects on crack closure level and/or slip reversibility.
4 Experimental

4.1 Materials

4.1.1 Chemical compositions

The materials used for the study were commercial Al-Li 8090 alloy plate of 12.7 mm thickness, and commercial Al-Cu 2024 alloy plate also of 12.7 mm thickness. The nominal chemical compositions [2,67,182] of the alloys are given in Table 4.1.

Table 4.1 Chemical Compositions (Nominal wt.%)  

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Li</th>
<th>Zr</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>8090</td>
<td>0.20</td>
<td>0.30</td>
<td>1.0-</td>
<td>0.10</td>
<td>0.6-</td>
<td>0.10</td>
<td>0.25</td>
<td>2.2-</td>
<td>0.04-</td>
<td>0.10</td>
<td>balance</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.6</td>
<td></td>
<td>1.3</td>
<td></td>
<td></td>
<td>2.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2024</td>
<td>0.50</td>
<td>0.50</td>
<td>3.8-</td>
<td>0.30</td>
<td>1.2-</td>
<td>0.10</td>
<td>0.25</td>
<td></td>
<td></td>
<td>0.15</td>
<td>balance</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.9</td>
<td></td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1.2 Mechanical Properties

The Al-Li alloy was received in the T8771 temper, which involves a solution treatment at 545 °C that is followed by a cold water quench, a 7% stretching operation, and a final aging treatment at 170 °C for 32 h [112]. The Al-Cu alloy was received in the T351 temper, which
generally consists of a solution treatment at 495 °C, a 1.5-3 % stretching and natural aging [182,183]. The actual and nominal mechanical properties [2,184,185] of the alloys in the as-received conditions are listed in Table 4.2.

Table 4.2 Physical and Mechanical Properties

<table>
<thead>
<tr>
<th></th>
<th>ρ (g/cm³)</th>
<th>E (GPa)</th>
<th>σ_{UTS} (MPa)</th>
<th>σ_Y (MPa)</th>
<th>ε (%)</th>
<th>K_{IC} (MPa.m^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T-L</td>
</tr>
<tr>
<td>8090-T8771 *</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8090-T8771 [2]</td>
<td>2.55</td>
<td>77</td>
<td>460-515</td>
<td>380-450</td>
<td>4-6</td>
<td>13-30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>S-L</td>
</tr>
<tr>
<td>2024-T351 *</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2024-T351 [185]</td>
<td>2.78</td>
<td>73</td>
<td>470</td>
<td>325</td>
<td>19</td>
<td>32</td>
</tr>
</tbody>
</table>

* Data supplied by Morrison [184].

4.1.3 Grain structures

The grain structures of both materials were examined in three orthogonal planes, with their normals in directions L, T and S, where L is the longitudinal or rolling direction, T is the transverse direction and S is the short-transverse or through-thickness direction. Subsequently,
planes normal to the L, T and S directions will be designated as the L-plane, T-plane and S-plane respectively. The specimens were ground with SiC paper down to 600 grit and subsequently polished with diamond suspensions to a 1 μm finish. The grain structures were revealed by immersion etching in Keller’s etchant for 10-20 seconds, followed by washing in a stream of warm water and ethanol, and drying in a stream of air. The Keller’s etchant is composed of the following reagents [186]:

1.0 ml HF, 1.5 ml HCl, 2.5 ml HNO₃ and 95 ml H₂O.

Both plates exhibited anisotropic grain structures that are characteristic of the commercial materials, as shown in the composite optical micrographs in Figure 4.1. The grain dimensions were not very uniform in the Al-Li alloy, even when measured and compared within each of the S, T, L directions, and indicated a partially recrystallized structure. The grain thickness in the S-direction varied by a factor of ~5 with a mean of ~7 x 10⁻³ mm. Grain diameters in the rolling plane (S-plane) were larger, but even less uniform, varying by a factor of ~19 with a mean of 2 x 10⁻² mm in the T direction, and varying by a factor of ~20 with a mean of ~7 x 10⁻² mm in the L direction. The grain dimensions were relatively uniform in each direction in the Al-Cu alloy, with a mean of ~3 x 10⁻² mm, ~7 x 10⁻² mm and ~1.3 x 10⁻¹ mm in the S, T and L directions respectively.

4.1.4 The re-aging treatment

A re-aging treatment was applied to the Al-Li alloy to investigate its effects on the S-L orientation corrosion fatigue crack propagation resistance. The denotation of crack plane follows the conventions as defined in ASTM E399-78a [188] and is shown here in Figure 4.2. It has been shown that a re-aging treatment at 230 °C for 10 minutes can largely improve the fracture
Figure 4.1 Grain structures of (a) Al-Li 8090-T8771 and (b) Al-Cu 2024-T351.
toughness in the short-transverse orientations with only minor decrease in strength [112]. In the present study, the re-aging treatment was conducted in a salt bath of ~50% NaNO\textsubscript{3} + ~50% KNO\textsubscript{3} [187] with coupons near the final size for the S-L orientation double cantilever beam (DCB) specimens. The salt bath was heated in an electric furnace at 230 °C. Each coupon was put in the salt bath for 10 minutes and then quenched in ambient temperature tap water (~20 °C). The DCB specimens were made from these coupons after the heat treatment.

4.2 Specimen design and preparation

4.2.1 Electrochemical test specimens

Small square samples of ~15 mm x 15 mm x 12.7 mm were cut from plates of both alloys to make the specimens for electrochemical tests. Each metal section was mounted in epoxy resin to leave only one surface exposed. The exposed surface was metallographically polished to a 1 \( \mu \)m finish and cleaned with ethanol. The exposed edges between the epoxy and alloy were masked with cellulose acetate lacquer to prevent crevice corrosion effects during the electrochemical tests. A copper wire was electrically connected to the unexposed rear face of each specimen and passed through a glass tube that was sealed into the epoxy mount, as shown schematically in Figure 4.3. The polished and lacquer masked specimens were stored in a desiccator before use.
Figure 4.2 Crack plane orientation identification code for plate [188].
Figure 4.3 Geometry of the electrochemical test specimen.
4.2.2 Fatigue specimens

Three types of specimens were used in the present fatigue study. The choice of specimen geometry was determined by the comprehensive consideration of intended crack orientations, environmental exposure feasibility, as well as the loading capability and applicability of the available fatigue machines.

4.2.2.1 Single edge notched specimen

Single edge notched (SEN) specimens with a T-L orientation cracking plane and direction, as defined by ASTM E399-78a [188] and shown in Figure 4.4 were used for high frequency fatigue testing at ~80 Hz on an Instron electromechanical resonant machine (Model 1603). Each specimen had a chevron-shaped machined starter notch, ~13 mm in length at the centre of the specimen and ~18 mm at the surfaces. The chevron-shaped starter notch was used in order to obtain a good starting crack front profile for the ensuing fatigue test after the fatigue precracking preparation procedures. The two side surfaces of each specimen were polished to a metallographic finish and fiducial lines were scribed on the surface to assist measurement of crack growth with a travelling microscope and the location of fractographic features. The stress intensity for opening mode loading for the SEN specimens were calculated from the following published $K$-calibration equations [41,189]:

\[
\Delta K = K_{\text{max}} - K_{\text{min}} = K_{\text{max}}(1 - R) \tag{4.1}
\]

\[
K = \frac{P(\pi a)^{1/2}f(a/W)}{WB} \tag{4.2}
\]
Experimental

\[ f(a/W) = \left( \frac{\tan Q}{Q} \right)^{1/2} \frac{0.752 + 2.202(a/W) + 0.37(1 - \sin Q)^{3}}{\cos Q} \]  
\[ Q = \left( \frac{a \pi}{2W} \right) \]  

where \( a \) is the crack length, \( P \) is the applied load, \( W \) is the specimen width and \( B \) is the specimen thickness.

4.2.2.2 Compact tension (CT) specimen

Compact tension specimens with the T-L crack plane orientation were used for low frequency fatigue testing at ~0.5 Hz on a motor driven, microswitch activated, modified Hounsfield tensile machine. The geometry of the specimen is shown in Figure 4.5. In a similar manner to the SEN specimens, a chevron-shaped starter notch, side surface polishing and scribed fiducial line were used on the CT specimens. The \( K \)-calibration for this specimen geometry under Mode I loading [190] is given by:

\[ K = \frac{P}{B \sqrt{W}} \left( 2 + \alpha \right) (0.086 + 4.46\alpha - 13.32\alpha^2 + 14.72\alpha^3 - 5.6\alpha^4) \]  
\[ \alpha = \frac{a}{W} \]  

where \( a \) is the crack length, \( W \) is the specimen width, \( B \) is the specimen thickness and \( P \) is the load.
Figure 4.4 Geometry of the single edge notched (SEN) specimen.

- $T = 12.7 \text{ mm}$
- $W = 55 \text{ mm}$
- $B = 12.7 \text{ mm}$
Figure 4.5 Geometry of the compact tension (CT) specimen.
4.2.2.3 Double cantilever beam (DCB) specimen

Double cantilever beam specimens were used for studying the corrosion fatigue crack propagation resistance of the Al-Li alloy in the S-L crack plane orientation, particularly the effects of the re-aging treatment. The same specimen geometry was also used to determine the effects of the re-aging treatment on the fracture toughness. The geometry of the specimen is shown in Figure 4.6. A chevron-shaped starter notch, \( \sim 6.4 \) mm at the centre and \( \sim 13 \) mm long at the surfaces, was introduced along the mid-plane of the plate to ensure a good starting crack front profile after precracking. Similar side surface polishing and fiducial line scribing were used as the SEN and CT specimens, concerned with crack length measurement and location of fractographic features. The \( K \)-calibration [191] for this specimen geometry is given below:

\[
K = \frac{Pa}{BH^{3/2}} \left( 3.45 + 2.415 \frac{H}{a} \right)
\]

(4.7)

where \( P \) is the load, \( a \) is the crack length, \( H \) is the half specimen height and \( B \) is the specimen thickness.

4.2.3 Preparation of specimens for transmission electron microscopy

Electron transparent specimens were prepared from the Al-Li alloy plate (in both the as-received and the re-aged tempers) by the following steps:

1. Thin strips of alloy, \( \sim 1 - 2 \) mm thick, with the surface normal to the T-direction were sectioned from the plate with a fluid-cooled saw.
2. Small disks of 3 mm diameter were cut out from the strips using a spark machine.
3. The disks were then thinned to \( \sim 100 \) \( \mu \)m by mechanically polishing on 600 grit sand paper using a special holder.
Experimental

4. The disks were then mechanically dimpled to remove about 30 μm of materials on both sides using a dimpling machine (Dimpler Model D500).

5. The final thinning was done by Ar ion beam sputtering with an ion beam thinner equipped with liquid nitrogen cooling specimen stage (Maxmill Model 703), operating at 6 KV and 40 μA beam intensities.

4.3 Test environment selection

Four environments were chosen for the corrosion fatigue studies. They were:

1. Desiccated air.
2. Distilled water.
3. Sodium chloride solution (0.6 M).
4. Aluminium chloride solution (1 M).

Desiccated air was used to eliminate any aqueous environmental effects and to allow studies to be made solely on the effects of mechanical factors on the crack propagation behaviour. This reproducible inert environment also served as the baseline condition for determining whether other environments significantly affected the corrosion fatigue behaviour. Distilled water was used to study the effect of this reproducible contaminant-free environment relative to that of dry air. Sodium chloride solution was used to study the effects of halide-anion-containing corrosive media on the crack propagation behaviour. Aluminium chloride simulates possible local chemistry conditions that form inside occluded (restricted) geometries such as pits, cracks and crevices. It is known that a local acidic chemistry, enriched in chloride ions forms inside restricted geometries for both the conventional Al-alloys and Li-containing Al-alloys when exposed to neutral bulk chloride solution [119,147,148,149].
Figure 4.6 Geometry of the double cantilever beam (DCB) specimen.

- \( B = 12.7 \text{ mm} \)
- \( 2H = 12.7 \text{ mm} \)
- \( W = 49 \text{ mm} \)
Experimental

All the aqueous solutions were prepared from regent grade chemicals and distilled water.

4.4 Test setup and procedures

4.4.1 Potentiodynamic polarization tests

Potentiodynamic polarization tests were conducted in the aqueous chloride environments, using a conventional three electrode system with one working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). The working and counter electrodes were placed in a single compartment electrochemical cell containing ~1 liter of test solution, and the reference electrode was interfaced to the test solution via a salt bridge and Luggin capillary that terminated ~2 mm from the working electrode surface. The potential was controlled by means of a microprocessor controlled potentiostat (PAR Model 350A) with automated recording of potential (E) and current density (i). The data were then transferred to a personal computer and the polarization curve, presented as log(i) versus E, was constructed using software, Lotus 123 and Lotus Freelance Graphics. Each test was conducted by first imposing a potential on the working electrode that was ~250 mV cathodic with respect to its open circuit potential (E_{oc}) and then scanning the potential in the anodic direction at 1 mV/s. All solutions were deaerated by purging with nitrogen before and during the polarization tests. A schematic set-up of the experiment is shown in Figure 4.7.
Figure 4.7 Schematic experimental set-up of the potentiodynamic polarization test.
4.4.2 Corrosion fatigue crack propagation tests

4.4.2.1 High frequency

High frequency fatigue tests with the SEN specimens were conducted on the Instron fatigue machine. The loading frequency of the fatigue machine depends on the stiffness of the testing specimen and the load level, with the frequency decreasing as the crack length increases. For the materials and specimen geometries used in the present study, the frequency change was less than 5%. The load cycled sinusoidally between maximum ($P_{\text{max}}$) and minimum ($P_{\text{min}}$) loads, and crack growth was monitored on the metallographically polished external surface with an internally illuminated travelling microscope having a micrometer stage resolution of 10 μm. The fatigue precracking and subsequent fatigue tests followed different loading sequences, as detailed below.

4.4.2.1.1 Precracking

Fatigue precracking was conducted in laboratory air at ~22 °C using a load shedding technique combined with an increasing $R$ ratio ($P_{\text{min}}/P_{\text{max}}$). This involved commencing the precracking at an initial cyclic stress intensity ($\Delta K$) of ~5 MPa. m$^{1/2}$ and an $R$ ratio of 0.1. The $\Delta K$ was gradually decreased by the incremental lowering of $P_{\text{max}}$ to reduce the maximum stress intensity ($K_{\text{max}}$), while slowly increasing the $R$ ratio to 0.5 by raising $P_{\text{min}}$ to increase the minimum stress intensity ($K_{\text{min}}$). Upon reaching $R = 0.5$, incremental decreases (~10%) of $\Delta K$ were continued at constant $R$ until no crack growth increment could be detected after $1 \times 10^6$ cycles (equivalent to $\leq 1 \times 10^8$ mm/cycle). At this point, the crack front was essentially straight and the overall length of crack ($a$) was ~22 mm. The above loading procedures were used to minimize
crack closure effects due to load shedding while approaching the threshold without causing large increases in crack length. The fatigue precracking was normally finished within a crack length increase of ~5mm.

**4.4.2.1.2 Fatigue tests**

During subsequent fatigue cracking studies at ~22 °C in the test environments, a constant R ratio of 0.5 was used throughout the test in order to minimize crack closure effects, and the initial Δ*K* was chosen to be ~10% lower than the final value used for precracking. The Δ*K* was then raised or lowered in small increments (≤ 10%) until a crack propagation rate close to 1 x 10^-8 mm/cycle (the lower limit of crack rate detectability) was detected. Thereafter, the cyclic loads, \( P_{\text{max}} \) and \( P_{\text{min}} \), were held constant, and the crack was allowed to propagate under rising Δ*K* conditions while recording the crack growth behaviour. Crack length (a) was monitored as a function of the number of load cycles (N) and the average crack growth rate per cycle, \( da/dN \), was obtained by the secant method described in ASTM E 647-78T [190].

The environments used during corrosion fatigue testing were contained in a transparent acrylic (Plexiglas) cell that was mounted around the mid-section of the specimen and sealed to the specimen by silicone rubber cement, as shown schematically in Figure 4.8. For tests in the aqueous environments, the top of the cell was left open and the external polished surface of the specimen was coated with a thin layer of transparent nitrocellulose lacquer to minimize surface corrosion and facilitate crack growth monitoring. For tests in desiccated air, the precracked specimen was first placed in a vacuum chamber (~1 x 10^5 torr) for over 60 hours to eliminate any possible reversible hydrogen embrittled effects caused by water moisture in the ambient air during precracking [192]. It was then placed in a test cell containing freshly baked silica gel
desiccant, and the top of the cell was closed with a rubber sheet.

The electrochemical potentials of the specimens were not controlled during the fatigue tests in the electrolyte solutions. However, the freely corroding potentials \( E_{\text{corr}} \) were measured with respect to the SCE electrode by means of a salt bridge assembly, similar to that used in the polarization tests, and a high impedance voltmeter.

High frequency loading tests are useful for fundamental studies of fatigue in aqueous environments, because the more rapid fluid flow and mass transfer effects inside the crack increase the probability of maintaining the crack solution chemistry close to that of the bulk solution [41], minimizing complications arising from changes in local solution chemistry that normally occur in static cracks and crevices.

4.4.2.2 Low frequency

It takes longer time at lower frequency to initiate and grow a fatigue crack to a certain length. Therefore, in order to speed up the specimen precracking processes, the CT specimens used for the low frequency tests were precracked at a different, relatively high frequency. In the ensuing low frequency tests, higher starting \( \Delta K \) were used for similar concern, i.e. to shorten the experimental time period.
Figure 4.8 Schematic environmental cell set up for the high frequency fatigue test.
4.4.2.2.1 Precracking

Precracking of the CT specimens was conducted in laboratory air at -22 °C on a Sontag electrical synchronous fatigue machine (Model SF-1-U) which has a fixed loading frequency of 30 Hz and sinusoidal load waveform. Similar load shedding (ΔK decreasing) technique to the high frequency precracking was used except that an R ratio of 0.5 was chosen right from the beginning. Precracking was proceeded until the ΔK value was lowered below the planned starting ΔK value for subsequent low frequency fatigue tests (the starting ΔK was higher than that used on the high frequency tests).

4.4.2.2.2 Fatigue tests

The low frequency fatigue tests with the precracked CT specimens were conducted on the modified Hounsfield tensile machine fitted with a microswitch activated DC reversing motor. The frequency was controlled to ~0.5 Hz by adjusting the motor speed and the load waveform was triangular. The load was applied horizontally and for testing in the aqueous environments, the uncracked portion and some of the cracked portion of the specimen was immersed in the solution, as shown schematically in Figure 4.9. For tests in desiccated air, the specimen was sealed in a plastic bag with freshly baked silica gel desiccant. All tests were conducted at room temperature (~22 °C). Crack growth was also monitored by a travelling microscope, similar to that used in the high frequency tests.

The starting ΔK values for the low frequency tests were relative high to compensate the longer time involved. Therefore the real threshold region of low cracking rate (≤ 10⁻⁷ mm/cycle as suggested by Bucci [37] and Taylor [38]) was never reached.
Figure 4.9 Schematic environmental cell set up for the low frequency fatigue test.
4.4.2.3 Intermediate frequency

The relatively low stiffness of the DCB specimens and the relatively high working load level of the Instron fatigue machine available prevented the fatigue tests from being conducted at the high frequency with the Instron fatigue machine. Therefore, the short-transverse (S-L) orientation fatigue crack propagation behaviour of the Al-Li alloy plate was studied at a frequency of 30 Hz with the Sontag fatigue machine. Studies on the effects of the re-aging treatment on the S-L orientation fatigue crack growth behaviour were also conducted with the same machine. To overcome the restriction by the limited size of the DCB specimens, the load was applied through two threaded eye-bolts which were screwed into the specimen (see Figure 4.10).

4.4.2.3.1 Precracking

Precracking of the DCB specimens was done in laboratory air at ~22 °C with load shedding (decreasing ΔK) technique on the Sontag fatigue machine at 30 Hz. An R ratio of 0.5 was used from the start and precracking was terminated at the point that no crack extension could be observed by the travelling microscope used to monitor the crack progress after 10^5 cycles (equivalent to ≤ 1 x 10^7 mm/cycle cracking rate). Precracking was normally finished with a crack extension of about 4 mm beyond the tip of the ~13 mm long chevron notch seen at the specimen surface.

4.4.2.3.2 Hardness and fracture toughness tests

Hardness and fracture toughness tests were conducted for materials in the as-received state and after the re-aging treatment, to ensure the accomplishment of a proper re-aging
treatment, which has been reported to be able to significantly improve (double or even triple) the toughness in the short-transverse orientations with only slight sacrifice in yield strength (~7%) [112]. Microhardness ($H_v$, Vickers hardness) tests were conducted across the plate thickness. The S-L orientation fracture toughness values were measured using some of the fatigue precracked DCB specimens. The specimen was tested on a Hounsfield Tensile Machine and the load continuously increased until fracture occurred. The load at this point and the crack length were used to calculate the toughness value via the stress intensity formula for the DCB specimen, equation (4.7).

4.4.2.3.3 Fatigue tests

Corrosion fatigue tests were conducted on the Sontag machine at 30 Hz at room temperature (~22 °C). An $R$ ratio of 0.5 was used throughout the tests. Testing environments were contained within a Plexiglas cell placed around the specimen, and Plexiglas sheaths, rubber gaskets and acetate cellulose lacquer were used to prevent the loading bolts from contacting the testing solutions, as shown schematically in Figure 4.10. Other experimental and data processing procedures were similar to those described for the high frequency tests.

At the end of each fatigue test, the specimen was rinsed with ethanol, dried in a stream of air and broken open on a Hounsfield Tensile Machine by tensile overload. This overload was recorded and used to calculate the apparent fracture toughness to re-confirm that its value was within the normal limits, and in the case of the re-aged material, to re-confirm that a proper re-aging treatment had been done.
Experimental

4.4.3 Fractographic study

After fatigue testing, the fracture surfaces were prepared for fractographic study. The fracture surfaces were normally cleaned with denatured ethanol ultrasonically. When necessary, the fracture surfaces were cleaned with an inhibited acid solution containing 70 ml phosphoric acid, 32 mg chromic acid and 130 ml distilled water [193]. Crack surface fractography was examined by standard scanning electron microscopy (SEM), using secondary electron imaging with 20 KV and 5 KV acceleration voltages. The 5 KV excitation was chosen because it was found sometimes that small details on the surface were more easily visible under low excitation conditions. Two scanning electron microscopes, a Hitachi S-570 equipped with energy dispersive X-ray (EDX) spectrometer and wavelength dispersive X-ray (WDX) spectrometer, and a Hitachi S-2300 were used in the studies.

4.4.4 Crack profile study

Metallographic sectioning procedures and conventional optical microscopy were used to study the crack front profiles in the plane normal to the direction of crack propagation. Sectioning was made at several $\Delta K$ values on specimens tested in different environments and conditions in order to study the changes of crack front profile. The sectioning was done by cutting with a fine jewelry saw, grinding with SiC paper down to 600 grit and then polishing to 1 $\mu$m finish. The polished surface was etched with Keller's etchant to reveal the grain structure.
Figure 4.10 Schematic environmental cell set up for the intermediate frequency fatigue test.
4.4.5 Microstructural and compositional study

4.4.5.1 TEM

Transmission electron microscopy was conducted to characterize the microstructures of the Al-Li alloy in the as-received temper and after the re-aging treatment. Bright field imaging, centred dark field imaging and selected area diffraction were used to observe and identify structures and phases in the material. The transmission electron microscope, Hitachi H-800, was operated at 200 KV.

4.4.5.2 STEM + EDX

Scanning transmission electron microscopy (STEM), combined with EDX analysis, was performed in order to detect composition profile across grain boundaries in the Al-Li alloy and the effect of the re-aging treatment. Quantitative analyses at points along a line across a grain boundary and directly on a precipitate, or between two precipitates, were conducted.

4.4.5.3 EELS

Lithium in the Al-Li alloy is a light element which is not detectable by the common analytical X-ray techniques like EDX analysis and WDX analysis. Therefore, electron energy loss spectroscopy (EELS) was used, in order to study the compositional distribution of Li in the material. Attempts were made to find the Li excitation edge and the shift of the plasmon peak energy which can be related to the local composition [194,195].
5 Results

5.1 Electrochemical behaviour

5.1.1 Al-Li alloy

The potentiodynamic polarization behaviour of the as-received Al-Li alloy (T8771) in the chloride solutions is shown in Figure 5.1. The alloy exhibited different polarization behaviour in the two chloride solutions, particularly with respect to the open circuit potential \(E_{\text{oc}}\), passivity and the pitting potential \(E_{\text{pt}}\). The polarization curve obtained in 0.6 M NaCl shows an \(E_{\text{oc}}\) near \(-1.025\) V \(V_{\text{SCB}}\) and a series of very low anodic current densities \(\leq 3 \times 10^{-8}\) A/mm\(^2\), as the potential is raised \(-350\) mV above \(E_{\text{oc}}\), that is consistent with the presence of a passive film. Near \(-0.705\) V \(V_{\text{SCB}}\), there is a pronounced increase in current that is characteristic of film breakdown and the onset of pitting, suggesting that the pitting potential \(E_{\text{pt}}\) is close to \(-0.705\) V \(V_{\text{SCB}}\). The curve obtained in 1 M AlCl\(_3\) shows a higher \(E_{\text{oc}}\) near \(-0.875\) V \(V_{\text{SCB}}\), a narrow poorly defined region of passivity with a higher current density of \(-5 \times 10^{-7}\) A/mm\(^2\), and a much lower \(E_{\text{pt}}\) near \(-0.785\) V \(V_{\text{SCB}}\). The differences in polarization behaviour are readily attributable to the large difference in chloride ion concentration between the two solutions, and the acidic nature of the 1 M AlCl\(_3\) (pH = 2.0) relative to the near neutral 0.6 M NaCl (pH = 6.0).

Thermodynamic equilibria in aqueous solutions at one atmospheric pressure and 25 °C [196] show that the potential, \(E_{\text{H}_2}\), below which it is possible to reduce H\(^+\) ions to hydrogen is given with respect to the standard hydrogen electrode (SHE) by Equation (5.1),

\[
E_{\text{H}_2} = -0.059pH, V_{\text{SHE}} \tag{5.1}
\]
Consequently, since the conversion from the SHE to the SCE scale is obtained via the relationship $V_{SCE} = -0.242 + V_{SHE}$, Equation (5.2) gives $E_{H_2}$ on the SCE scale,

$$E_{H_2} = -0.242 - 0.059pH, V_{SCE}$$  (5.2)

Therefore, with respect to Figure 5.1, hydrogen can be evolved on the alloy surface at potentials $\leq -0.360 \ V_{SCE}$ in 1 M AlCl$_3$, and $\leq -0.596 \ V_{SCE}$ in 0.6 M NaCl.

Electrochemical studies were conducted with specimens of different exposed surface orientations (S and T). Changing the orientation did not produce any obvious effect on the polarization behaviour, even though the material has an anisotropic grain structure so that specimens of different orientations expose different portions of grain and grain boundary regions. The orientation-independence of the polarization behaviour of the highly textured material is consistent with the study of Yasuda et al. [200] on Al-Cu single crystals, where it was shown that the presence of alloyed Cu reduces the dependence of $E_{ph}$ on surface orientation so that $E_{ph}$ becomes invariant at Cu level above $\sim$1 wt.%. The re-aged alloy showed no difference in electrochemical polarization behaviour either.

The appearances of metallographically polished T-surfaces of both the as-received and re-aged materials, after immersion in 1 M AlCl$_3$ under freely corroding conditions at room temperature ($\sim$22 °C) for $\sim$20 hours, are shown in Figure 5.2. It is seen that the materials were attacked preferentially along lines which delineate the grain boundaries. However, no significant difference can be seen in the intergranular attack between the two tempers. Figure 5.3 shows the same surfaces after continuing the immersion in 1 M AlCl$_3$ solution to 170 hours. It is obvious that the material is not as badly corroded in the re-aged temper as in the as-received temper. When sectioning was made perpendicular to these surfaces, as shown in Figure 5.4, it revealed that the intergranular attack depth was much larger for material in the as-received
Figure 5.1 Potentiodynamic polarization behavior of Al-Li alloy 8090-T8771 in 0.6 M NaCl and 1 M AlCl₃.
Results

temper than in the re-aged temper. These differences indicate that the short time re-aging treatment was able to cause changes in the material which affect its corrosion behaviour. Analyses of the sectioned surfaces by SEM + EDX suggested that the corrosion may be related to the local Cu content distribution, because Cu-rich particles were unattacked while materials around them were eaten away, as shown, for example, in Figure 5.5. Further studies were conducted with precipitates-containing intergranular fracture surface obtained by monotonic loading, in order to locate the sites where corrosion starts preferentially. The results are illustrated in Figure 5.6, where a comparison is made between the same location before and after immersion (corrosion) in 1 M AlCl₃ for ~12 hours. It is evident that corrosion occurred preferentially at sites where there were precipitates and/or where precipitates had been pulled out during the previous mechanical fracture. One Cu-rich precipitate (identified by EDX) remained while the others disappeared after the immersion. The disappearance of the particles may be due to either the corrosion of the particles themselves or the corrosion of the materials around them that the particles fall out subsequently. With regard to the cavity growth at Site A in Figure 5.6 and consistent with Figure 5.5, the corrosion of the materials around the particles is considered more likely. The sites where corrosion starts preferentially are likely to be associated with Cu-depleted regions in the matrix around Cu-rich precipitates, based on the effects of local Cu concentration on localized corrosion of aluminium alloys [200,201].
Figure 5.2 Appearance of polished surfaces (T orientation) of Al-Li 8090 after freely corroding in 1 M AlCl₃ for ~20 hours.

(a) As-received; (b) re-aged.
Figure 5.3 Appearance of polished surfaces (T orientation) of Al-Li 8090 after freely corroding in 1 M AlCl₃ for ~170 hours.

(a) As-received; (b) re-aged.
Figure 5.4 Sectioning parallel to the L plane showing depths of intergranular corrosion after corroding in 1 M AlCl₃ for 170 hours.

(a) As-received; (b) re-aged.
Figure 5.5 SEM + EDX analysis of the intergranularly corroded slots in the re-aged Al-Li alloy, showing uncorroded Cu-containing particle.

(a) Line scan position; (b) Cu X-ray line scan.
Figure 5.6 SEM micrographs showing location of Cu-rich particle containing intergranular surface of the re-aged Al-Li alloy before and after corroding in 1 M AlCl₃ for ~12 hours.

(a) Before the corrosion; (b) after the corrosion.
5.1.2 Al-Cu alloy

The potentiodynamic polarization behaviour of the Al-Cu alloy in the chloride solutions was similar to the Al-Li alloy. Representative polarization curves for the Al-Cu alloy are shown in Figure 5.7, where the test in the acidic 1 M AlCl₃ shows a higher \( E_{\infty} \), a lower \( E_{pc} \) and a narrow poorly defined region of passivity with a higher current density than in the neutral 0.6 M NaCl. Also, in 1 M AlCl₃, \( E_{\infty} \) of the Al-Cu alloy is \(-0.725\) V\(_{SCB}\), \( E_{pc} \) is \(-0.670\) V\(_{SCB}\) and the passivation current density is \( \leq 10^{-6} \) A/mm\(^2\). Corresponding values in 0.6 M NaCl are \( E_{\infty} = \sim-0.960\) V\(_{SCB}\), \( E_{pc} = \sim-0.650\) V\(_{SCB}\) and the passivation current is \( \leq 3 \times 10^{-8} \) A/mm\(^2\).

The Al-Cu alloy exhibited slightly higher pitting potential than the Al-Li alloy in both chloride solutions, suggesting a slightly better resistance to pitting corrosion.
Figure 5.7 Potentiodynamic polarization behavior of Al-Cu alloy 2024-T351 in 0.6 M NaCl and 1 M AlCl₃.
5.2 Crack growth behaviour

5.2.1 Al-Li alloy

5.2.1.1 T-L crack plane orientation, 80 Hz loading frequency

The corrosion fatigue crack propagation behaviour of the as-received Al-Li alloy in the chloride solutions, distilled water and desiccated air at about 80 Hz loading frequency is shown in Figure 5.8. Crack growth rates \( (da/dN) \) increased with rising \( \Delta K \) in all the aqueous environments, with the AlCl₃ solution producing the highest rates and causing the most deleterious effects in the very low \( \Delta K \) region. The threshold of cyclic stress intensity \( (\Delta K_{th}) \) was reproducibly close to 1.05 MPa.m\(^{1/2}\) in 1 M AlCl₃, whereas \( \Delta K_{th} \) was higher and close to 1.7 MPa.m\(^{1/2}\) in 0.6 M NaCl and distilled water. Between a \( \Delta K \) of 2.2 and 4.0 MPa.m\(^{1/2}\), crack growth rates in both chloride solution were similar and slightly higher than those in distilled water. Above a \( \Delta K \) of \(~4.0\) MPa.m\(^{1/2}\), the fatigue curves obtained in the aqueous environments converged and crack growth kinetics became independent of solution composition. In this region, the aqueous fatigue curves obeyed a power law relationship, \( da/dN \propto (\Delta K)^n \) with \( n = -4 \), that is typical of Stage II fatigue behaviour.

Changing the environment to desiccated air caused a remarkable and reproducible difference in crack growth behaviour. In particular, the crack growth rates became essentially independent of \( \Delta K \) above \(~3\) MPa.m\(^{1/2}\), resulting in a crack rate plateau where \( da/dN \) was \(~2 \times 10^{-6}\) mm/cycle. This plateau extended into the region of Stage II cracking. Consequently, at \( \Delta K \sim 9 \) MPa.m\(^{1/2}\) (where \( \Delta K \) is based on crack length measurements made at the specimen
Figure 5.8 Effect of environment and $\Delta K$ on the growth of fatigue cracks in Al-Li alloy 8090-T871 at ~80 Hz.

$\Delta K$ (MPa.m$^{1/2}$)

$d\alpha/dN$ (mm/cycle)

($R=0.5$, ~22°C, ~80 Hz, T-L Orientation)

- $1$ M AlCl$_3$, Ecorr
- $0.6$ M NaCl, Ecorr
- Distilled Water
- Desiccated Air

Results
Results

surface), crack growth rates in desiccated air were \( \sim 100 \) times lower than those in the aqueous environments\(^1\). However, the near-threshold behaviour was indistinguishable from that in 0.6 M NaCl and distilled water, where \( \Delta K_{th} \) was \( \sim 1.7 \) MPa.m\(^{1/2}\).

The average \( E_{corr} \) potentials of specimens fatigued in 0.6 M NaCl and 1.0 M AlCl\(_3\) were \( \sim -0.730 \) V\(_{SCC}\) and \( \sim -0.780 \) V\(_{SCC}\), respectively. Comparison with Figure 5.1 shows that these are close to or coincident with the \( E_{pit} \) potentials in each solution, indicating the possibility of localized electrochemical dissolution processes during fatigue. In addition, comparison of each \( E_{corr} \) with Equation (5.2) confirms that hydrogen could have been evolving simultaneously on the alloy surface.

Some modified fatigue tests were conducted to study the effect of changing the testing environment from aqueous to the dry air condition on the crack growth behaviour of the same test specimen. Figure 5.9 shows the result of a fatigue test conducted in two different environments consecutively. The test was first conducted in distilled water until the \( \Delta K \) reached the value of 5 MPa.m\(^{1/2}\). Then the distilled water environment was removed and the specimen was put in a vacuum chamber for 72 hours to remove remaining water and any possible reversible hydrogen embrittlement effects\([192]\). The fatigue test was then continued in desiccated air environment. It is clear that the cracking rate dropped an order of magnitude abruptly from the value in distilled water to that in desiccated air, and was followed up by a crack rate plateau. Another fatigue test in desiccated air was started from a \( \Delta K \) of 5 MPa.m\(^{1/2}\) and exhibited the crack rate plateau right from the onset of cracking, which continued to an apparent \( \Delta K \) value of 50 MPa.m\(^{1/2}\) at the finish of the test (Figure 5.10). The corresponding apparent \( K_{max} \) value

\(^1\) It will be shown later in Section 5.4.1.1 that at \( \Delta K > 3 \) MPa.m\(^{1/2}\), the crack front in desiccated air is non-linear and that the \( \Delta K \) values in this environment are apparent values and not true values.
Results

at the termination of the test was ~100 MPa.m$^{1/2}$ and is well above the fracture toughness ($K_{IC}$) value reported in Table 4.2. Additional high frequency tests were conducted with a hydrogen precharged specimen, and a specimen subjected to continuous hydrogen charging. The fatigue crack propagation behaviour of the hydrogen precharged specimen in desiccated air is shown in Figure 5.11, where the crack growth rate plateau still persists. The fatigue crack propagation behaviour of the specimen under constant hydrogen charging condition is shown in Figure 5.12. With continuous on-site hydrogen production at the crack tip, the crack propagation curve is similar to those obtained in the aqueous testing environments, where a crack rate plateau is absent. The test conditions for Figure 5.12 were such that the specimen was controlled at a potential of -2.1 V$_{SCE}$ in 1 M HCl solution which was circulated around the specimen with a pump. The potential was chosen to place the alloy in the corrosion immunity region for Al ($E_{Al^{+++}/Al} = -2.02$ V$_{SCE}$ for [Al$^{+++}$] = 10$^{-6}$ [196]) so that hydrogen effects were dominant. The circulated acidic solution was chosen in order to maintain the pH at the metal surface and avoid severe corrosion of the specimen surface caused by local alkalization. Under highly hydrogen charging conditions the reduction of hydrogen ions can increase the local surface pH and tarnish the specimen surface, making crack monitoring with the travelling microscope very difficult.
Figure 5.9 Consecutive fatigue crack growth behaviour in Al-Li alloy 8090-T8771 when the testing environment is changed from distilled water to desiccated air.
Figure 5.10 Fatigue crack growth behaviour in Al-Li alloy 8090-T8771 at -80 Hz in desiccated air, starting from $\Delta K = 5\,\text{MPa.m}^{1/2}$. (Note: $\Delta K$ values are apparent values.)
Figure 5.11 Fatigue crack growth behaviour in Al-Li alloy 8090-T8771 at ~80 Hz in desiccated air after hydrogen precharge. (Note: \( \Delta K \) values are apparent values.)
Figure 5.12 Fatigue crack growth in Al-Li alloy 8090-T871 at −80 Hz in 1 M HCl solution under controlled potential of −2.1 V vs. In this potential and pH condition, Al is in the immunity region and the rate of hydrogen evolution is high.
5.2.1.2 T-L crack plane orientation, 0.5 Hz loading frequency

The corrosion fatigue crack propagation behaviour in the chloride solutions, distilled water and desiccated air at a loading frequency of 0.5 Hz is shown in Figure 5.13. The cracking rates in 1 M AlCl₃ and 0.6 M NaCl solutions showed similar behaviour in the range of ΔK investigated. The cracking rates in distilled water and desiccated air were not largely different from each other, however they were lower than those in the chloride solutions. Also, the crack growth rate curves in distilled water and desiccated air show an apparent cyclic stress intensity threshold of about 5.5 MPa.m¹⁄₂, which is much higher than the threshold values observed during the high frequency tests. The average $E_{\text{corr}}$ potentials monitored during fatigue at ~0.5 Hz in 0.6 M NaCl and 1 M AlCl₃ were ~0.810 V_{SCB} and ~0.780 V_{SCB} respectively.

5.2.1.3 S-L crack plane orientation, 30 Hz loading frequency

The microhardness and fracture toughness values of Al-Li 8090-T8771 before and after the re-aging treatment are listed in Table 5.1. The re-aging treatment doubled the fracture toughness with only ~8% decrease in hardness, consistent with reported data in the literature [112]. The data confirm that the re-aging treatment is an effective way to improve the S-L orientation fracture toughness with only minor sacrifice in strength (hardness).

The fatigue crack propagation behaviour of the Al-Li alloy in both the as-received and re-aged states when tested in a desiccated air environment is shown in Figure 5.14. It is obvious that fatigue crack propagation is faster and the threshold stress intensity ($\Delta K_{\text{th}}$) for crack propagation is lower in the re-aged temper in desiccated air. Figure 5.15 shows the crack growth behaviour in 1 M AlCl₃ solution under free corrosion condition, where it is seen that there is no
Figure 5.13 Effect of environment and $\Delta K$ on the growth of fatigue cracks in Al-Li alloy 8090-T8771 at -0.5 Hz.
difference between the as-received and re-aged tempers. Figure 5.16 shows the cracking behaviour in distilled water and again there is no observable difference between the two tempers. However, when compared with the crack propagation behaviour in desiccated air, it is seen that the AlCl₃ environment accelerated crack growth of both tempers by both increasing the cracking rate and decreasing the threshold value ΔKₐ₀, whereas the distilled water only increased the cracking rates of both tempers at ΔK ≥ −2 MPa.m¹/². Below ΔK value of −2 MPa.m¹/² the cracking rates were decreased in distilled water and showed a higher ΔKₐ₀ than in desiccated air. The ΔKₐ₀ values of the two tempers in the different environments are summarized in Table 5.2. The cracking in 0.6 M NaCl solution under free corrosion condition was not well defined and the data were very scattered because of problems arising from crack retardation effects. The average $E_{corr}$ potentials during fatigue at 30 Hz in 0.6 M NaCl and 1 M AlCl₃ were −0.730 V_sc and −0.780 V_sc respectively.

| Table 5.1 Values of Microhardness ($H_v$) and Short Transverse (S-L) Orientation Fracture Toughness ($K_{IC}$) |
|---------------------------------|---------------------------------|
| **As-received (T8771)**         | **Re-aged (230 °C, 10 minutes)** |
| $H_v$                          | $K_{IC}$ (MPa.m¹/²)              |
| 159                            | ~14.7                           |
| $H_v$                          | $K_{IC}$ (MPa.m¹/²)              |
| 146                            | ~29.8                           |
Table 5.2 Threshold Cyclic Stress Intensities ($\Delta K_{th}$) for S-L Fatigue Cracking in the Two Tempers of the Al-Li Alloy in Different Environments

<table>
<thead>
<tr>
<th>Environment</th>
<th>As-received $\Delta K_{th}$ (MPa.m$^{1/2}$)</th>
<th>Re-aged $\Delta K_{th}$ (MPa.m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desiccated Air</td>
<td>~1.6</td>
<td>~1.3</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>~1.8</td>
<td>~1.8</td>
</tr>
<tr>
<td>1 M AlCl$_3$</td>
<td>~1.0</td>
<td>~1.0</td>
</tr>
</tbody>
</table>

When compared to the T-L orientation fatigue crack growth data at ~80 Hz, crack propagation resistance in the S-L orientation is lower by showing faster cracking rates and lower $\Delta K_{th}$ values.

5.2.2 Al-Cu alloy

5.2.2.1 T-L crack plane orientation, 80 Hz loading frequency

The T-L orientation crack propagation behaviour of the as-received Al-Cu alloy in 1 M AlCl$_3$, 0.6 M NaCl, distilled water and desiccated air environments at the testing frequencies of ~80 Hz is shown in Figure 5.17. There was little difference between the cracking behaviour in 0.6 M NaCl, distilled water and desiccated air. While in 1 M AlCl$_3$, the crack propagation threshold $\Delta K_{th}$ was reduced to ~1 MPa.m$^{1/2}$, with respect to the value of ~2 MPa.m$^{1/2}$ in the other environments. In the relatively high $\Delta K$ region (i.e $\Delta K > ~4$ MPa.m$^{1/2}$), the cracking rates in 1
Results

M AlCl$_3$ converged with those in the other environments. The average $E_{\text{corr}}$ potentials monitored during fatigue at $\sim$80 Hz in 0.6 M NaCl and 1 M AlCl$_3$ were $-0.640$ $V_{\text{SCB}}$ and $-0.700$ $V_{\text{SCB}}$ respectively.

The crack growth rate curves of the Al-Cu alloy are very similar to those of the Al-Li alloy in the respective aqueous environment.

5.2.2.2 T-L crack plane orientation, 0.5 Hz loading frequency

The crack growth behaviour of Al-Cu alloy in the same four environments at 0.5 Hz loading frequency is shown in Figure 5.18. Crack growth rates were similar in 0.6 M NaCl, distilled water and desiccated air environments over the whole range of $\Delta K$ investigated. Crack propagation was accelerated in 1 M AlCl$_3$ in the lower end of the $\Delta K$ range investigated (i.e. near $\sim$5 MPa.m$^{1/2}$), and merged with cracking rates in the other environments at the higher $\Delta K$ end (i.e. above $\sim$8 MPa.m$^{1/2}$). For tests in distilled water and desiccated air, the curve shows an apparent threshold cyclic stress intensity of $\sim$5.5 MPa.m$^{1/2}$. When compared to the high frequency results, the major difference in behaviour is the decreased crack growth per cycle at the low frequency in the low end of the $\Delta K$ range investigated. The average $E_{\text{corr}}$ potentials during fatigue at $\sim$0.5 Hz in 0.6 M NaCl and 1 M AlCl$_3$ were $-0.700$ $V_{\text{SCB}}$ and $-0.710$ $V_{\text{SCB}}$ respectively.
Figure 5.14 Fatigue crack growth in the S-L orientation of the Al-Li alloy plate in desiccated air at -30 Hz.
Figure 5.15 Fatigue crack growth in the S-L orientation of the Al-Li alloy plate in 1 M AlCl₃ at ~30 Hz.
Figure 5.16 Fatigue crack growth in the S-L orientation of the Al-Li alloy plate in distilled water at -30 Hz.
Figure 5.17 Effect of environment and $\Delta K$ on the growth of fatigue cracks in Al-Cu alloy 2024-T351 at ~80 Hz.
Figure 5.18 Effect of environment and $\Delta K$ on the growth of fatigue cracks in Al-Cu alloy 2024-T351 at ~0.5 Hz.
5.3 Fractography

5.3.1 Al-Li alloy

5.3.1.1 T-L crack plane orientation, 80 Hz loading frequency

Transgranular cracking was the predominant mode of crack propagation in both the near threshold Stage I region and the linear Stage II region (or Paris law region) for the Al-Li alloy when tested in all four environments at the high loading frequency (~80 Hz). With the exception of the AlCl₃ solution, the threshold fractography was very similar in the different environments, consistent with the similarity in their crack growth behaviour near ΔKₐ. A representative fractograph, typical of the desiccated air, distilled water and NaCl environments, is shown for distilled water in Figure 5.19a. Numerous fine scale tear and shear ridges (river lines) are evident which are inclined to the macroscopic direction of propagation. Therefore, assuming that these ridges are normal to the local direction of the propagating crack front, the fractography indicated that the crack front was not straight on the microscopic scale; instead, it was composed of a series of tongues that linked together by the widening of the tongues in the wake of the propagating crack tip. A schematic diagram illustrating the tongue-like nature of the propagating crack front is shown in Figure 5.19b.

The near threshold fractography obtained in the AlCl₃ was different from the other environments. A distinguishing feature was the large degree of secondary cracking (splitting) normal to the primary crack plane (i.e. the splits were consistent with S-L orientation cracking). The splitting was microstructure dependent and occurred along grain boundaries, whereas the primary crack plane (T-L orientation cracking) followed a transgranular path. Figure 5.20 shows
Figure 5.19 (a) SEM fractograph showing transgranular fracture surface of Al-Li alloy specimen fatigued at ~80 Hz in distilled water near $\Delta K_{th}$. Macroscopic direction of crack propagation is from the right to the left of the page.

(b) Schematic diagram of the transgranular crack front in the primary crack plane showing tongues extending into uncracked material, with uncracked ligaments between the tongues.
Results

the characteristic splitting (delamination) features observed near $\Delta K_n$ (i.e. near $\Delta K \approx 1$ MPa.m$^{1/2}$).

Increasing the $\Delta K$ caused significant change in the degree of S-L splitting in all environments. Splitting was quantified by measuring the number ($N_b$) of splits across the width of the specimen, using linear intercept analyses conducted in the SEM. In the cases of distilled water and 0.6 M NaCl, the number of splits was found to increase from near zero at $\Delta K_n$ and reached a peak at $\Delta K$ values of $\sim5$ to $\sim6$ MPa.m$^{1/2}$. This was followed by a decreasing number of splits as $\Delta K$ continued to increase. Tests in 1 M AlCl$_3$ showed that the number of splits decreased from a maximum at $\Delta K_n$ to a minimum as $\Delta K$ increased to $\sim3$ MPa.m$^{1/2}$. Thereafter, the splitting behaviour imitated that in the other aqueous environment by exhibiting a peak at $\sim5$ MPa.m$^{1/2}$. Splitting effects in desiccated air were very small relative to the aqueous environments and were virtually independent of $\Delta K$. Details of the splitting analyses are presented in Figure 5.21.

The large number of splits at $\Delta K_n$ in the AlCl$_3$ solution appeared to be related primarily to localized stress-independent dissolution of the grain boundaries, because the precracked fracture surface, which was not fatigued in AlCl$_3$, also exhibited the same degree of splitting. An example of this phenomenon is shown in Figure 5.22. The precracked fracture surface of specimens tested in the other environments did not show the splits. Consequently, it follows that the decreasing degree of splitting as $\Delta K$ increased to $\sim3$ MPa.m$^{1/2}$ was due primarily to the fact that the propagating crack front spent increasingly smaller amounts of time in contact with the solution, thereby causing increasingly smaller amounts of grain boundary dissolution. Localized dissolution processes are consistent with the observation that $E_{\text{corr}}$ during fatigue was close to $E_{\text{p pit}}$ and that the anodic dissolution current at $E_{\text{p pit}}$ was much higher in the 1 M AlCl$_3$ solution than in NaCl (see Figure 5.1). The result of severe intergranular corrosion in the AlCl$_3$
Figure 5.20 SEM fractograph of Al-Li alloy specimen fatigued at ~80 Hz in 1 M AlCl₃ near ΔKₐ, showing transgranular cracking on the primary crack plane and S-L splitting of grain boundaries normal to the primary plane. Macroscopic direction of crack propagation is from the right to the left of the page.
local crack front. The average spacing of these striations is $\sim 1 \times 10^{-4}$ mm corresponding very well with an average crack propagation rate of $\sim 1 \times 10^{-4}$ mm/cycle for the testing conditions (see Figure 5.8) and providing further support for the interpretation of Figure 5.25.

Figure 5.26 shows the region of fracture surface when the test environment is changed from distilled water to desiccated air. The secondary cracks (splits) produced in distilled water disappeared in the desiccated air environment, and the fracture surface changed to contain large facets. Fracture surfaces from the fatigue test conducted under constant hydrogen charging at -2.1 $V_{SCB}$ also contained splits, as shown by the results of the SEM analyses in Figure 5.27. In a similar manner to behaviour in distilled water and 0.6 M NaCl environments, the number of splits increased from about zero at $\Delta K_b$ and peaked at intermediate $\Delta K$ values of $\sim 7$ MPa.m$^{1/2}$.

In addition, detailed studies of the near-threshold fractography were conducted by examining stereo pairs of opposing fracture surfaces. In this manner, it was found that the fractographic features on the opposing surfaces interlocked (i.e. matched peak to valley). An example is shown in Figure 5.28 for a test conducted in distilled water. The production of this fractography is easily explainable by the restricted slip reversibility (RSR) model [41,42] for fatigue cracking, where alternative slip systems are operating in the near threshold region. However, using the same matching surface techniques, it is less certain whether the fractographic striations produced in Stage II are matching on opposing fracture surfaces in a peak to peak or peak to valley mode, as shown in Figure 5.29. From the crack tip blunting and re-sharpening model [43] for Stage II fatigue crack growth, it would be expected that the match on opposing fracture surfaces should be peak to peak and valley to valley (i.e. mirror images).
Figure 5.21 Effect of environment and AK on the number of splits (N^p) across the thickness of the T-L orientation Al-Li 8090-T8771 specimen fatigued at ~80 Hz.
immersion tests supports the above conclusion. Furthermore, consistency of reasoning leads to the conclusion that the increasing degree of splitting as \( \Delta K \) rises to values of \(-5\) to \(-6\) MPa.m\(^{1/2}\), observed in all the aqueous environments, was due to a synergism between the cyclic load and the environment.

Optical microscopy studies of sectioned specimens showed that the depth of penetration of the splits below the primary crack plane often reached \(~200\ \mu\text{m}\) or more in Stage II. This is seen in Figure 5.23 for a specimen fatigued at \(~80\) Hz in 0.6 M NaCl and then sectioned through the primary crack plane at the position corresponding to \( \Delta K = 5\) MPa.m\(^{1/2}\). The grain structure was revealed by Keller's etchant and shows the intergranular path followed by the splits. Some tests were terminated in Stage II after reaching a \( \Delta K \) condition corresponding to the formation of the peak number of splits. In these cases, each specimen was sectioned behind the leading edge of the main crack and carefully polished towards the crack front until the first tongue-like penetrations of the crack could be detected. The result is shown in Figure 5.24 for a test in the NaCl solution and clearly shows a section through two tongues, one on the left and one on the right side of the micrograph. A vertical split is present that is not connected to either tongue, confirming that the split extends ahead of the crack front. Consequently, it is possible that such splits can assist linkage of uncracked ligaments between the crack front tongues by acting as initiation sites for microcracks which subsequently propagate away from the split along the primary crack plane. Detailed SEM fractography observations supported this possibility, as shown in Figure 5.25 for \( \Delta K = 6\) MPa.m\(^{1/2}\), where the orientation of river lines clearly indicates that local microcracks initiated at a split and propagated away from the split in a direction that was inclined to the overall direction of macroscopic crack propagation. Furthermore, very faint striations are detectable normal to the river lines and they indicate successive positions of the
Results

Figure 5.22 SEM micrograph of Al-Li alloy 8090-T8711 specimen precracked surface exposed to 1 M AlCl₃ during -80 Hz test. Area shows localized dissolution of grain boundaries.
Figure 5.23  Optical micrograph of sectioned and etched Al-Li alloy 8090-T8771 specimen fatigued at \(-80\) Hz in 0.6 M NaCl. Sectioned normal to the primary crack plane in Stage II at \(\Delta K = 5\) MPa.m\(^{1/2}\).
Figure 5.24 Optical micrograph of sectioned and etched Al-Li alloy 8090-T8771 specimen fatigued at ~80 Hz in 0.6 M NaCl. Test terminated in Stage II and sectioned normal to the primary crack plane very close to the main crack front.
Figure 5.25 SEM fractograph of Stage II cracking ($\Delta K = 6 \text{ MPa.m}^{1/2}$) of Al-Li 8090-T8771 in 0.6 M NaCl at ~80 Hz, showing river patterns running away from the S-L split. Note very faint striations normal to the river lines. Macroscopic cracking direction is from the right to the left of the page.
Figure 5.26 SEM fractograph showing change of fatigue fracture surface of Al-Li 8090-T771 produced at ~80 Hz in distilled water and desiccated air consecutively. Macroscopic cracking direction is from the right to the left of the page.
Figure 5.27 Change of the number of splits ($N_b$) across the thickness of the T-L orientation Al-Li 8090-T8771 specimen with $\Delta K$, when fatigued at ~80 Hz under continuous hydrogen charging at -2.1 $V_{SCF}$. 
Figure 5.28 SEM fractographs of near $\Delta K_{th}$ cracking of Al-Li alloy 8090-T8771 in distilled water at ~80 Hz. The opposing fracture surfaces indicating a "peak to valley" match of small details. Macroscopic cracking direction is from the top to the bottom of the page.
Figure 5.29 SEM fractographs of matching fatigue fracture surfaces of Al-Li alloy 8090-T8771 produced by Stage II cracking ($\Delta K = 6 \text{ MPa.m}^{1/2}$) in distilled water at ~80 Hz. Macroscopic cracking direction is from the top to the bottom of the page.
5.3.1.2 T-L crack plane orientation, 0.5 Hz loading frequency

Changing the loading frequency of the fatigue tests to ~0.5 Hz did not cause any obvious change in the fractography obtained. In the ΔK range tested, the fractography was still predominantly transgranular, as shown in Figure 5.30 for fracture surfaces produced in desiccated air. Similar split number analyses to those at the high loading frequency were conducted, the result is shown in Figure 5.31.

5.3.1.3 S-L crack plane orientation, 30 Hz loading frequency

Fractographic studies of surfaces obtained from the fracture toughness tests and fatigue tests in the S-L orientation showed that the crack path followed the "pan cake" grain boundaries, i.e. the cracking was intergranular. Figure 5.32 shows the fracture surfaces from the $K_{IC}$ tests of the material in both the as-received and re-aged tempers, with the transition between the fatigue precracked region and the monotonic loading cracked region located near the centre of the respective micrograph. Careful SEM examination close to the transition region of the re-aged specimen showed that the monotonically loaded fracture surface exhibited continuous fine scale dimples, characteristic of a ductile microvoid coalescence process, whereas the adjacent precracked surface was relatively featureless with no dimples. In addition, trenches were observed lying normal to the primary crack in the transition region. For the as-received material, the fracture surface showed discontinuous patches of dimple features on the monotonically loaded side of the transition region. These were interspersed with patches of featureless surface. Also no trenches were found in the transition region. At locations more distant from the transition region, the monotonically overloaded fracture surface of both the as-received and re-aged tempers showed a patchy fractographic mixture of dimpled and smooth features.
Figure 5.30 SEM fractograph showing transgranular fracture surface of Al-Li 8090-T8771 specimen fatigued at ~0.5 Hz in desiccated air. \( \Delta K = \sim 6 \text{ MPa.m}^{1/2} \), location near the mid-thickness of the specimen. Macroscopic direction of crack propagation is from the right to the left of the page. Micrograph (b) shows the central region of Micrograph (a) in higher magnification.
Figure 5.31 Effect of environment and $\Delta K$ on the number of splits ($N_B$) across the thickness of the T-L orientation Al-Li 8090-T8771 specimen fatigued at ~0.5 Hz.
Figure 5.32 SEM fractographs showing transition from fatigue precracking to monotonic overload fracture in the S-L orientation fracture toughness test specimens of Al-Li alloy 8090. Macroscopic cracking direction is from the right to the left of the page.

(a) As-received; (b) re-aged.
The S-L fatigue crack fractographies of the as-received and re-aged Al-Li alloys were very similar to each other when obtained in the same environment. The fractography was generally flat and featureless, and followed an intergranular path along the S-L orientation grain boundaries. Detailed differences in fractography between different environments could be related to environmental effects on the crack propagation rates. For example, Figure 5.33 compares the near threshold fatigue fracture surfaces of the re-aged material tested in distilled water and desiccated air. Dark features indicative of rubbing or fretting, and corrosion products are visible on the fracture surface obtained in distilled water, while a clean intergranular fracture surface was obtained in desiccated air. These differences are consistent with the higher threshold value in distilled water than in desiccated air, as displayed in the \( \frac{da}{dN} - \Delta K \) curves (Figure 5.14 and Figure 5.16), and can be attributed to corrosion product induced crack closure [38,58,59].

5.3.2 Al-Cu alloy

5.3.2.1 T-L crack plane orientation, 80 Hz loading frequency

The T-L fractography of the Al-Cu alloy tested in the different environments was also predominantly transgranular. Fractography in the near threshold cracking region showed a similar irregular crack front to the Al-Li alloys, with numerous tongues extending into the uncracked material and uncracked ligaments between the tongues. Figure 5.34a shows a micrograph obtained from a test in distilled water, and is typical of the other environments except AlCl₃. In the AlCl₃ environment, the fracture surface was more corroded (Figure 5.34b). As the crack grew into Stage II with increasing \( \Delta K \), well defined ductile striations began to
Results

appear on the fatigue crack surface in all environments. A characteristic striated fractography is shown in Figure 5.35, a test conducted in distilled water. Similar striations were observed in the other environment.

5.3.2.2 T-L crack plane orientation, 0.5 Hz loading frequency

Decreasing the loading frequency of the fatigue test from ~80 Hz to ~0.5 Hz did not cause any obvious change in fractography. When compared to the Al-Li alloy, no secondary cracking (splitting) effects were observed in the Al-Cu alloy. This is the major difference in fractography between the Al-Li and Al-Cu alloys.
Figure 5.33 SEM micrographs showing fatigue fracture surfaces of Al-Li alloy 8090 in the S-L orientation in the re-aged temper near $\Delta K_{\text{th}}$. Macroscopic cracking direction is from the right to the left of the page.

(a) In distilled water;  (b) in desiccated air.
Figure 5.34 SEM fractographs of near $\Delta K_{th}$ cracking of Al-Cu alloy 2024-T351 in the T-L orientation at $\sim 80$ Hz.

(a) In distilled water;  (b) in 1 M AlCl$_3$. 
Figure 5.35 SEM fractograph of Stage II cracking ($\Delta K = 8$ MPa.m$^{0.5}$) in Al-Cu alloy 2024-T351 in the T-L orientation in distilled water at ~80 Hz.
Results

5.4 Macroscopic fracture surface appearance, roughness and crack profile

5.4.1 Al-Li alloy

5.4.1.1 T-L crack plane orientation, 80 Hz loading frequency

For the Al-Li alloy tested at ~80 Hz, the T-L fatigue fracture surfaces produced in the aqueous environments were relatively flat on a macroscopic scale and remained in the initial crack plane, with no particular tendency for the crack to lead at the centre or edge of the specimen. A typical example is shown in Figure 5.36a for two opposing fracture surfaces of a specimen tested in the AlCl₃ solution. The fatigue crack was allowed to propagate until the overall crack length (a) was ~48 mm, after which the test was terminated and the specimen opened by increasing the load monotonically until unstable crack propagation occurred upon reaching $K_{IC}$.

Fatigue surfaces obtained in desiccated air exhibited a characteristically different macroscopic appearance from other tests, as shown for opposing fracture surfaces in Figure 5.36b. Initially, the crack remained relatively flat and stayed in the original crack plane until $\Delta K$ reached ~3 MPa.m$^{1/2}$, corresponding to $a = 31$ mm in Figure 5.36b. Beyond this point, the crack started to deviate (climb out of the cracking plane) near the centre of the specimen. As the crack continued to propagate, the deviation increased in height and width in the central region while the outer sections of the crack front remained in the original macroscopic cracking plane. The result was the production of a centrally ridged fracture surface as shown in Figure 5.37a, and the angle of the ridge with respect to the original macroscopic crack plane is ~60° (Figure 5.37b). With reference to the crack length scale in Figure 5.36b and the $\Delta K$ values in Figure 5.8, the ridge was 2 mm in height at $a = 34$ mm and $\Delta K = 4.6$ MPa.m$^{1/2}$, and 4 mm in
Figure 5.36 Macroscopic appearance of opposing fracture surfaces of Al-Li alloy 8090-T8771 tested in the T-L orientation at ~80 Hz. Scale shows crack length.

(a) In 1 M AlCl₃; (b) in desiccated air.
Results

height at \( a \approx 40 \text{ mm} \) and 8.4 MPa.m\(^{1/2}\). Furthermore, the formation of the ridge caused the crack front to trail in the centre of the specimen so that when the crack length at the surface was \( \approx 46 \text{ mm} \) it was only \( \approx 40 \text{ mm} \) at the centre. This trailing effect is clearly seen from the shape of the crack front in Figure 5.36b, where the specimen was fatigued until the surface length of the crack was \( \approx 46 \text{ mm} \) before terminating the test and opening the specimen. The trailing effect was confirmed by additional tests where the fatigue crack was allowed to reach a length of \( \approx 35.5 \text{ mm} \) at the surface, corresponding to an apparent \( \Delta K \) near 5.6 MPa.m\(^{1/2}\), after which the unopened specimen was sectioned and polished on a plane passing through \( a = 34.6 \text{ mm} \), corresponding to an apparent \( \Delta K \) near 5.0 MPa.m\(^{1/2}\). No crack was visible in the central \( \approx 46\% \) of the section width, but was present in each outer \( \approx 27\% \) (Figure 5.38), confirming that the crack was leading at the edges of the specimen and trailing at the centre. Furthermore, continued grinding and polishing of the specimen back to the plane where the apparent \( \Delta K \) was \( \approx 4 \text{ MPa.m}^{1/2} \) revealed a crack that was continuous across the thickness and ridged in the mid-thickness region (Figure 5.38), supporting the proposal that the trailing effect was directly associated with out-of-plane cracking. All of these observations show that at \( \Delta K > 3 \text{ MPa.m}^{1/2} \) the reported \( \Delta K \) values are apparent values only, due to the non-linearity of the crack front developed in this desiccated air environment.
Figure 5.37 (a) Schematic diagram of ridge formation in mid-thickness of specimens fatigued in the T-L orientation in desiccated air at ~80 Hz. Arrow shows direction of macroscopic crack propagation.

(b) The angle of the central ridge with respect to the original macroscopic crack plane.
Figure 5.38 Optical micrographs of sectioned and etched Al-Li 8090-T8771 specimen fatigued at −80 Hz in the T-L orientation in desiccated air. Sectioned normal to the primary crack plane.

(a) $\Delta K = 5 \text{ MPa.m}^{1/2}$; (b) $\Delta K = 4 \text{ MPa.m}^{1/2}$. 
Another significant observation arising from the study of surface roughness is that the $\Delta K$ value at which the central ridge began to form in desiccated air also corresponded very closely with the value of $\Delta K$ at which the crack rate plateau commenced in this environment (Figure 5.8). Fatigue test in desiccated air that commenced from a $\Delta K$ value of 5 MPa.m$^{1/2}$ is consistent with this observation because they exhibited a cracking rate plateau (Figure 5.10) and rough ridged fracture surface immediately. Ridge formation and an associated crack rate plateau were also observed in the hydrogen precharged specimen tested in desiccated air, whereas the continuously hydrogen charged specimen showed no ridge and no crack rate plateau (c.f. Figure 5.11 and Figure 5.12).

5.4.1.2 T-L crack plane orientation, 0.5 Hz loading frequency

The macroscopic fractography produced at 0.5 Hz loading frequency in the aqueous environments was similar to that of the ~80 Hz tests. The fracture surface produced in desiccated air at 0.5 Hz was much rougher than those in the other environments at the same loading frequency. However, the same large scale ridge as that in the centre of the specimen tested at ~80 Hz in desiccated air was not observed for the 0.5 Hz test. This is also consistent with the fact that no cracking rate plateau was observed for the 0.5 Hz test in desiccated air. This absence of the large ridge and the related crack growth rate plateau may be associated with the longer exposure times and lower crack tip deformation rates at the lower loading frequency, thereby allowing a greater degree of interaction between the environmental and mechanical effects during each load cycle.
5.4.1.3 S-L crack plane orientation, 30 Hz loading frequency

The S-L orientation fatigue cracking fracture surfaces were very flat on a macroscopic scale, and no obvious difference in surface roughness was observed among fatigue fracture surfaces produced in the different aqueous and dry environments. Also no obvious difference in surface roughness was observed between the as-received and the re-aged tempers.

5.4.2 Al-Cu alloy

For the Al-Cu alloy tested at ~80 and ~0.5 Hz in the T-L crack plane orientation, the macroscopic appearance of fatigue fracture surfaces produced in the different environments were much flatter than those of the Al-Li alloy produced in the aqueous environments. Figure 5.39 shows the macroscopic fracture surfaces of a specimen tested in 0.6 M NaCl at ~80 Hz that are typical of the other environments. Specimens sectioned at different $\Delta K$ values showed very linear crack front profiles as compared to the crack front profiles of the Al-Li alloy. A comparison of the sectioned alloys at $\Delta K = 5 \text{ MPa.m}^{1/2}$ is shown in Figure 5.40 for tests in 0.6 M NaCl.

Unlike the Al-Li alloy, fatigue tests on the Al-Cu alloy in desiccated air did not produce a ridged fracture surface and associated crack rate plateau at ~80 Hz. Similar to the Al-Li alloy, no ridge and no crack rate plateau were observed at ~0.5 Hz.
Figure 5.39 Macroscopic appearance of opposing fracture surfaces of Al-Cu alloy 2024-T351 fatigued in the T-L orientation in 0.6 M NaCl at ~80 Hz. Scale shows crack length.
Figure 5.40 Optical micrographs showing crack front profiles of specimens fatigued in the T-L orientation in 0.6 M NaCl at ~80 Hz. Sectioned normal to the primary crack plane at $\Delta K = 5$ MPa.m$^{1/2}$.

(a) Al-Cu alloy 2024-T351;  (b) Al-Li alloy 8090-T8771.
5.5 Microstructure and compositional distribution

Figure 5.41a shows the finely dispersed, precipitation hardening \( \delta' \) phase in the Al-Li alloy in the as-received temper (T8771). The appearance is the same as that reported by Blankenship *et al.* [113] for 8090-T8771. For the Al-Li alloy after the re-ageing treatment, similar micrographs were obtained (Figure 5.41b). Figure 5.42 shows the grain boundaries with precipitates on them. From TEM studies with both bright field and centred dark field imaging techniques, no difference was noticed regarding either the size or the distribution of the strengthening phases between the two tempers of materials. However, small changes in chemical composition between the two tempers were detected by STEM + EDX analyses. For example, Figure 5.43 compares changes in the Cu concentration of precipitates and matrix in the grain boundary region of the as-received and re-aged material. It is apparent that the grain boundary precipitates have become enriched in Cu in the re-aged alloy. Electron diffraction analyses were conducted to identify the Cu-containing precipitates in the boundary of the as-received and re-aged alloy. Analyses of the limited patterns obtained, and comparison with reported data in the literature [197-199], led to the conclusion that the precipitates in the boundary were close to the \( T_2 (Al_6CuLi_3) \) phase, as shown in detail in Appendix II.

The BELS analyses, conducted by searching the excitation edges and the plasmon peak energy shifts to detect Li distribution, did not produce useful results in the present study. The plasmon peak energy shifts measured with the Al-Li specimens relative to a pure Al (99.9995\%) indicated a change in the correct direction. However, no reproducible and sensible compositional profile could be drawn out from the multiple measurements conducted, due to the limited attainable resolution of the equipment and the accuracy of the energy shift measurements from the energy loss spectra (see Appendix III for detail).
Figure 5.41 TEM micrograph showing 8' phase in Al-Li alloy 8090. Centered dark field image. (a) As-received; (b) re-aged.
Figure 5.42 TEM micrograph showing precipitates containing grain boundaries in Al-Li alloy 8090-T8771. Bright field image.

(a) As-received; (b) re-aged.
Figure 5.43 STEM + EDX analyses showing Cu content profiles across a grain boundary containing precipitates.

(a) Grain boundary containing precipitates in the re-aged Al-Li alloy. The contamination cycles mark the locations of composition analyses;

(b) Cu content profiles through precipitates (average from 4 tests);

(c) Cu content profiles between or near precipitates (average from 4 tests).
Results

(b)

Distance from the Grain Boundary (nm)

Cu Content (wt. %)

As-received

Re-aged
6 Discussion

6.1 Corrosion fatigue crack propagation in the Al-Li alloy in the T-L orientation and comparison with the Al-Cu alloy

6.1.1 Role of splitting

It is clear from the experimental studies that the S-L splitting phenomenon plays an important role in the T-L orientation fatigue cracking behaviour of the Al-Li alloy at the high frequency (~80 Hz) and that the splitting tendency is influenced by environmental effects. Any tensile stress-dependent effects causing S-L splitting must arise from through-thickness stresses. It is well established that the stress state near the tip of a crack is significantly different from regions remote from the crack tip [32]. With respect to the T, L and S directions, three principal tensile stresses $\sigma_T$, $\sigma_L$, and $\sigma_S$ may be present due to constraints imposed by the less stressed material outside the crack tip region, as shown in Figure 6.1. The value of $\sigma_S$ drops to zero under plane stress conditions (relatively thin specimens) and has a value equal to $V(\sigma_T + \sigma_L)$ under plane strain conditions (relatively thick specimens), where $V$ is Poisson’s ratio [32]. Consequently, the through-thickness stress component contributing to the S-L splitting is due to $\sigma_S$. The significant effect of the environment on splitting is apparent from a comparison between the different test conditions. For example, significant splitting was observed in all the aqueous environments and the lowest $\Delta K_{th}$ was observed in the aqueous solution of AlCl$_3$, which promoted the largest degree of splitting in the low $\Delta K$ region. In contrast, out-of-plane cracking, the greatest macroscopic surface roughness, and a cracking rate plateau at $\Delta K$ values above ~3 MPa.m$^{1/2}$ were observed only in the non-aqueous environment (desiccated air), where negligible amounts of splitting occurred.
Figure 6.1 Schematic diagram showing the triaxial stress state near the tip of a crack.
The fractography indicated that splitting influences crack propagation by assisting the linkage of uncracked ligaments between crack front tongues, as shown schematically in Figure 6.2. Assuming that linkage occurs by slip dominated shear processes, then the implication is that additional local slip systems become operative during the linkage process. These additional systems are different variants of \( \{111\}<110> \) slip in the face centred cubic (FCC) matrix and operate simultaneously with other variants that control slip reversibility advance [41, 42] of the propagating crack front tongues. The situation may be envisaged as a change in the stress state in the local crack tip region, whereby a smaller degree of crack tip plasticity and lower number of slip systems are present under plane strain conditions, whereas a larger degree of crack tip plasticity and a larger number of slip systems are present under plane stress conditions. For example, with respect to Figure 6.1 and shown in Figure 6.3 [32], under plane strain conditions the principal shear stress planes at the crack tip are confined to planes that are parallel to the S-direction and inclined 45° with respect to the L-direction, with the maximum of the shear stress being \((\sigma_T - \sigma_L)/2\). Only slip plane variants oriented closely to these planes will be operative and the orientation of these planes are not conducive to shear linkage of uncracked ligaments. In contrast, under plane stress conditions, other principal shear stress planes become dominant. These are parallel to the L-direction and inclined 45° to the S direction, with the maximum of the shear stress being \(\sigma_T/2\) (which is higher than in the plane strain condition). Slip plane variants oriented closely to these planes now become operative, and the orientation of these planes favours the shear linkage of the uncracked ligaments. Consequently, splitting may exert its influence on crack propagation behaviour by changing the stress state in the crack tip region from one that is predominantly plane strain to one that includes plane stress. An equivalent way of envisaging these changes in stress state is to consider that splitting causes a change in the cyclic loading mode near the crack tip from a combination of Model I (opening) and Model...
II (in-plane shear) to a more complex combination of Mode I, II and III (anti-plane shear). This is consistent with the results of a recent study by Kamat and Prasad [202] on an Al-Li 8090-T3 alloy plate that fatigue crack propagation resistance is lower under mixed Mode I and Mode III loading as compared to that under pure Mode I loading.

The concept of a change in local stress state due to S-L splitting may be tested by comparing the required number of splits to produce such a change against the number of splits observed during fatigue. The generally accepted thickness criterion [188] for plane strain testing conditions at the tip of a crack is given by Equation (6.1),

$$t_B \geq 2.5 \left( \frac{K}{\sigma_T} \right)^2$$

where $t_B$ is the minimum specimen thickness above which plane strain conditions are dominant and below which plane stress conditions become increasingly important, and $\sigma_T$ is the tensile yield stress. Consequently, if there are $N_B$ splits along the crack front, the average thickness of the material between each free surface, or split, will be decreased from the initial specimen thickness of $B$ to $B/(N_B + 1)$. Also, under cyclic loading conditions, the value of $K$ governing the minimum thickness criterion will be $K_{\text{max}}$, as given by equation (4.1). Therefore, substituting $t_B = B/(N_B + 1)$ and $K = \Delta K/(1 - R)$ into Equation (6.1), and rearranging, leads to a $N_B$ controlled boundary condition for the cyclic stress intensity ($\Delta K_b$) above which plane stress conditions start to become an important consideration in the crack tip region. The boundary condition is given by Equation (6.2),

$$\Delta K_b = \left[ \frac{B}{(N_B + 1)(2.5)} \right]^{1/2} [(1 - R)\sigma_T]$$
Figure 6.2 Schematic diagram showing effect of S-L splitting on linkage of uncracked ligaments near the crack front.

Arrow shows direction of macroscopic crack propagation.

(a) Before linkage; (b) after linkage.
Figure 6.3 Deformation patterns [32].
(a) 45° shear deformation in plane stress; (b) hinge type deformation in plane strain.
Discussion

Calculated values of $\Delta K_b$ for different $N_b$ values, using the relevant $\sigma_f$ (480 MPa) in Table 4.2, are listed in Table 6.1. Comparisons of the data in Table 6.1 with the splitting analyses in Figure 5.21, and the crack propagation rates in Figure 5.8, clearly show that the observed $N_b$ in the threshold region leads to plane stress conditions ($\Delta K_a \geq \Delta K_b$) in the AlCl₃ solution and to plane strain conditions ($\Delta K_a \leq \Delta K_b$) in all the other environments. Thus, the lower $\Delta K_{bb}$ of 1.05 MPa.m$^{1/2}$ in the AlCl₃ solution, relative to $\sim$1.7 MPa.m$^{1/2}$ in the other environments, may be attributed primarily to differences in the crack tip stress state caused by the presence of S-L splitting, leading to the conclusion that $\Delta K_a$ is near $\sim 1$ MPa.m$^{1/2}$ under plane stress conditions and closer to $\sim 1.7$ MPa.m$^{1/2}$ under plane strain conditions. These two situations are analyzed in more detail in Appendix IV. In addition, comparison of Table 6.1 with Figure 5.8 and 5.21 confirms that fatigue in the AlCl₃ solution occurred under conditions of $\Delta K > \Delta K_b$ over the whole range of $\Delta K$ values investigated, suggesting that the crack tip was always subjected to some degree of plane stress. Similar comparisons and analyses of the splitting data in Figure 5.21, fatigue data in Figure 5.8 and the boundary stress intensity data in Table 6.1 show that plane stress crack tip conditions become important at $\Delta K$ above $\sim 3$ MPa.m$^{1/2}$ in all the other aqueous test environments, and indicates that the great similarity in Stage II behaviour between these environments and the AlCl₃ solution was due primarily to plane stress state conditions at the crack tip.

In contrast, for tests in desiccated air, there was a general absence of splitting and $N_b \rightarrow 0$ over a wide $\Delta K$ range. This resulted in plane strain dominated condition, $\Delta K < \Delta K_b$, up to $\Delta K$ values at least as high as 7 MPa.m$^{1/2}$. Consequently, examination of Figure 5.8 shows that the crack rate plateau, which commenced near a $\Delta K$ of $\sim 3$ MPa.m$^{1/2}$, developed and grew under plane strain crack tip conditions. These conditions should affect the number of operative slip systems at the crack tip and contribute to significant out-of-plane cracking and ridge formation.
Table 6.1 Boundary Conditions, $\Delta K_b$, above Which Plane Stress Conditions Become Important in the Presence of $N_b$ Splits

<table>
<thead>
<tr>
<th>$N_b$</th>
<th>$K_{\text{max}}$ (MPa.m$^{1/2}$)</th>
<th>$\Delta K_b$ (MPa.m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.97</td>
<td>0.99</td>
</tr>
<tr>
<td>275</td>
<td>2.06</td>
<td>1.03</td>
</tr>
<tr>
<td>250</td>
<td>2.16</td>
<td>1.08</td>
</tr>
<tr>
<td>200</td>
<td>2.41</td>
<td>1.21</td>
</tr>
<tr>
<td>150</td>
<td>2.78</td>
<td>1.39</td>
</tr>
<tr>
<td>100</td>
<td>3.40</td>
<td>1.70</td>
</tr>
<tr>
<td>75</td>
<td>3.92</td>
<td>1.96</td>
</tr>
<tr>
<td>50</td>
<td>4.79</td>
<td>2.39</td>
</tr>
<tr>
<td>25</td>
<td>6.71</td>
<td>3.36</td>
</tr>
<tr>
<td>10</td>
<td>10.32</td>
<td>5.16</td>
</tr>
<tr>
<td>5</td>
<td>13.97</td>
<td>6.98</td>
</tr>
<tr>
<td>2</td>
<td>19.75</td>
<td>9.88</td>
</tr>
<tr>
<td>1</td>
<td>24.19</td>
<td>12.10</td>
</tr>
<tr>
<td>0</td>
<td>34.21</td>
<td>17.10</td>
</tr>
</tbody>
</table>
in the mid-thickness region of the specimen. The resulting crack morphology inevitably leads to the retardation of cracking by significantly reducing the effective cyclic stress intensity ($\Delta K_{eff}$) at the crack tip to a value significantly below that calculated from Equations (4.1) to (4.4). Several processes may decrease $\Delta K_{eff}$, including crack deflection effects, lower stress components acting on the inclined surfaces of the ridged crack plane, and significant roughness induced closure effects caused by the macroscopically large ridge. Another probable contributing factor to ridge formation is the tendency for the commercial Li-containing alloys to exhibit marked differences in crystallographic texture in the mid-thickness of plate products [169]. The study of Yoder et al. [169] showed that in highly textured 2090 Al-Li alloy material ([110] <112> and {123} <634>), large slip band ([111] type) shear facets can form due to planar slip across many closely oriented grains (i.e. the effective grain size is larger than the actual grain size), resulting in unusual height of asperities on the fatigue fracture surface and thus roughness induced crack closure. Tromans and Mogamedze [203] observed a dominant {110} <112> texture in the mid-thickness region of the same Al-Li 8090-T8771 plate used in the present study. This {110} <112> texture in the 8090-T8771 plate may lead to the ridge formation on the fatigue fracture surface produced in desiccated air at ~80 Hz. Detailed analysis is given below.

Because of the pronounced {10\overline{1}} < \overline{T2T} > rolling texture in the mid-section of the Al-Li 8090-T8771 plate, the T-L orientation crack plane in this region exhibits a texture that is {111} < \overline{T2T} >, as shown in Figure 6.4a where the macroscopic crack plane is parallel to (111) and the macroscopic cracking direction is parallel to [\overline{T2T}]. The {111} < \overline{T10} > slip systems are expected to be operative in Al-Li alloys [169]. The texture in the 8090-T8771 plate is such that one slip plane, (111), is parallel to the crack plane, and three others, (\overline{T1}), (\overline{T11}) and (\overline{T11}), are
symmetrically oriented with respect to the load axis, [111], as shown in Figure 6.4b. The operative slip systems and their corresponding Schmid factors under uniaxial ([111] direction) loading conditions are list in Table 6.2.

Therefore, considering an applied stress parallel to the T-direction (i.e. normal to the (111) plane), together with the Schmid factors listed in Table 6.2, the following combination of four slip systems will be required for a slip-dominated (slip reversibility) cracking process to produce a macroscopically flat fracture plane (i.e. parallel to (111)) with a <12T> direction of crack propagation:

\[
(1\bar{T}1)[110] + (1\bar{T}1)[011] = (1\bar{T}1)[121]
\]

\[
(1\bar{T}1)[121] + (1\bar{T}1)[101] + (11\bar{T})[10\bar{T}] = (111)[1\bar{T}2]
\]

The respective orientations of the slip planes and slip directions are shown schematically in Figure 6.5.

Macroscopic flat fracture surfaces were obtained during fatigue in the aqueous environments, and may be attributed to the operation of the above four slip systems. However, under plane strain conditions (i.e. in desiccated air with no splitting phenomena), the hinge type deformation occurs (Figure 6.3b), favouring slip on (1\bar{T}1), rather than on (11\bar{T}) and (11\bar{T}) planes. Hence, the crack will tend to move out of the T-plane, onto (1\bar{T}1) in the mid-thickness region of the plate. The planar slip characteristics of Al-Li alloys, coupled with the out-of-plane cracking, will form large slip band facets on (1\bar{T}1) planes, leading to ridge formation in the mid-thickness region, as observed (see Figures 5.36 and 5.37). Consistent with this, the measured angle between the climbing ridge and the initial crack plane is ~60° (Figure 5.37b), which compares favourably with the 70.5° angle between (1\bar{T}1) and (111) planes.
Table 6.2 The Operative \{111\} < \overline{1} \overline{1} 0 > Slip Systems and Schmid Factors Under Uniaxial Loading (\{111\} Direction)

<table>
<thead>
<tr>
<th>Slip Plane</th>
<th>Slip Direction</th>
<th>ϕ (Degree)</th>
<th>λ (Degree)</th>
<th>Schmid Factor or (\cos \phi \cos \lambda)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>[01\overline{1}]</td>
<td>0</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>[\overline{1}0\overline{1}]</td>
<td>0</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>[\overline{1}10]</td>
<td>0</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>(11\overline{1})</td>
<td>[\overline{1}10]</td>
<td>70.53</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>[011]</td>
<td>70.53</td>
<td>35.26</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>[\overline{1}0\overline{1}]</td>
<td>70.53</td>
<td>35.26</td>
<td>0.27</td>
</tr>
<tr>
<td>(1\overline{1}1)</td>
<td>[\overline{1}01]</td>
<td>70.53</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>[011]</td>
<td>70.53</td>
<td>35.26</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>[110]</td>
<td>70.53</td>
<td>35.26</td>
<td>0.27</td>
</tr>
<tr>
<td>(\overline{1}11)</td>
<td>[01\overline{1}]</td>
<td>70.53</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>[\overline{1}0\overline{1}]</td>
<td>70.53</td>
<td>35.26</td>
<td>0.272</td>
</tr>
<tr>
<td></td>
<td>[110]</td>
<td>70.53</td>
<td>35.26</td>
<td>0.272</td>
</tr>
</tbody>
</table>

ϕ = angle between the loading direction and the normal of the slip plane

λ = angle between the loading direction and the slip direction
Figure 6.4 (a) Schematic diagram showing the relation of the initial T-L macroscopic crack plane with the texture in the mid thickness of the Al-Li 8090-T8771 plate.

(b) Standard (111) projection for a face-centred cubic crystal.
Figure 6.5 Relative orientations of the operative slip systems in the overall (111)[121] cracking.
In the desiccated air environment at ~80 Hz load frequency, the fatigue crack growth rate plateau and the corresponding ridge formation on the fracture surface commence at a $\Delta K$ of ~3 MPa.m$^{1/2}$. At this $\Delta K$ value, the monotonic crack tip plastic zone size in the $(1\bar{1}1)$ plane under plane strain conditions in the mid-thickness region of the plate, can be calculated from the following formula \[32\],

$$r_Y(\theta) = \frac{K_{max}^2}{4\pi\sigma_Y^2} \left[ \frac{3}{2} \sin^2 \theta + (1 - 2v)^2(1 + \cos \theta) \right]$$  \hspace{1cm} (6.3)

where, in the present case, $\theta$ is the angle between the $(1\bar{1}1)$ and the T-plane. Substituting $\theta = 70.5^\circ$, Poisson’s ratio $\nu = 1/3$, $K_{max} = 6$ MPa.m$^{1/2}$ and $\sigma_Y = 480$ MPa from Table 4.2, Equation (6.3) gives, $r_Y (70.5^\circ) = 1.8 \times 10^{-2}$ mm. This value is very close to the T-direction grain size of the Al-Li alloy plate (~2 $\times$ 10$^{-2}$ mm). The similarity between these values may indicate that the central ridge starts to form when the extent of plastic deformation reaches the point such that the planar slip on $(1\bar{1}1)$ planes is extending fully across one grain to the neighbouring grain. In the situation of textured material with closely oriented grains, the planar slip band can cut through the grain boundary and extend into the next grain without being diverted. As the extent of plastic deformation at the crack tip increases with increasing $\Delta K$, due to crack growth, the planar slip band can cut through many closely oriented grains and create a large asperity on the fracture surface, resulting in the large ridge formation in the mid-thickness region of the specimen, as observed in the present study.

The effects of texture on fracture surface roughness are largely reduced in the aqueous environments when the splitting effects are present, due to the change in stress state ahead of the crack tip from plane strain to plane stress. The $45^\circ$ shear deformation under plane stress conditions (Figure 6.3a) is more uniformly distributed among $(\bar{1}11)$, $(1\bar{1}1)$ and $(1\bar{1}1)$ planes. In
Discussion

this situation, the above slip systems are likely to operate coordinately to produce overall macroscopic cracking on (111) i.e. the T-plane. Therefore, the presence of splitting effects will decrease roughness on the fatigue fracture surface.

It is worth noting that, Rao et al. [107,108] have reported that splitting effects, which they described as crack divider delamination, may occur at the onset of unstable (critical) crack propagation in some commercial Al-Li alloys and increase the fracture toughness ($K_{IC}$). They interpreted the improved toughness as being due to a change in stress state from plane strain to plane stress and a consequent increase in energy required for fracture. The present study considers stable (subcritical) crack propagation under fatigue conditions where splitting has been obtained at stress intensities well below $K_{IC}$. The splitting phenomenon, and development of a plane stress state will not lead to improved resistance to fatigue cracking when the fatigue crack propagation process is slip controlled, because plane stress conditions enhance the degree of plastic deformation and facilitate crack tip linkage.

6.1.2 Role of environment

It seems reasonably clear from the observations of the T-L orientation fatigue cracking behaviour of the Al-Li alloy at ~80 Hz and the related fractography that the large degree of splitting in the AlCl$_3$ solution at $\Delta K_a$, and as $\Delta K$ increased to ~3 MPa.m$^{1/2}$, was associated with significant stress-independent dissolution of grain boundaries lying in the rolling plane (i.e. the S-plane containing the T and L directions). Such localized dissolution is almost certainly due to chemical heterogeneities in the grain boundary region, which cause the boundary to be anodic relative to the grain, and this is enhanced by the acidic pH of the test solution. Direct evidence for the above assertion is provided by the immersion test in the AlCl$_3$ solution in which the
initial corrosion delineated the grain boundaries and extended corrosion period led to deep intergranular corrosion. The intergranular penetration rate on the fracture surface of the fatigue specimen may be relatively faster than that on the immersion test specimen, because the dislocation movements inside the cyclic crack tip plastic zone during the previous fatigue fracture process may have further enriched the grain boundaries near the fatigue fracture surface with solute or impurity elements.

Indirect evidence for solute segregation effects at the S-plane boundaries is provided by the low $K_{ic}$ value of $\sim 14.7$ MPa.m$^{1/2}$ obtained in the S-L orientation (short transverse fracture toughness), which is listed in Table 4.2. Lynch [112] has studied the toughness of 8090 Al-Li alloy plate in this orientation and his work strongly indicates that low S-L toughness values of $\sim 15$ MPa.m$^{1/2}$ are associated with solute segregation effects at the grain boundary. He was unable to positively identify the segregant, but concluded that lithium segregation effects were consistent with his experimental results. The general absence of splitting phenomenon at $\Delta K_a$ in the NaCl solution and distilled water (see Figure 5.21) is attributable to the fact that these neutral pH environments are sufficiently less aggressive than the AlCl$_3$ solution that local dissolution rates at the grain boundaries are too small relative to the plane strain threshold cracking rates to produce any significant grain boundary penetration.

The increase in degree of splitting as $\Delta K$ rises from $\sim 3$ to $\sim 5$ MPa.m$^{1/2}$ in the AlCl$_3$ solution, and as $\Delta K$ rises from $\Delta K_a$ to $\sim 5$ or $6$ MPa.m$^{1/2}$ in the other aqueous environments (see Figure 5.21), appears to be due to a synergism between the cyclic load and the environment that results in grain boundary cracking (splitting) ahead of the main crack front. The lower $\Delta K_a$ value in the AlCl$_3$ solution and the higher cracking rates in AlCl$_3$ and distilled water, as shown in the S-L orientation fatigue cracking behaviour of the Al-Li alloy, are consistent with the splitting
results. While this may possibly be due to preferential dissolution of the grain boundaries arising from a combination of film rupture and grain boundary segregation effects, the role of dissolution may be less important than that of hydrogen embrittlement, because the \( E_{\text{corr}} \) potentials observed during fatigue testing were fully consistent with thermodynamic conditions that allowed hydrogen evolution. Also, dissolution and hydrogen evolution need not be confined solely to the grain boundaries during each load cycle. Local slip processes at the crack tip should enhance corrosion along the whole crack front by rupturing corrosion films to expose newly generated metal surface to the environment, although the more actively corroding grain boundary regions may put the other part of the grains under a certain degree of cathodic protection. Some of the hydrogen generated during the corrosion process will be absorbed into the metal lattice as monatomic hydrogen, which is mobile at room temperature, and will permeate slowly through the metal. For example, Gest and Troiano [204] have clearly demonstrated room temperature permeation of hydrogen through thin stressed membranes of a high strength 7075 Al-alloy under freely corroding conditions in aqueous NaCl. Consequently, it may be the absorbed hydrogen that is promoting the grain boundary splitting. Therefore, it is important to estimate the diffusion distance, \( x \), of monatomic hydrogen into the crack tip region during each load cycle and to compare this distance with the average crack growth increment per cycle \( (da/dN) \).

If the assumption is made that the concentration of dissolved hydrogen at the crack tip surface is held at a reasonably constant value, \( C_s \), by local corrosion processes, mathematical solutions to the mass transport problem in one dimension [205] show that the concentration of hydrogen, \( C_x \), at a distance \( x \) ahead of the crack tip after time \( t \) is given by Equation (6.3):

\[
C_x = C_s \left[ 1 - \text{erf} \left( \frac{x}{2(Dt)^{1/2}} \right) \right]
\]

(6.4)
where $D$ is the diffusion constant for monatomic hydrogen in the metal lattice. Also, error function tables [205] show that $C_x = 0.5\ C_e$ when

$$x = (Dt)^{1/2}$$

Thus, Equation (6.5) provides a reasonable estimate of the distance at which a significant concentration of hydrogen, relative to $C_e$, is present in the metal lattice.

For the present purposes, $t$ is the period of one load cycle at 80 Hz, $1.25 \times 10^{-2}$ second, and Ricker and Duquette [206] concluded that values of $D$ for hydrogen in aluminium, based on the published literature, should lie between $1 \times 10^{-12}$ and $1 \times 10^{-14}$ m$^2$/s. In a later paper, Chen and Duquette [179] considered $1 \times 10^{-13}$ m$^2$/s to be an appropriate value of $D$ for Al-Li alloys. Consequently, using the latter value, Equation (6.5) shows that $x$ is $3.54 \times 10^{-5}$ mm. Examination of Figure 5.21 shows that a peak in the number of splits occurs between cyclic stress intensities of 5 and 6 MPa.m$^{-1/2}$ when tested in the aqueous environments, corresponding to crack propagation rates between $2 \times 10^{-5}$ and $6 \times 10^{-5}$ mm/cycle in Figure 5.8. The good agreement between these cracking rates and the magnitude of the computed value of $x$ strongly suggests that the diffusion of hydrogen during each load cycle is sufficiently rapid to influence grain boundary splitting up to $\Delta K$ values of 5 to 6 MPa.m$^{-1/2}$. At higher cracking rates, the overall advance of the crack front per cycle will become larger than $x$ and the degree of splitting should decline, consistent with the decreasing amounts of splitting that were observed at $\Delta K > 6$ MPa.m$^{-1/2}$ in Figure 5.21. It is possible that other transport processes may influence the distribution of hydrogen in the cyclic plastic zone, such as dislocation transport and grain boundary diffusion processes. Also, the amount of hydrogen absorption at the crack tip, and the actual concentrations $C_e$ and $C_x$, will be dependent on such factors as the local pH and hydrogen overvoltage [207], and the area fraction of surface that is covered by corrosion films.
These, in turn, will affect the prevalence of splitting in different solutions. Nevertheless, within these limitations, the simple calculation based on Equation (6.5) is considered to be sufficiently adequate to demonstrate that splitting effects are reasonably consistent with the presence of dissolved hydrogen.

The experimental results from the high frequency fatigue test under continuous hydrogen charging provided more support to the above argument. From the change of split number with $\Delta K$ (Figure 5.27), it is evident that splitting is caused by the synergistic interaction between hydrogen embrittlement and the lateral stress arising from through-thickness constraints. At low $\Delta K$ values near the threshold, the acidic solution ($\text{pH} = 1$) did not cause a large number of splits to form by anodic dissolution, because the dissolution process was sufficiently suppressed by the cathodic polarized potential (-2.1 $V_{SCB}$). While at a relatively higher $\Delta K$, a large number of splits were observed at the splitting peak due to the interaction of hydrogen and the cyclic load. This peak was reached at a higher $\Delta K$ value relative to the other test conditions, and is probably associated with the higher hydrogen production rate occurring under the hydrogen charging conditions.

Considering the test conditions of all the high frequency tests on the Al-Li alloy, it appears that a continuous hydrogen source is required at the crack tip to produce the splitting effect and to maintain the crack in its initial macroscopic cracking plane. If this hydrogen source is removed, the splitting process will stop. This was shown by the combined test conducted consecutively in distilled water and desiccated air, where the splits produced at the crack tip in water disappeared when the test was continued in desiccated air and cracking did not continue in the previous macroscopic plane at the previous growth rate (see Figure 5.26 and Figure 5.9).
It is concluded that the hydrogen precharged specimen contained insufficient absorbed hydrogen to have any significant effect, because subsequent fatigue of the specimen in desiccated air remained free from the splitting phenomenon.

The precise mechanism by which hydrogen promotes splitting is not established, but it may be related to the low S-L toughness caused by the possible segregation of Li at the grain boundaries [112]. Electronic interactions between Li and the monatomic hydrogen in the metal lattice could reduce the cohesive energy between the atoms at the boundary so that the through-thickness stresses produced by lateral restraint in the crack tip region during fatigue loading are sufficient to cause boundary decohesion (splitting). Strong interactions between the Li segregant and the dissolved hydrogen are expected because of the stability of the hydride, LiH [208]. Balasubramaniam et al. [137,138] showed by transmission electron diffraction techniques that a brittle hydride, LiAlH₄, can form from grain boundary precipitates of δ (AlLi) phase in hydrogen charged Al-Li alloys, and they suggested that the hydride plays a major role in stress corrosion cracking of these alloys.

It is possible that impurities (mainly Na and K) contained in the Li alloying addition may also play a role. There has always been a strong argument that the 3 to 10 ppm Na and K impurities contained in commercial purity Al-Li alloys could be responsible for their lower short-transverse fracture toughness [81,82,209].

6.1.3 Effects of loading frequency

Lowering the loading frequency may lead to the following changes:

1. Decreased strain rate at the crack tip;
2. Increased time for environmental exposure during each load cycle;
3. Increased time for material recovery and increased probabilities for other thermally activated processes (e.g., cross slip) during each load cycle;

4. Change of local environment chemistry due to relatively poor mixing with the surrounding bulk solution.

Interactions among the changes 1 to 4 may lead to different consequences depending on which factor is dominant. For example, the similarity in crack growth behaviour between the Al-Li alloy fatigued in 0.6 M NaCl and that tested in 1 M AlCl₃ at ~0.5 Hz indicates that their crack tip chemistries may be similar. This suggests that the crack tip solution in the neutral NaCl moves towards an acidic AlCl₃ composition due to the hydrolysis of dissolved Al during the corrosion fatigue process,

\[ Al^{3+} + nH_2O \rightleftharpoons Al(OH)_{n-3}^{3-n} + nH^+ \quad (6.6) \]

The higher apparent threshold values at lower frequency may be associated with crack closure effects due to increased amounts of corrosion product at the crack tip and/or the increased time for the material at the crack tip to recover from deformation damage during each load cycle. However, the thresholds observed at ~0.5 Hz are possibly overestimated because time constraints did not allow fatigue to be studied at the same low crack growth rates per cycle as those conducted at ~80 Hz.

Although the fatigue fracture surface of Al-Li 8090-T8771 produced at 0.5 Hz in desiccated air was much rougher than those produced at 0.5 Hz in the aqueous environments, it did not show an obvious large central ridge as those observed on fatigue fracture surfaces of the as-received Al-Li alloy tested at 80 Hz in desiccated air. Consistently, the crack growth curve for the 0.5 Hz test in desiccated air did not show a crack rate plateau. Study of the fatigue fracture surfaces of the Al-Li alloy produced at 0.5 Hz in desiccated air revealed that the ridge
Discussion

still tended to form but the scales were much smaller as shown in Figure 5.30, and the faces of the small ridge correlated very well with the operative slip planes drawn in Figure 6.5. The ridge was terminated at small scales when slip deformation on the three slip planes ((111), (111) and (111)) intercepted and combined. A convincing explanation on why the ridge formation at 0.5 Hz loading frequency did not develop to the same large scales as that at ~80 Hz loading frequency has not be reached, but it may be related to fact that the split number is slightly higher at the low frequency than at the high frequency (see Figure 5.31 and Figure 5.21). Although the increased number of splits at 0.5 Hz is not yet high enough to change the crack tip stress state from plane strain to plane stress (see Figure 5.31 and Table 6.1), it is closer to plane stress conditions which produce a flatter fracture surface in this Al-Li plate, as discussed in Section 6.1.1 regarding the effects of the presence of splits on crack tip stress state and fracture surface roughness. The increased number of splits at 0.5 Hz may be attributed to the longer time for interaction between the remaining moisture in the environment and the lateral stress during each cycle. Other factor, such as increased probability for cross slip at lower frequency, may also play a role in restricting the scales of the ridge. Therefore, the fatigue crack growth curve at 0.5 Hz in desiccated air did not show a crack rate plateau as that at 80 Hz which was caused by the severe roughness induced crack closure from the large ridge formation.

6.1.4 Effects of microstructure and deformation behaviour

The Al-Cu alloy exhibited different high frequency fatigue characteristics from those in the Al-Li alloy. The difference were more significant for tests conducted in desiccated air, where a crack rate plateau and ridge formation were not observed in the Al-Cu alloy. Differences
Discussion

were less evident in the aqueous environments, but still detectable, as shown by the flatter crack front profiles in the Al-Cu alloy relative to the Al-Li alloy (c.f. Figure 5.40) and the absence of splitting effects.

The behaviour of the Al-Li alloy is closely related to the planar slip characteristics conferred by the coherent $\delta'$ (Al$_3$Li) phase, the anisotropic grain structure, and the strongly textured microstructure, as explained in the previous section (Section 6.1.1). In contrast, the Al-Cu has a more equi-axed grain structure, is less strongly textured and is not expected to exhibit strong planar deformation characteristics [11,13]. These factors probably contribute to the similarity in behaviour of the Al-Cu alloy in the desiccated air, distilled water and NaCl environments.

The lower $\Delta K_m$ of the Al-Cu alloy in the AlCl$_3$ solution, relative to $\Delta K_m$ in the other environments, is likely associated with the higher corrosion and accompanying hydrogen generation rates at the crack tip in this solution. Such processes are enhanced at the crack tip due to the generation of freshly exposed metal by the cyclic deformation, and more time is available per cycle for environmental effects to exert an effect at low crack growth rates. As the $\Delta K$ value increases, the mechanical effects on fatigue cracking become more and more dominant so that the environmental effects are overshadowed, and the crack rates converge with those in the other environments.

The above explanation for the low $\Delta K_m$ of the Al-Cu alloy in the AlCl$_3$ in the absence of splitting effects does not contradict the explanation proposed for the low $\Delta K_m$ of the Al-Li alloy in AlCl$_3$, where a change of stress state was attributed to splitting effects. In the Al-Li alloy, the sensitive grain boundary region dissolves preferentially and the other part of the fresh metal exposed by cyclic slip deformation is under a certain degree of cathodic protection caused by
Discussion

the higher dissolution rate of the grain boundary regions, as illustrated schematically in Figure 6.6. Therefore, the direct contribution from anodic dissolution to transgranular crack tip advance in the Al-Li alloy is not as large as that in the Al-Cu alloy.

Fatigue crack propagation behaviour of the Al-Li and Al-Cu alloys at the low test frequency is more similar, with the Al-Li alloy showing a slightly higher environmental sensitivity.

In summary, when compared to the Al-Cu alloy, the Al-Li alloy showed very superior T-L orientation fatigue crack propagation resistance in the dry air environment, and slightly better or equivalent fatigue crack propagation resistance in the aqueous environments at the same $\Delta K$ values. (Note that the Al-Cu alloy has a slightly higher $K_{IC}$ and is able to sustain a longer critical crack length before unstable fracture.)
Figure 6.6 Schematic theoretical polarization diagram showing possible cathodic protection on the other part of the grains by the active dissolution of the grain boundary regions. $I_p < I_u$ due to enhanced corrosion at the grain boundaries ($I_{GB}$).
6.2 Corrosion fatigue crack growth in the Al-Li alloy in the S-L orientation and effects of the re-aging treatment

6.2.1 Possible changes in the material caused by the re-aging treatment

It is clear from the fracture toughness and hardness tests that the short time re-aging treatment can largely increase the short transverse toughness of the material with only a slight decrease in hardness, confirming that the re-aging treatment is an effective way to improve the short-transverse fracture toughness.

Two mechanisms have been proposed to explain the effects of the re-aging treatment on the short-transverse fracture toughness value in the literature:

1. Transient decrease of Li segregation at the grain boundaries, by Lynch [112].
2. Reduced slip planarity due to a combination of $\delta'$ (Al$_3$Li) phase dissolution and S' (Al$_5$CuMg) growth, by Blankenship et al. [113] and Slavik et al. [114].

In the study of short transverse fracture toughness of 8090 Al-Li plates, Lynch [112] proposed that Li segregation along the grain boundaries is responsible for the low fracture toughness of the T8771 heat treatment. He rationalized that the short time re-aging treatment increases the fracture toughness because it allows the Li segregant to diffuse from the grain boundaries to nearby precipitates at the grain boundaries before bulk diffusion from the matrix replenishes the segregant at the grain boundaries. Re-embrittlement occurs when the grain boundaries are re-segregated with Li due to the diffusion of Li from the matrix. However, Lynch provided no direct evidence to support his proposal. In his fractographic study, Lynch noticed that fracture surfaces of the as-received material consisted of a mixture of well defined dimples
and relatively smooth facets, while that of the 230 °C, 5 minutes re-aged material was completely covered with well defined dimples. Our SEM studies of the transition region between the fatigue precracked and monotonic fractured surfaces showed similar features to those in Lynch's observations. In addition, lines of trenches along part of the transition region were observed in the re-aged material in the present study, which were not reported in Lynch's article [112]. These trenches may cause blunting of the crack and provide an additional contribution to the increased fracture toughness.

In studies by Blankenship and Starke [113] and Slavik et al. [114], the increased fracture toughness obtained by the re-aging treatment was attributed to a combination of δ' (Al3Li) phase dissolution and S' (Al2CuMg) phase growth. They proposed that these microstructural changes lead to a transition from a coarse planar deformation mode to more homogeneous deformation and results in the increased fracture toughness of the re-aged material. They pointed out that their TEM study did not reveal any differences in δ' distribution between T8771 and the re-aging tempers, although they could identify an increase of S' phase in the re-aging temper. The decreased δ' volume fraction in the re-aging temper was documented by Guinier X-ray analysis [113] and small angle neutron scattering (SANS) [210].

Consistently, the TEM observation in the present study showed no discernible differences in δ' phase distribution between the two tempers (Figure 5.39). Attempts to measure Li compositional profiles by EELS, using Li absorption edge measurements and plasmon peak energy shifts, were unsuccessful, as explained in Appendix III.

Intergranular segregation effects were suggested by the immersion etching tests in 1 M AlCl3 solution, where a detectable improvement in intergranular corrosion resistance was observed after the re-aging treatment. The SEM + EDX and STEM + EDX analyses indicated
a possible relationship between corrosion resistance and the effects of re-aging on the Cu
distribution. It is known that alloyed Cu in solid solution ennobles Al-alloys against corrosion
[200]. The improved intergranular corrosion resistance of the re-aged material may be related
to a local increase of Cu in solid solution. The re-aging temperature (230 °C) is higher than the
original aging temperature (170 °C), and the increased solubility at higher temperature may put
more Cu back into solution by dissolving some small precipitates during the re-aging treatment.
The obvious increase of Cu concentration in the grain boundary precipitates after re-aging
(Figure 5.43b) indicates that a diffusion controlled re-distribution of Cu is achievable during
the re-aging treatment. This possibility is supported by the fact that the Cu content that was
detected near the grain boundary region was slightly higher in the re-aged material (Figure
5.43c).

It is known that localized corrosion starts at sites with the lowest Cu concentration (Cu
depleted zone) in binary Al-Cu alloys [201]. The grain boundary regions in the as-received
material were only slightly more active than those in the re-aged material, and the difference
was not easily discernible in the early stage of corrosion (Figure 5.2). However, as corrosion
proceeds, Cu enrichment will occur on the side surfaces of the corrosion sites, allowing these
surfaces to act as cathodes in the local corrosion cells. The Cu enrichment will accelerate the
local cathodic evolution of hydrogen because the hydrogen overpotential on Cu is lower than
that on Al [154], resulting in accelerated dissolution of the local anodic sites at the tip of the
propagating corrosion slots. Therefore, deeper corrosion slots and larger differences between
the intergranular corrosion rates of the as-received and re-aged tempers were observed in the
later stages of the intergranular corrosion tests (Figure 5.3 and Figure 5.4).
Difference in intergranular corrosion behaviour may also be accounted for via changes in Li segregation at grain boundaries, as proposed by Lynch [112]. A decreased concentration of the reactive Li element at the grain boundaries should lead to reduced sensitivity to corrosion. Unfortunately, it was not possible to confirm the presence or absence of Li segregation in the present work.

Moreover, during corrosion the $\delta'$ phase is likely to be anodic to the Al matrix in the corrosion process [123], like the $\delta$ (AlLi) phase. The decreased volume fraction of $\delta'$ phase in the re-aged material, as proposed in the studies by Blankenship et al. [113] and Slavik et al. [114], may also be reflected in the less generally corroded appearance of the re-aged material. Although, the present study detected no significant changes in the volume fraction of $\delta'$ phase.

The low $K_{IC}$ of the as-received material and its improvement is similar to classical temper embrittlement phenomena in steels that are caused by segregation of tramp elements. In Al-Li alloys, tramp Na and K elements are introduced with Li. There have always been arguments that these tramp elements could be responsible for the lower short-transverse fracture toughness of commercial purity Al-Li alloys [81,82,209].

6.2.2 Effects of re-aging on the S-L crack growth rates

It is interesting to see that the fatigue crack propagation resistance of the re-aged material in desiccated air is inferior to that of the as-received material, showing a lower threshold stress intensity value for cracking and faster crack growth rates.

Considering the possible changes in the material caused by the re-aging treatment, the decreased fatigue crack propagation resistance in the dry air environment caused by the re-aging
treatment may be due to one or more of the following reasons:

1. Decrease of strength (hardness): A decreased yield strength produces a larger crack tip opening displacement, leading to faster cracking rate and a lower $\Delta K_{th}$ value [160].

2. Reduced planarity of slip: The superior fatigue crack propagation resistance of Li-containing alloys is attributed mainly to the "extrinsic toughening" effects from crack deflection, crack branching and roughness-induced crack closure [6-11]. These effects stem from the planar slip characteristics of Li-containing alloys. Therefore, reduced planarity of slip [113,114] can lead to reduced fatigue crack propagation resistance.

3. Replenishment of the embrittling element(s): According to Lynch's theory [112], the re-aging treatment caused a transient decrease of Li segregation at the grain boundaries. However, it may be argued that during the fatigue process, the slip movement at the crack tip and the associated dislocation motion can facilitate the re-segregation of embrittling species from the matrix to the grain boundaries. Grain boundaries inside the cyclic crack tip process zone can be replenished with the embrittling element(s) by dislocation transportation during fatigue. Therefore, similar fatigue resistance could result for both the re-aged and as-received materials, if other related material properties (e.g. yield strength) were not changed by the heat treatment.

6.2.3 Effects of environments on the S-L crack growth rates

Interestingly, no obvious difference in fatigue crack propagation resistance was observed between the as-received and re-aged materials when tested in each aqueous environment. The similar fatigue crack propagation resistance between the two tempers of materials in the aqueous
environments may be attributed to the combination of the inferior "mechanical fatigue" resistance with the superior intergranular corrosion resistance (accompanied by lower hydrogen production during corrosion) of the re-aged material relative to the as-received material.

When comparing the fatigue crack growth in both tempers of materials in different environments, large differences were observed. The higher threshold ($\Delta K_{th}$) in distilled water than in desiccated air is attributed to corrosion product induced crack closure [15,17-19,58,59,179]. The SEM observation showed the blackening marks of rubbing or fretting and a thicker layer of corrosion product on the fatigue fracture surface produced in distilled water near $\Delta K_{th}$ (Figure 5.33a), while no such marks were observed on fracture surface in desiccated air (Figure 5.33b). However, at relatively higher $\Delta K$, the closure effect was largely overcome [7,9,98], and the embrittling effect of water dominated, resulting in faster cracking rates in distilled water. In the AlCl$_3$ solution, no crack closure resulted, because the corrosion product is less stable and is soluble in the acidic environment. Moreover, the higher corrosion and hydrogen production rates, and their interaction with cyclic deformation at the crack tip, combined together to produce a lower threshold ($\Delta K_{th}$) and higher cracking rates in this environment.

The S-L fatigue cracking fractography was predominantly intergranular for both tempers (Figure 5.33). The easier cracking along the grain boundaries in distilled water and AlCl$_3$ solution is consistent with the observation that fatigue crack propagation in the T-L orientation was accompanied by lateral splitting along the S-L orientation in these environments. Furthermore, the lower S-L fatigue resistance in AlCl$_3$ also corresponds to the higher splitting tendency (see Figure 5.21 and Figure 5.31).


Discussion

Considering the faster crack propagation rates and the lower threshold \( \Delta K_{th} \) of the re-aged material in desiccated air, the beneficial effects of the re-aging treatment on improved fracture toughness may be largely compromised in regard to the overall lifetime of a structure or component. Although a higher fracture toughness value means that unstable cracking will be delayed to a longer critical crack length, the lower threshold \( \Delta K_{th} \) and higher cracking rate will reduce the time period (lifetime) required to reach this critical length. Near threshold fatigue crack growth behaviour is important in determining service lifetime, because this period occupies the largest fraction of the lifetime under normal situations.

In summary, a re-aging treatment that has been shown to be effective in increasing the short-transverse fracture toughness does not improve the corrosion fatigue crack propagation resistance. This means that the re-aging treatment is less promising for commercial applications where fluctuating loads prevail.
7 Summary and Conclusions

(1) Regarding the T-L orientation crack propagation behaviour, the following conclusions emerge:

(i) The T-L orientation fatigue crack propagation resistance of Al-Li 8090-T8771 is superior to Al-Cu 2024-T351 in a desiccated (dry) air environment, and slightly better than or equivalent to Al-Cu 2024-T351 in the aqueous environments.

(ii) The superior crack growth resistance of the Al-Li alloy in desiccated air comes mainly from the crack deviation and roughness induced crack closure.

(iii) The presence of corrosive environments can largely accelerate the fatigue crack propagation rate. For Al-Li 8090-T8771, the primary effect of aqueous environments is to promote S-L splitting (delamination) along grain boundaries normal to the initial crack plane in the crack tip region. Splitting does not occur in the Al-Cu alloy.

(iv) The splitting occurs ahead of the main crack front and affects the main crack growth by changing the local stress state, keeping the main fatigue crack in the original crack plane and restricting the fracture surface roughness induced crack closure.

(v) In the absence of an aqueous environment, S-L splitting is avoided. A large degree of crack deviation and fracture surface roughness result, leading to severe crack growth retardation. The central ridge formation on the fatigue fracture surface is related to the strong texture in the mid-thickness of the Al-Li 8090 plate.
(vi) Splitting arises from both localized anodic dissolution and hydrogen embrittlement processes. The occurrence of significant splitting at $\Delta K_a$ is due to anodic dissolution, whereas the increased splitting that occurs with rising $\Delta K$ is attributed mainly to hydrogen embrittlement.

(2) Regarding the S-L orientation fatigue crack propagation behaviour of Al-Li alloy 8090, the following conclusions are reached:

(i) The fatigue crack propagation resistance is lower in the S-L orientation than in the T-L orientation. The easier intergranular cracking along the S-L orientation is consistent with the observed S-L splitting phenomenon in the aqueous environments during the T-L crack orientation tests.

(ii) The re-aging treatment, effective in increasing the short-transverse fracture toughness, does not improve the corrosion fatigue crack propagation resistance. This makes the re-aging treatment less promising for commercial applications, especially in situations where fluctuating loads prevail.

(iii) The re-aging treatment improves the intergranular corrosion resistance of the material.

(iv) Dislocation transport processes during fatigue may facilitate re-segregation of the embrittling species from the matrix to grain boundaries inside the cyclic crack tip process zone. The similar crack growth behaviour between the two tempers of materials in each environment is due to the combination of the inferior "mechanical fatigue" resistance with the superior intergranular corrosion resistance (accompanied by lower hydrogen production during corrosion) of the re-aged material relative to the as-received material.
8 References


17. Peters, M., K. Welpmann, W. Zink and T.H. Sanders, Jr., "Fatigue Behaviour of Al-Li-Cu-Mg Alloy", see ref. 73, pp. 239-246.


References
References


References


References


80. Vasudevan, A.K., A.C. Miller, M.M. Kersker, "Contribution of Na-Segregation to Fracture Behaviour of Al-11.4 At.% Li Alloys", see ref. 72, pp. 181-199.


87. Harris, S.J., B. Noble and K. Dinsdale, "Effect of Composition and Heat Treatment on Strength and Fracture Characteristics of Al-Li-Mg Alloys", see ref. 72, pp. 219-233.


89. Miller, W.S., M.P. Thomas, D.J. Llord and D. Creber, "Deformation and Fracture in Al-Li Base Alloys", see ref. 73, pp. 584-594.

90. Tosten, M.H., A.K. Vasudevan and P.R. Howell, "Grain Boundary Precipitation in Al-Li-Cu alloys", see ref. 73, pp. 490-495.
References


99. Suresh, S., A.K. Vasudevan, "Influence of Composition and Aging Treatment on Fracture Toughness of Lithium-Containing Aluminium Alloys", see ref. 73, pp. 595-601.


101. Webster, D., "Temperature Dependence of Toughness in Various Aluminium-Lithium Alloys", see ref. 73, pp. 602-609.


References


References


References


133. Gray, A., "Factors Influencing the Environmental Behaviour of Aluminium-Lithium Alloys", see ref. 74, pp. 891-904.


143. Ahmad, M., "Correlation between Aging Heat Treatments, Microstructure and Stress Corrosion Properties of Al-Li-Cu-Mg Alloys", see ref. 73, pp. 871-879.


References

146. Holroyd, N.J.H., A. Gray, G.M. Scamans and R. Hermann, "Environment-Sensitive Fracture of Al-Li-Cu-Mg Alloys", see ref. 73, pp. 310-320.


158. Coyne, Jr., E.J., T.H. Sanders, Jr., and E.A. Starke, Jr., "The Effect of Microstructure and Moisture on the Low Cycle Fatigue and Fatigue Crack Propagation of Two Al-Li-X Alloys", see ref. 71, pp. 293-305.
References


165. Ruch, W. and E.A. Starke, Jr., "Fatigue Crack Propagation in Mechanically Alloyed Al-Li-Mg Alloys", see ref. 73, pp. 121-130.


170. Lespinasse, C and C. Bathias, "Fatigue Crack Growth of 8090 Alloy under Overloading", see ref. 73, pp. 793-799.


References


174. Haddleton, F.L., S. Murphy and T.J. Griffin, "Fatigue and Corrosion Fatigue of 8090 Al-Li-Cu-Mg Alloy", see ref. 74, pp. 809-815.


176. Magnin, T. and M. Rebiere, "The Effect of Hydrogen During Stress Corrosion Cracking and Corrosion Fatigue of Al-Li-Cu Alloys in 3.5 % NaCl Solution", see ref. 74, pp. 835-841.


References


References


9 Appendix

9.1 Appendix I. Increased stiffness of Al-Li alloys

The stiffness of a simple beam of rectangular cross section under 3-point bending load is given by the formula,

$$S = \frac{4Ebh^3}{l^3}$$  \hspace{1cm} (A1)

where $E$ is the elastic modulus, $b$ is the beam thickness, $h$ is the beam height, and $l$ is the supporting distance. Consider a beam of a conventional Al-alloy (of elastic modulus $E_1$ and density $\rho_1$) and let it be replaced with a beam of an Al-Li alloy (of elastic modulus $E_u$ and density $\rho_u$) of equal weight. Further, allow the beam height to change while maintaining $b$ and $l$ at their original sizes. The stiffness ($S_1$) of the conventional beam relative to the stiffness ($S_u$) of the Al-Li beam is then given by,

$$\frac{S_u}{S_1} = \frac{E_u(h_u)^3}{E_i(h_i)^3}$$  \hspace{1cm} (A2)

With equal weight, $\rho_i h_i = \rho_u h_u$, therefore,

$$\frac{S_u}{S_1} = \frac{E_u(\rho_i)^3}{E_i(\rho_u)^3}$$  \hspace{1cm} (A3)

For each weight percent lithium added to an aluminium alloy, the density is reduced approximately 3% and the elastic modulus is increased approximately 6%, i.e., $\rho_u/\rho_i = 0.97$, $E_u/E_i = 1.06$. Substitution into Equation (A3) leads to $S_u/S_1 = 1.16$, that is, the stiffness can be increased 16 percent by one percent lithium addition. Alternatively, the stiffness may be kept
constant by changing the beam thickness \( b \), then the weight \( W_i \) of the conventional Al-alloy beam is changed to \( W_n \) for the Al-Li alloy beam, where

\[
\frac{W_n}{W_i} = \frac{\rho_n b_n}{\rho_i b_i} = \frac{\rho_n E_i}{\rho_i E_n}
\] (A4)

Consequently, each weight percent lithium addition can lead to \( \sim 8 \) percent weight saving.

9.2 Appendix II. Identification of grain boundary precipitate by selected area electron diffraction

The grain boundary precipitates in the as-received Al-Li alloy and the re-aged alloy were investigated by selected area electron diffraction during the TEM studies. Figure A1 shows the limited part of a selected area diffraction pattern obtained from a grain boundary precipitate in the as-received materials, 8090-T8771. Using the known camera length, the pattern was indexed and possible plane spacings were calculated. Table A1 lists the comparison between the calculated spacing \( d \) and angle values with known values of a possible phase from the X-ray Powder Diffraction File \(^{[ii]}\). It is seen that it is a close match to the \( \text{Li}_3\text{CuAl}_5 \) phase which has a body-centred cubic structure.

Usually, the larger grain boundary particles are referred to in the literature \([79,92,118,121,198,199]\) as \( T_2 \)-phase. Only one article \(^{[iii]}\) describes \( T_2 \) as \( \text{Li}_3\text{CuAl}_5 \) (hereafter designated as \( (T_2)_1 \)), most \([79,92,118,121,198,199]\) describe \( T_2 \) as \( \text{Al}_6\text{CuLi}_3 \) (hereafter designated \( (T_2)_2 \)). Unfortunately, very little crystallographic data is available for \( (T_2)_2 \); it is


\(^{[iii]}\) Glazer, J. and J.W. Morris, Jr., "Thermomechanical Processing of Two-Phase Al-Cu-Li-Zr Alloy", see ref. 74, pp. 191-198.
Figure A1 Selected area diffraction pattern obtained from a grain boundary precipitate.

(a) TEM micrograph; (b) schematic diagram showing the pattern of interest and the indexing.
Appendix

reported to have an icosahedral structure, but is not indexed in the latest X-ray Powder Diffraction File. Some authors [197] reported that the morphology and $d$-spacings of $(T_2)_2$ are not markedly different from those of the cubic $\delta$ (AlLi) phase, which has a well established crystal structure. However, several grain boundary precipitates were found to have a "five-fold" symmetry, as shown in Figure A2. This symmetry is impossible for $\delta$ (AlLi), but such patterns have been reported for $(T_2)_2$ [198,199]. Therefore, on this basis it is believed that grain boundary precipitates of $(T_2)_2$ phase were present.

Table A1  Comparison of Calculated Spacing and Angle Values with Known Values of a Possible Phase

<table>
<thead>
<tr>
<th>Calculated and Measured Values</th>
<th>Known Values for Li$_3$CuAl$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2R_c d = 2L\lambda = 40 \text{ mm} \cdot \text{Å}$</td>
<td></td>
</tr>
<tr>
<td>$2R_1 = 10.0 \text{ mm} \to d_1 = 4.00$</td>
<td>$d_{222} = 4.06$</td>
</tr>
<tr>
<td>$2R_2 = 11.5 \text{ mm} \to d_2 = 3.46$</td>
<td>$d_{222} = 3.50$</td>
</tr>
<tr>
<td>$2R_3 = 10.0 \text{ mm} \to d_3 = 4.00$</td>
<td>$d_{400} = 4.06$</td>
</tr>
<tr>
<td>$\angle_{R_1,R_2} = 55^\circ$</td>
<td>$\angle_{222,400} = 54.7^\circ$</td>
</tr>
<tr>
<td>$\angle_{R_1,R_3} = 110^\circ$</td>
<td>$\angle_{222,222} = 109.5^\circ$</td>
</tr>
</tbody>
</table>

It is noticed that the concentrations of Cu in the grain boundary precipitates detected by the STEM + EDX analyses (~7 wt.% in the as-received state and ~16 Wt.% in the re-aged state,
Figure A2 Selected area diffraction pattern obtained from a grain boundary precipitate, showing five-fold symmetry.
as shown in Figure 5.43) are all much lower than the concentrations of Cu in Li₃CuAl₅ (~29 wt.%) and in Al₄CuLi₃ (~26 wt.%). This may be due to the contribution from the Al matrix enclosed in the sampling region of the analysis.

9.3 Appendix III. EELS analyses

EELS analysis is useful for detecting light elements, such as lithium, by examining the Li K-excitation edge. However, when attempting to detect Li in Al-alloys, complications arise from the overlapping of the Li K-edge at ~55 eV with the high background tails of the very well defined Al plasmon loss peaks at 15, 30 and 45 eV, making the analysis particularly difficult [194]. Consistently, no excitation edge was observed in the EELS analyses conducted in the present study.

Another attempt to conduct compositional microanalysis was made by examining the plasmon peak energy shift from the energy loss spectrum. A schematic diagram of the electron energy loss spectrum is shown in Figure A3. The average quantum loss $E_p = \frac{1}{2} \left( E_1 + \frac{1}{2} E_2 \right)$ can be determined from the spectrum, where $E_1$ and $E_2$ are the measured energies of the first and second plasmon loss peaks. This energy loss is related to the concentration of the alloying element. Williams and Edington [195] reported a relation between the Li atomic concentration ($C_L$) in binary Al-Li alloys and the plasmon energy loss ($E_p$ in eV) as, $E_p = 15.3 - 4.0 C_L$, and used the equation to measure the composition profile across a grain boundary. With regard to
Figure A3 Schematic diagram of an electron energy loss spectrum.
the other major alloying elements in Al-Li alloy 8090 (i.e. Cu and Mg), similar equations were found, \( E_p = 15.3 - 10 \, C_{Cu} \) for Cu \(^{[v]} \) and \( E_p = 15.3 - 4.4 \, C_{Mg} \) for Mg \(^{[v]} \). It is seen that these three alloying elements shift the plasmon peak in the same direction.

The \( E_p \) value for pure Al is 15.3 eV and was used to calibrate the equipment. For example, the system gave \( E_p \) values for 99.9995% purity Al that varied between 17.1 eV and 17.7 eV during repeated measurements at the same location on the Al specimen. Hence, it was not possible to say with certainty whether a system measurement of 17.1 eV or 17.7 eV corresponded to a \( E_p \) value of 15.3 eV. Therefore, when searching for \( E_p \) shifts due to alloying effects, only measurements outside the 17.1-17.7 eV limits were likely to be meaningful. In practice, plasmon energy losses measured from the as-received and re-aged Al-Li alloys ranged between 17.1 eV and 16.1 eV, indicating a definite decrease in \( E_p \) of uncertain value. These shifts were in the right direction according to the above equations for Li, Cu and Mg concentrations, but were not useful for quantitative purposes. Point-by-point measurements along a straight line across a grain boundary were conducted many times. However, no sensible and reproducible compositional profile could be drawn from the data obtained. The scattering and the poor reproducibility of the data may be due to several reasons:

(i) Large systematic error associated with determining \( E_p \) from the measurements of \( E_1 \) and \( E_2 \) on the obtained spectra, which were plotted on chart paper. The systematic error was estimated to be \(-0.2\) eV, and based on equation \( E_p = 15.3 - 4.0 \, C_{Li} \), this means that a change of Li concentration of less than 5 at.% will not be detectable.

---


Appendix

(ii) Drift of the specimen during the data collecting time period. It was found quite often that the point of analysis had moved from the intended position during the collection of the spectrum, leading to poor spatial resolution.

(iii) The resolution achievable with the ordinary tungsten filament gun equipped with the scanning transmission electron microscope is limited. To obtain a resolution of ~0.1 eV (such as those indicated in the reported work [195, 196]), a field emission gun is required.

9.4 Appendix IV. Threshold stress state

The generally accepted formulae for the average crack tip plastic zone size along the crack front under Mode I monotonic loading are,

plane strain conditions: \[ r_y = \frac{1}{6\pi} \left( \frac{K}{\sigma_y} \right)^2 \]

plane stress conditions: \[ r_y = \frac{1}{2\pi} \left( \frac{K}{\sigma_y} \right)^2 \]

Accordingly, the corresponding formulae for the average cyclic plastic zone size under Mode I cyclic loading are,

plane strain conditions: \[ \Delta r_y = \frac{1}{6\pi} \left( \frac{\Delta K}{2\sigma_y} \right)^2 \]

plane stress conditions: \[ \Delta r_y = \frac{1}{2\pi} \left( \frac{\Delta K}{2\sigma_y} \right)^2 \]
Consequently, if the onset of fatigue crack propagation at $\Delta K_a$ is a slip dominated process that is associated with a specific size of reversed plastic zone (i.e. a specific amount of slip reversibility), then Equation (A7) and Equation (A8) indicate that for a constant $\Delta r_Y$ at threshold,

$$\left[ \frac{(\Delta K_{th})_{\text{plane strain}}}{(\Delta K_{th})_{\text{plane stress}}} \right]^2 = 3 \quad (A9)$$

The experimental data for fatigue tests at the high frequency in the AlCl$_3$ solution, the other aqueous environments (AQ), and desiccated air (DA) show that,

$$\left[ \frac{(\Delta K_{th})_{AQ}}{(\Delta K_{th})_{AlCl_3}} \right]^2 \approx \left[ \frac{(\Delta K_{th})_{DA}}{(\Delta K_{th})_{AlCl_3}} \right]^2 \approx \left[ \frac{1.7 \text{MPa.m}^{1/2}}{1.05 \text{MPa.m}^{1/2}} \right] = 2.62 \quad (A10)$$

Consequently, the reasonably good correlation between Equation (A9) and (A10) is consistent with the conclusion that the lower $\Delta K_a$ in the AlCl$_3$ is due to the development of a plane stress situation at the crack tip that is caused by significant S-L splitting effects.

9.5 Suggestions for further work

Based on the present study of the S-L splitting effects on the T-L orientation fatigue crack growth and of the effects of the re-aging treatment on the S-L orientation fatigue crack propagation, it will be intriguing to investigate the effects of the re-aging treatment on the T-L orientation corrosion fatigue crack propagation behaviour of Al-Li alloy 8090-T8771 plate. Such a study will determine whether there is any influence of the re-aging treatment on the occurrence of the S-L splitting phenomenon and the consequent effects on the T-L orientation fatigue crack growth.