STRESS CORROSION CRACKING OF ALUMINUM ALLOYS

BY

RAJESHWAR SINGH PATHANIA

B.Sc. (Hons.) Delhi University, 1963
B.E. (Met.) Indian Institute of Science, Bangalore, 1965

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

in the Department
of
METALLURGY

We accept this thesis as conforming to the
required standard

The University of British Columbia
February, 1970.
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 representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Metallurgy

The University of British Columbia
Vancouver 8, Canada

Date April 6, 1970
ABSTRACT

The stress corrosion behaviour of precipitation hardened Al-9Mg, Al-22Zn and Al-3Mg-6Zn alloys has been studied in aqueous environments and ethanol. The stress corrosion susceptibility defined as the reciprocal of failure time has been investigated as a function of alloy-environment system, isothermal aging treatment, microstructure, applied tensile stress, and temperature using smooth and notched specimens. Constant load tests, load-relaxation tests and tensile tests in different environments have been used to evaluate the stress corrosion characteristics of aluminum alloys. A limited study of Mg-9Al has also been carried out in aqueous environments.

The process of stress corrosion generally consisted of three parts: 1) A slow initiation stage 2) a rapid propagation stage 3) mechanical fracture due to tensile overload. With a few exceptions, the initiation time was greater than the propagation time.

The crack initiation and propagation rates were stress and thermally activated and could be expressed by a general equation of the form

\[
\text{Rate} = A_0 \sigma^n \exp \left( \frac{Q}{RT} \right)
\]

where \( \sigma \) is the applied tensile stress, \( Q \) is the apparent activation energy of the rate controlling process and \( A_0 \) and \( n \) are constants for a given alloy-environment system. The apparent activation energy of the rate controlling process was different in the two environments. It also changed between initiation and propagation stages.
The aluminum alloys when ranked in order of increasing susceptibility were: 1) Al-3Mg-6Zn, 2) Al-9Mg, 3) Al-22Zn. The alloys which were given heat treatments correlating to the presence of coherent or partially coherent phases, were found to be most prone to stress corrosion cracking.

The environments placed in an order of increasing aggressiveness were dessicant-dried air, double distilled water, ethanol, ambient air, deionized water and NaCl/K₂CrO₄ solution. The ductility of susceptible aluminum alloys was found to be significantly decreased by NaCl/K₂CrO₄ and deionized water at low strain rates and enhanced by dessicant-dried air.

Fractography showed the cracking to be intergranular in aluminum alloys and transgranular in the Mg-Al alloy. The stress corrosion surface was characterised by a rough or corroded appearance while the mechanically fractured surface exhibited slip steps and dimples caused by void formation.

The hydrogen mechanism of cracking was examined in light of hydrogen charging experiments and other evidence and was found to be unsatisfactory. Models involving either dissolution or deformation alone were also inadequate in explaining the present results. Therefore a new model was postulated which involves the generation of a continuous path of chemical heterogeneity by shearing and link up of coherent precipitates followed by their dissolution. The rate controlling step in the deformation process is believed to change during the transition from initiation to propagation.
The postulated model is consistent with the present results but its further development must await better knowledge of the kinetics of dissolution of precipitates and that of deformation processes at the crack tip.
# TABLE OF CONTENTS

## Chapter 1. INTRODUCTION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Critical Review of Stress Corrosion Theories</td>
<td>3</td>
</tr>
<tr>
<td>1.2. Film Rupture Mechanisms</td>
<td>4</td>
</tr>
<tr>
<td>1.3. Mechanisms Involving Precipitate Distribution and Precipitate Free Zone</td>
<td>5</td>
</tr>
<tr>
<td>1.4. Stress Concentration Hypotheses</td>
<td>7</td>
</tr>
<tr>
<td>1.5. Environmental Factors</td>
<td>9</td>
</tr>
<tr>
<td>1.6. The Unresolved Points</td>
<td>9</td>
</tr>
<tr>
<td>1.7. Objectives of the Present Work</td>
<td>10</td>
</tr>
</tbody>
</table>

## Chapter 2. EXPERIMENTAL PROCEDURE

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1. Starting Materials and Alloy Preparation</td>
<td>12</td>
</tr>
<tr>
<td>2.2. Fabrication by Rolling</td>
<td>13</td>
</tr>
<tr>
<td>2.3. Extrusion</td>
<td>13</td>
</tr>
<tr>
<td>2.4. Heat Treatment</td>
<td>15</td>
</tr>
<tr>
<td>2.5. Polishing, Degreasing and Tensile Tests</td>
<td>17</td>
</tr>
<tr>
<td>2.6. Constant Load Stress Corrosion Tests</td>
<td>17</td>
</tr>
<tr>
<td>2.7. Load Relaxation Tests</td>
<td>19</td>
</tr>
<tr>
<td>2.8. Strain Rate Tests</td>
<td>19</td>
</tr>
<tr>
<td>2.9. Hydrogen Charging Experiments</td>
<td>20</td>
</tr>
<tr>
<td>2.10. Optical Microscopy</td>
<td>20</td>
</tr>
<tr>
<td>2.11. Electron Microscopy</td>
<td>21</td>
</tr>
</tbody>
</table>

## Chapter 3. RESULTS AND OBSERVATIONS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1. Isothermal Aging of Al-9Mg</td>
<td>22</td>
</tr>
</tbody>
</table>
3.2. Al-3Mg-6Zn ........................................ 22
3.3. Mg-8.5Al ........................................... 26
3.4. Stress Corrosion Testing Techniques ........... 26
  3.4.1. Stress Corrosion Susceptibility............ 30
  3.4.2. Constant Load Tests ......................... 30
    3.4.2.1. Al-9Mg ................................. 30
    3.4.2.2. Al-3Mg-6Zn ............................ 34
    3.4.2.3. Mg-8.6Al ............................... 34
  3.4.3. Strain Rate Tests ............................ 39
    3.4.3.1. Al-2.6Mg-6.3Zn ........................ 39
    3.4.3.2. Al-21.5Zn ............................... 42
  3.4.4. Load Relaxation Tests for Different
        Alloy-Environment Systems .................. 42
  3.5. The pH of the NaCl/K₂CrO₄ Solution ............ 50
  3.6. Activation Energy Analysis ....................... 50
    3.6.1. Al-21.5Zn .................................. 52
    3.6.2. Applied Stress vs Failure Time .......... 55
    3.6.3. Al-2.6Mg-6.3Zn ........................... 57
    3.6.4. Al-8.6Mg ................................. 61
    3.6.5. Apparent Activation Energy During
            Propagation ............................... 61
  3.8. Electron Microscopy ............................. 68
    3.8.1. Precipitation Distribution After
            Aging ..................................... 68
3.8.2. Fractography ........................................ 77

Chapter 4. DISCUSSION ........................................ 93

4.1. Precipitation Hardening and Mechanical Properties ........................................ 93

4.1.1. Al-9Mg Aged at 200°C ............................ 93
4.1.2. Al-3Mg-6Zn Aged at 160°C ....................... 95
4.1.3. Al-21.5Zn Aged at Room Temperature. .......... 96
4.1.4. Mg-8.5Al Aged at 200°C .......................... 97
4.1.5. Aged Hardening Mechanism ....................... 98
4.1.6. Effect of Aging on Mechanical Properties of Aluminum Alloys .......... 100

4.2. Parameters Affecting Stress Corrosion Cracking in Aluminum Alloys ..................... 105

4.2.1. Stress Corrosion Cracking and Microstructure in Al-9Mg Alloys ... 105
4.2.2. Applied Stress and Stress Corrosion Susceptibility ......................... 106
4.2.3. Nature of Slip and Stress Corrosion Susceptibility ......................... 107
4.2.4. Stress Corrosion Susceptibility and Microstructure in Al-3Mg-6Zn Alloy 108
4.2.5. Applied Stress and Stress Corrosion Susceptibility ......................... 111

4.3. Stress Corrosion Susceptibility of Mg-8.5Al 118
\begin{table}[h]
\centering
\begin{tabular}{|l|l|}
\hline
4.4. Variation in Stress Corrosion Susceptibility with the Alloy System & 120  \\
4.5.1. Initiation and Propagation of Stress Corrosion Cracks in NaCl/K₂CrO₄ Solution & 123  \\
4.5.2. The Relative Lengths of Initiation and Propagation Times in NaCl/K₂CrO₄ Solution & 129  \\
4.6. The Effect of Different Environments on the Stress Corrosion Behaviour of Aluminum Alloys & 130  \\
4.6.1. Stress Corrosion in Alcohols & 136  \\
4.6.2. Effect of Environment on Mechanical Properties of Al-2.6Mg-6.3Zn & 137  \\
4.6.3. Effect of Environment and Strain Rate on Mechanical Properties of Al-21.5Zn & 140  \\
4.6.4. Effect of Strain Rate on Serrated Yielding & 140  \\
4.7. Temperature Dependence of the Stress Corrosion Process & 143  \\
4.8. The Hydrogen Mechanism & 145  \\
4.9. The Requirements of a Satisfactory Model & 154  \\
4.9.1. Models Involving Either Dissolution or Deformation and Their Drawbacks & 155  \\
4.10. The Proposed Model & 158  \\
\hline
\end{tabular}
\end{table}
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.10.1. The Observations Explained by the Proposed Model</td>
<td>165</td>
</tr>
<tr>
<td>4.11. Conclusions</td>
<td>167</td>
</tr>
<tr>
<td>4.12. Suggestion for Further Work</td>
<td>168</td>
</tr>
<tr>
<td>Appendix I</td>
<td>169</td>
</tr>
<tr>
<td>Appendix II</td>
<td>177</td>
</tr>
<tr>
<td>Bibliography</td>
<td>180</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Types of tensile and stress corrosion specimens used in the present work</td>
</tr>
<tr>
<td>2</td>
<td>Stress corrosion cells used in the present work</td>
</tr>
<tr>
<td>3</td>
<td>Modified creep stand for constant load tests</td>
</tr>
<tr>
<td>4</td>
<td>Precipitation hardening of Al-9Mg, aged at 200°C</td>
</tr>
<tr>
<td>5</td>
<td>Precipitation hardening of Al-3Mg-6Zn, aged at 200°C</td>
</tr>
<tr>
<td>6</td>
<td>Precipitation hardening of Mg-8.6Al, aged at 200°C</td>
</tr>
<tr>
<td>7</td>
<td>Failure time vs aging time for Al-9Mg aged at 200°C</td>
</tr>
<tr>
<td>8</td>
<td>Applied stress vs failure time for Al-9Mg aged for 7 hours at 200°C</td>
</tr>
<tr>
<td>9</td>
<td>Effect of aging time at 160°C on the failure time of Al-3Mg-6Zn in NaCl/K$_2$CrO$_4$</td>
</tr>
<tr>
<td>10</td>
<td>Applied stress vs failure time for the aged Al-3Mg-6Zn alloy</td>
</tr>
<tr>
<td>11</td>
<td>Failure time vs aging time for Mg-8.6Al aged at 200°C</td>
</tr>
<tr>
<td>12</td>
<td>Effect of applied stress on the failure time of solution treated and quenched Mg-8.6Al</td>
</tr>
<tr>
<td>13</td>
<td>Strain rate vs uniform and total elongation for solution treated and quenched Al-2.6Mg-6.3Zn alloy</td>
</tr>
<tr>
<td>14</td>
<td>Strain rate vs uniform and total elongations for an overaged Al-2.6Mg-6.3Zn alloy</td>
</tr>
<tr>
<td>15</td>
<td>Effect of different media on crack initiation and propagation times in Al-2.6Mg-6.3Zn alloy in solution treated and overaged conditions</td>
</tr>
<tr>
<td>16</td>
<td>Effect of different media on initiation and propagation times in Al-21.5Zn alloy</td>
</tr>
<tr>
<td>17</td>
<td>Logarithm of crack initiation rate vs 1/T for Al-21.5Zn in ethyl alcohol</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-------------</td>
</tr>
<tr>
<td>18.</td>
<td>Logarithm of crack initiation rate vs 1/T for Al-21.5Zn in ethyl alcohol</td>
</tr>
<tr>
<td>19.</td>
<td>The effect of applied stress on log failure time of Al-21.5Zn alloy in 99.9% ethyl alcohol</td>
</tr>
<tr>
<td>20.</td>
<td>Logarithm of crack initiation rate vs 1/T for an overaged Al-2.6Mg-6.3Zn alloy</td>
</tr>
<tr>
<td>21.</td>
<td>Logarithm of crack initiation rate vs 1/T for Al-2.6Mg-6.3Zn in NaCl/K₂CrO₄ solution and water</td>
</tr>
<tr>
<td>22.</td>
<td>Logarithm of crack initiation rate vs 1/T for aged Al-8.6Mg alloy in ethyl alcohol</td>
</tr>
<tr>
<td>23.</td>
<td>Logarithm of propagation rate vs 1/T for Al-2.6Mg-6.3Zn in NaCl/K₂CrO₄ and D. water</td>
</tr>
<tr>
<td>24.</td>
<td>Logarithm of propagation rate vs 1/T for Al-Mg-Zn and Al-Mg alloys in ethyl alcohol</td>
</tr>
<tr>
<td>25.</td>
<td>Logarithm of propagation rate vs 1/T for Al-21.5Zn in 95% ethyl alcohol</td>
</tr>
<tr>
<td>26.</td>
<td>Logarithm of propagation rate vs 1/T for Al-21.5Zn in 99% ethyl alcohol</td>
</tr>
<tr>
<td>27.</td>
<td>Al-9Mg aged 7 hours at 200°C. Matrix precipitate distribution, 10,000 x</td>
</tr>
<tr>
<td>28.</td>
<td>Al-9Mg aged 7 hours at 200°C. G.b. ppt 10,000 x</td>
</tr>
<tr>
<td>29.</td>
<td>Al-9Mg aged 5 hours at 200°C. G.b. ppt and dislocations, 20,000 x</td>
</tr>
<tr>
<td>30a,b</td>
<td>Al-9Mg aged at 200°C. Showing the precipitate free zone</td>
</tr>
<tr>
<td>31a-d</td>
<td>Al-9Mg aged at 200°C. Precipitate distribution</td>
</tr>
<tr>
<td>32a,b</td>
<td>Difference in precipitate size between the aged Al09Mg and Al-3Mg-6Zn</td>
</tr>
<tr>
<td>33a,b</td>
<td>Al-3Mg-6Zn aged at 160°C for a) 1 hour b) 3 hours</td>
</tr>
<tr>
<td>34a-c</td>
<td>Al-9Mg aged 5 hours at 200°C. Strained a) 1.3% b) 4%, c) 4%</td>
</tr>
<tr>
<td>35.</td>
<td>Mg-8.6Al aged for 1 hour at 200°C. Transgranular stress corrosion crack 40 x</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>36.</td>
<td>Mg-8.6Zn, solution treated and water quenched. Transgranular stress corrosion crack 80 x .........</td>
</tr>
<tr>
<td></td>
<td>76</td>
</tr>
<tr>
<td>37a-e</td>
<td>Aged Al-22Zn alloy, stress corroded in NaCl/K₂CrO₄ at 10,000 psi. Complete stress corrosion failure....</td>
</tr>
<tr>
<td></td>
<td>81</td>
</tr>
<tr>
<td>38a-h</td>
<td>Al-22Zn, hydrogen charged for 30 minutes and stress corroded in NaCl/K₂CrO₄ at 10,000 psi ..............</td>
</tr>
<tr>
<td></td>
<td>84</td>
</tr>
<tr>
<td>39a-e</td>
<td>Al-2.6Mg-6.3Zn, solution treated and water quenched, stress corroded in NaCl/K₂CrO₄ at 55,000 psi. Predominantly stress corrosion surface ..........</td>
</tr>
<tr>
<td></td>
<td>87</td>
</tr>
<tr>
<td>40a-d</td>
<td>Aged Al-9Mg, stress corroded in NaCl/K₂CrO₄ at 7,000 psi. Predominantly stress corrosion surface...</td>
</tr>
<tr>
<td></td>
<td>89</td>
</tr>
<tr>
<td>41a-f</td>
<td>Al-22Zn stress corroded in 99.9% ethanol at 30,000 psi. Stress corrosion and tensile overload modes of failure ..........</td>
</tr>
<tr>
<td></td>
<td>91</td>
</tr>
<tr>
<td>42.</td>
<td>Phase diagrams of Al-Mg and Al-Zn systems ..........</td>
</tr>
<tr>
<td></td>
<td>92</td>
</tr>
<tr>
<td>43.</td>
<td>Plates of equilibrium Mg₁₇Al₁₂ phase with basal habit plane ........................................</td>
</tr>
<tr>
<td></td>
<td>99</td>
</tr>
<tr>
<td>44.</td>
<td>Schematic variation of yield stress with aging time for an age-hardening system .........................</td>
</tr>
<tr>
<td></td>
<td>102</td>
</tr>
<tr>
<td>45.</td>
<td>Log-log plot of applied stress vs failure time for Al-9Mg in NaCl/K₂CrO₄ ................................</td>
</tr>
<tr>
<td></td>
<td>113</td>
</tr>
<tr>
<td>46.</td>
<td>Log-log plot of applied stress vs failure time for Al-9Mg in NaCl/K₂CrO₄ ................................</td>
</tr>
<tr>
<td></td>
<td>114</td>
</tr>
<tr>
<td>47.</td>
<td>Log-log plot of applied stress vs initiation time for Al-22Zn in ethanol ................................</td>
</tr>
<tr>
<td></td>
<td>116</td>
</tr>
<tr>
<td>48.</td>
<td>Log-log plot of applied stress vs propagation rate for Al-22Zn in ethanol ................................</td>
</tr>
<tr>
<td></td>
<td>117</td>
</tr>
<tr>
<td>49.</td>
<td>Applied stress vs failure time for three systems studied under constant load in NaCl/K₂CrO₄ .............</td>
</tr>
<tr>
<td></td>
<td>122</td>
</tr>
<tr>
<td>50a-c</td>
<td>Three types of load relaxation curves observed in the present work ........................................</td>
</tr>
<tr>
<td></td>
<td>125</td>
</tr>
<tr>
<td>51.</td>
<td>Variation in stress intensity factor K_I during sub-critical crack propagation ............................</td>
</tr>
<tr>
<td></td>
<td>128</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>52.</td>
<td>Illustration of the proposed model</td>
</tr>
<tr>
<td>53a-h</td>
<td>Tensile fracture surface of aged, notched Al-22Zn alloy fractured in dessicant dried air at cross-head speeds of 20 in/min (a-e) and 0.01 in/min (f-h).</td>
</tr>
<tr>
<td>54a-f</td>
<td>Notched, aged Al-2.6Mg-6.3Zn alloy pulled to fracture in air at 0.01 in/min</td>
</tr>
<tr>
<td>55a,b</td>
<td>Aged Al-9Mg pulled to fracture in air at 0.01 in/min.</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.</td>
<td>Chemical Analysis of Fabricated Alloys</td>
</tr>
<tr>
<td>2.</td>
<td>Extrusion Condition of Alloys</td>
</tr>
<tr>
<td>4.</td>
<td>Effect of Strain Rate on Ductility and Yield Strength, of Al-21.5Zn in Dry Air and Deionized Water</td>
</tr>
<tr>
<td>5.</td>
<td>Crack Initiation and Propagation Times for Al-3Mg-6Zn in NaCl/K₂CrO₄ Solution</td>
</tr>
<tr>
<td>6.</td>
<td>Crack Initiation and Propagation Times in Different Environments</td>
</tr>
<tr>
<td>7.</td>
<td>Crack Initiation and Propagation Times for Al-8.6Mg in NaCl/K₂CrO₄ Solution</td>
</tr>
<tr>
<td>8.</td>
<td>Crack Initiation and Propagation Times for Mg-8.6Al in NaCl/K₂CrO₄ Solution</td>
</tr>
<tr>
<td>10.</td>
<td>Activation Energies of Crack Initiation for Al-21.5Zn in Ethanol-Water Mixtures</td>
</tr>
<tr>
<td>11.</td>
<td>Activation Energies for Al-21.5Zn From Log Rate/T vs 1/T Plot</td>
</tr>
<tr>
<td>12.</td>
<td>Hydrogen Charging Experiments on Al-21.5Zn in NaCl/K₂CrO₄ at 10,000 psi</td>
</tr>
<tr>
<td>13.</td>
<td>Hydrogen Charging Experiments on Aged Al-2.6Mg-6.3Zn Alloy in NaCl/K₂CrO₄ at 76,500 psi</td>
</tr>
<tr>
<td>14.</td>
<td>Relative Fractions of Initiation and Propagation Times of Different Alloys in NaCl/K₂CrO₄ Solution</td>
</tr>
<tr>
<td>15.</td>
<td>Relative Lengths of Initiation and Propagation Times in Various Alloy Environment Systems</td>
</tr>
<tr>
<td>16.</td>
<td>The Apparent Activation Energies for Crack Initiation and Propagation and the Possible Rate Controlling Processes</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>17.</td>
<td>Apparent Activation Energies of Crack Initiation and Propagation for Aluminum Alloys</td>
</tr>
<tr>
<td>18.</td>
<td>Proposed Activation Energies</td>
</tr>
<tr>
<td>19.</td>
<td>The Correlation Coefficient and Error in Apparent Activation Energy from the Arrhenius Plots</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

The author wishes to thank his research advisor Dr. D. Tromans for his keen interest and valuable advice throughout this project. Thanks are also extended to the members of his Ph.D. committee, Dr. Peters and Dr. Lund and to other members of the department for their useful suggestions. The assistance of the technical staff particularly Mr. Arvid Lacis is appreciated.

The financial support in the form of a National Research Council Scholarship is gratefully acknowledged.
Errata

p. 6  last line    enhanced
p. 8  line 18     reiterate
p. 10 line 2      but is immune
p. 13 line 2      homogenized
p. 20 line 2      part
p. 33 Abcissa     Failure time sec. 10^4
p. 50 line 9      alloys
p. 54 Ordinate    log Initiation Rate/T
p. 57           \[ t_f = k_1 \sigma^{-n} \]
 p. 61 line 20    fatigue in aluminum
p. 62 line 22    carried out
p. 96 line 11    comparable
p. 120 line 9    matrix
     line 14    overaged
p. 150 line 24   0.1\mu radius
1. INTRODUCTION

Stress corrosion cracking can be defined as the rupture of metal, taking the form of cracks that may occur under the conjoint influence of a specific corrosive environment and applied or residual tensile stresses (1) well below the ultimate tensile strength. A "crack" can further be defined as a penetration, in which the depth is several order of magnitude greater than the width. Failures promoted by cross sectional area reduction by corrosion, are excludes from the term stress corrosion cracking (SCC).

Metals of high strength and ductility can fail catastrophically by stress corrosion cracking. The phenomenon is insidious, because there may be no macroscopic indications of impending failure and yet it may result in the explosion of a boiler, the failure of a steel hook on a building site or the failure of landing gear struts on an airplane (2). Many stress corrosion failures are undramatic and include leaks in tanks, unspectacular failures of bolts and failure of stainless steel vessels used in various industries.

Some other features which make stress corrosion cracking a major problem are (3):

(i) Alloys subject to cracking are normally considered passive
and may take years to be corroded to unusable dimensions and yet in the presence of a stress may fail in several hours.

(ii) Extremely small quantities of apparently innocuous environments may cause cracking; e.g. water may cause cracking in aluminum alloys and high strength steels; salt water may stress corrode austenitic stainless steel and titanium alloys.

(iii) The stress corrosion cracking of aluminum and magnesium alloys assumes special importance in view of the fact that these alloys are widely used in aircraft fittings and in applications where a high strength to weight ratio is required. The most susceptible aluminum alloys are those that can be strengthened by heat treatment and these are, of course, most useful as load carrying members in aerospace industry (2), automotive applications, railroad and marine applications and chemical process application.

The objective of this project was to study the stress corrosion characteristics of aluminum base alloys, specifically Al-9Mg, Al-3Mg-6Zn, and Al-21.5Zn with a view to developing a mechanism of stress corrosion cracking. A limited study of Mg-8.5Al was also carried out. The precipitate in Al base alloy is believed to be anodic to the matrix (4) whereas in Mg base alloy it is cathodic (5) to the solid solution.

No general mechanism of stress corrosion is believed to exist (6). There are a number of processes operating under specific metallurgical and environmental conditions and only a few of these operating together may be necessary for cracking to occur. Stresses may give rise to elastic and plastic deformations resulting in film rupture, dislocation-precipitate interaction and crack-stress field interaction. The
environment may cause ionic diffusion into oxide layers, dissolution of layers, adsorption reactions at cracktip or fresh metal surface, embrittlement by hydrogen and anodic dissolution by chemical or electrochemical processes.

1.1. Critical Review of Stress Corrosion Theories

A number of mechanisms have been put forward to explain the stress corrosion cracking of aluminum base alloys. The generalized theory of stress corrosion of aluminum alloys described by Mears, Brown and Dix (7) is as follows:

"Corrosion occurs along localized paths such as grain boundaries producing fissures. These preferentially corroded paths may represent strata of low inherent resistance to corrosion or they may be anodic to the adjoining metal. Components of tensile stress normal to the path create a stress concentration at the base of the fissure. At sufficient concentration of stress, the fissures open further, thus exposing unfilmed metal to the corrosion attack. The fresh metal is anodic and there is an acceleration of corrosion resulting in further separations of metal". Thus the effects of corrosion and stress are mutually reinforcing and result in an accelerating crack which leads to a reduction in area sufficient to cause mechanical fracture.

The model proposed by Mears et al., does not give a detailed mechanistic interpretation of the stress corrosion phenomenon. Other models have been proposed, which interpret the observed stress corrosion behaviour in terms of the rupture of protective oxide, the size of the
precipitate free zone (PFZ) next to the grain boundary, the deformation in the PFZ, and the nature of precipitate produced during aging. Some of the results and their interpretations are contradictory. There is no single theory which can completely explain the stress corrosion characteristics of aluminum base alloys.

1.2. **Film Rupture Mechanisms**

Logan (11) believes that the protective oxide film must be ruptured by plastic deformation in order for corrosive attack to proceed. Corrosion results in repair of the film which is once again ruptured by plastic deformation, leading to more corrosion. According to this theory stress corrosion crack in the alloy proceeds by electrochemical processes alone and no mechanical rupture of the alloy takes place.

Film rupture by itself is not sufficient to cause stress corrosion cracking. Pure aluminum does not stress corrode even when the passive oxide film is ruptured by slip step formation. Many ductile aluminum alloys exhibit excellent stress corrosion resistance. Another objection is raised by the work of Farmery and Evans (14). They allowed a crack to propagate part of the way through a specimen of susceptible Al-7Mg alloy and then arrested the crack by application of cathodic current for 30 minutes. When the current was stopped, the crack did not propagate again although 25 hours later fresh cracks appeared elsewhere. If mechanical film rupture at the crack tip was the determining factor for propagation, the crack should have resumed
after the discontinuation of the protective current, because of the heavy plastic deformation at the crack tip.

Gruhl (15) describes stress corrosion cracking as a two stage process. The first stage is largely chemical or electrochemical, whereas the true crack formation is determined in the second stage by a metal physical process. However, it fails to explain the behaviour of some aluminum alloys that can tolerate initiation of intergranular fissures in some environments and yet possess excellent resistance to stress corrosion cracking. Another point that conflicts with Gruhl's theory is that there appears to be no correlation between stress corrosion cracking and fracture toughness (12).

1.3. Mechanisms Involving Precipitate Distribution and Precipitate Free Zone.

In certain models, the precipitate-free zone adjacent to the grain boundary is believed to be responsible for intergranular stress corrosion. This model is espoused by Pugh and Jones (13), McEvily et al (16) and Thomas (17). These workers believe that the precipitate free zone undergoes preferential plastic deformation on application of stress. As a result the deforming metal within the PFZ becomes anodic to the rest of the grain. Stress corrosion cracking proceeds by preferential dissolution of metal within the PFZ (17). Pugh and Jones (13) suggest that localized plastic deformation initiates a grain boundary crack which propagates mechanically through the PFZ.

However, studies conducted by Holl (18) on similar alloys with small additions of copper (0.5%), silicon and iron (0.3%) did not show the precipitate free zone in most cases. It is significant that the
two most susceptible conditions were free of denuded zones but contained Guinier Preston (G.P.) zones or coherent precipitates, whereas the two resistant conditions did show very narrow (500 Å) denuded zones. Dislocations in highly susceptible condition formed uniformly distributed tangles.

Gruhl and Cordier (19) obtained results on an Al-5Zn-3Mg (plus 1% other elements) which indicated that stress corrosion was caused mainly by metastable, redissolvable precipitates such as coherent \( \eta' \) phase and improved markedly when these precipitates were replaced by the stable \( \text{MgZn}_2 \) phase. Jacobs (20) proposes that the initiation of a stress corrosion crack can take place at the interface between a pitted precipitate particle and the aluminum matrix. The crack propagates intergranularly via a series of corrosion-mechanical steps. Both precipitate and aluminum matrix are believed to alternate as anodic phases. In a recent study Helfrich (21) demonstrated that stress corrosion cracking does initiate at the particle matrix interface in an Al-2.6Mg-4Zn alloy tested in 6% NaCl solution.

The precipitate free zone hypothesis is also opposed by Speidel (22). He observed long straight narrow bands of high dislocation density, with the dislocations piled up against the grain boundaries in materials of high susceptibility. In materials aged to a reduced susceptibility, the slip bands contain dislocations of irregular curvature and dislocation loops. Speidel concluded that susceptibility to stress corrosion cracking in high strength aluminum alloys is enhanced by precipitates which are sheared during plastic deformation.
such as G.P. zones and intermediate precipitates. The shearing results in an increase in slip step height and stress concentrations at the grain boundaries as a result of pile ups of unpinned dislocations adjacent to the grain boundary.

1.4. Stress Concentration Hypotheses

According to Robertson and Tetelman (8) suitably oriented dislocation pile ups adjacent to grain boundary produce tensile stress components normal to the grain boundary. They derive their results from the analysis by Stroh (9) who concludes that the maximum normal stress occurs across a plane at 70° to the slip plane and diminishes with distance from the barrier.

\[ \sigma_m = \tau_e \left( \frac{L}{r} \right)^{1/2} \]  

where

- \( \sigma_m \) = maximum normal stress
- \( \tau_e \) = effective shear stress
- \( L \) = length of an array of \( n \) dislocations
- \( r \) = distance from the barrier at which normal stress is calculated

Stroh has put this expression into the Griffith criterion for fracture leading to the result that a crack will nucleate when

\[ n\tau_e > 1.5G \]  

where \( G \) is the rigidity modulus.
From equation (1) and (2) a crack will be formed when the maximum tensile stress due to a pile up of \( n \) dislocations is such that

\[
\frac{n \cdot \sigma_m \sqrt{L}}{L} > 1.5 \, G
\]  

Uhlig (23) and Johnson (24) et al believe that the adsorption of corrosive environment or its constituents lowers the strength of the strained atomic bonds at the crack tip (stress-sorption cracking). Both the shear modulus and the surface energy are thought to be reduced by the presence of environment at the crack tip.

The stress concentration at a grain boundary on a free surface is likely to be less than in the interior since the surface atoms are under a smaller constraint.

Haynie and Boyd (25) suggest that hydrogen concentrates at the grain boundaries. Under localized high stresses these hydrogen rich areas are then assumed to become anodic with respect to the surrounding grains and thus create susceptible paths. Their model, however, does not account for the prevention of stress corrosion cracking by cathodic charging.

In a recent paper Pugh et al (26) reiterate the idea that the stress corrosion susceptibility of Al-Mg-Zn depends on the width of the precipitate free zone, increasing significantly with decreasing zone width. This seems to contradict the results of Beck and Sperry (27) who obtain a positive correlation between the zone width and stress corrosion susceptibility for Al-7Mg.
The stress corrosion surface is shown to be rough textured, both by Pugh (26) and Jacobs (10). This indicates that dissolution is taking place either during or after the propagation of the crack.

1.5. Environmental Factors

Gilbert and Hadden (28) showed that Al-7Mg alloy did not crack in 3.5% NaCl in the absence of oxygen while admission of oxygen resulted in rapid cracking. During stress corrosion of this alloy a stream of fine bubbles of hydrogen was seen to evolve.

The time for cracking increases with pH in a 3.5% NaCl solution. It seems to decrease with increasing salt concentration and a susceptible Al-7Mg would stress corrode even in a 50 ppm NaCl solution (29).

In spite of the tremendous amount of work done on the stress corrosion behaviour of high strength aluminum alloys and a multitude of proposed mechanisms, a reasonably satisfying mechanism can hardly be said to exist.

1.6. The Unresolved Points

1. If the nature of precipitate distribution is important in SCC, then why do similar precipitate distributions result in a widely different stress corrosion susceptibilities (12)?

2. Why is it, that different dislocation arrangements can result in identical stress corrosion characteristics? A number of models relate susceptibility to dislocation configurations.

3. While a number of alloys susceptible to intergranular attack also stress corrode in the same medium, there are two other
classes of aluminum alloys. One of these undergo intergranular corrosion but are immune to stress corrosion while the others show no intergranular attack but are highly susceptible to stress corrosion (12).

4. The role of the precipitate free zone (PFZ) is not clear. Robinson and Holl have observed widely different stress corrosion behaviour in alloys of similar width of PFZ.

Ductile crack propagation through the PFZ is not supported by fractographic evidence on account of an absence of dimpling in this region.

5. The role of hydrogen in stress corrosion of aluminum alloys is not clear (25).

6. Aluminum alloys can be stress corroded in organic liquids such as ethyl alcohol, methyl alcohol and carbon tetrachloride. It is not known whether the mechanism of stress corrosion in organic liquids is the same as in aqueous solutions.

1.7. Objectives of the Present Work

Historically the approach to stress corrosion has been largely phenomenological. Most of the work has been carried out to evaluate the stress corrosion susceptibility as a function of alloy composition and test variables. Experimental measurements of the stress corrosion susceptibility have involved either time-to-failure for uncracked or precracked specimen; or the determination of the rate of crack growth as a function of stress intensity factor $K_I$ (82).

There is a scarcity of kinetic data for initiation and propagation stages as a function of temperature. While Gruhl (73) and
Helfrich (72) have studied the temperature dependence of stress corrosion in aluminum alloys, they have not distinguished between initiation and propagation times. Therefore, it is not clear whether the apparent activation energies they observe are for the initiation or propagation stage. Wei (82) has determined the kinetics of fatigue crack growth in a high strength aluminum alloy immersed in different environments. The apparent activation energy for the process decreases with increasing stress concentration factor $K_I$.

1. The first objective of the present work was to determine the effect of isothermal ageing treatment, alloy composition, stress level, environment and specimen geometry on the stress corrosion susceptibility of aluminum alloys.

2. The next objective was to study the kinetics of stress corrosion cracking as a function of temperature and environment, in order to determine the apparent activation energy and to correlate the kinetic observations with processes possibly occurring during the initiation and propagation of stress corrosion cracking.

3. A third objective of this work was to carry out fractographic studies to determine the relative roles of dissolution and mechanical fracture processes during stress corrosion.
2. PROCEDURE

2.1. Starting Materials and Alloy Preparation

High purity aluminum (99.99), high purity magnesium (99.99), and high purity zinc (99.95) were used in the present investigation. Melting was carried out at 700°C in a cylindrical graphite mold, enclosed in a stainless steel bomb and housed in a vertical resistance heated furance. The steel bomb was shaken vigorously to stir the melt. The melt was then solidified by sharp unidirectional cooling by placing it on a large steel block while the upper part of the mold was still kept inside the furance. Pipe formation was kept to a minimum by this technique.

Four types of alloys were made. The compositions were checked by Coast Eldridge Co. and were found to be close to nominal. The compositions are listed in Table (1).

Table (1)
CHEMICAL ANALYSIS OF FABRICATED ALLOYS

<table>
<thead>
<tr>
<th>Nominal Composition (wt %)</th>
<th>Actual Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-9Mg</td>
<td>Al-9Mg</td>
</tr>
<tr>
<td>Al-9Mg</td>
<td>Al-8.6Mg</td>
</tr>
<tr>
<td>Al-3Mg-6Zn</td>
<td>Al-3Mg-6Zn</td>
</tr>
<tr>
<td>Al-3Mg-6Zn</td>
<td>Al-2.6Mg-6.3Zn</td>
</tr>
<tr>
<td>Al-22Zn</td>
<td>Al-21.5Zn</td>
</tr>
<tr>
<td>Mg-9Al</td>
<td>Mg-8.6Al</td>
</tr>
<tr>
<td>Mg-9Al</td>
<td>Mg-9.1Al</td>
</tr>
</tbody>
</table>

All the alloy compositions in this thesis are stated in weight percent of solute.
2.2. Fabrication by rolling

The castings were approximately 1" in diameter and 6" long. They were homogenised and subsequently hot rolled or extruded.

Considerable difficulty was encountered in rolling Al-9Mg which showed hot shortness at temperatures between 300° to 400°C. It was therefore rolled at 150°C at a slow roll speed with an initial reduction of 10% per pass. Intermittent anneals of 10 minutes were given between each pass. Any edge cracks formed during rolling were ground off before the annealing. When the sheet reached a thickness of 0.05", it was solution heat treated at 430°C for 20 minutes and water quenched. It was then cold rolled 50% to a final thickness of 0.025". The heat treatment before cold rolling resulted in the desired grain size of 90 μ.

Al-3Mg-6Zn was similarly rolled at 200°C to a thickness of 0.050" then cold rolled to 0.025". The rolled alloys were used for preliminary age hardening, stress corrosion and slip line studies.

The rolled sheet was sheared into 2.5" long by 0.75" wide strips, which in turn were punched into tensile test specimens having a reduced gauge length of 0.8" with a width of 0.21". The tensile axis of specimen was parallel to the rolling direction, fig. (1a).

2.3. Extrusion

3" long billets were machined to diameter of 0.96" and extruded at high temperature. The following table gives the extrusion variables. The diameter of the extruded wire was 0.152".
Figure (1). Types of tensile and stress corrosion specimens, used in the present work.
Table (2)

EXTRUSION CONDITIONS OF ALLOYS

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temp. °C</th>
<th>Pressure</th>
<th>Extrusion ratio</th>
<th>Average extrusion speed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>Al-8.6Mg</td>
<td>390</td>
<td>116,000</td>
<td>141,000</td>
<td>38.5:1</td>
</tr>
<tr>
<td>Al-2.6Mg-6.3Zn</td>
<td>415</td>
<td>81,500</td>
<td>106,000</td>
<td>38.5:1</td>
</tr>
<tr>
<td>Al-22%Zn</td>
<td>380</td>
<td>45,000</td>
<td>60,000</td>
<td>38.5:1</td>
</tr>
<tr>
<td>Mg-8.6Al</td>
<td>360-370</td>
<td>49,000</td>
<td>62,000</td>
<td>38.5:1</td>
</tr>
</tbody>
</table>

Two types of specimens were made from the wire. They are shown in fig. 1b and 1c.

The notched specimens were machined after the solution heat treatment while the tensile specimens were machined before. This procedure was made necessary by the fact that specimens notched prior to solution heat treatment bent or developed cracks during quenching.

No cracks were found in specimens notched after solution heat treatment.

2.4. **Heat Treatment**

Al-9Mg was solution treated at 450°C for 15 minutes in air and water quenched. It was aged at 200°C for different times.

Al-3Mg-6Zn and Al-2.6Mg-6.3Zn were solution treated at 460°C for 4 hours, water quenched, then aged at 160°C.

Al-21.5Zn was solution treated at 500°C for 1 hour, step quenched to 300°C for 1/2 hour, water quenched and aged at room temperature (15).
Figure (2). Stress corrosion cells used in the present work.
Mg-8.6Al was solution treated at 420°C for 70 hours in Argon, water quenched, then aged at 200°C.

2.5. Polishing and Degreasing

The machined and ground specimens were electropolished in a solution containing 45 vol.% nitric acid, 45 vol.% methanol and 5 vol.% concentrated hydrochloric acid at 15°C. The polishing was carried out at 4 to 6 volts and 2.5 to 3 amperes (2 amp/cm²).

A bright surface was obtained after electropolishing. The specimens were then washed in water and ultrasonically degreased for 15 minutes in chlorotheene.

Tensile Tests

Tensile tests were done on the Instron machine. Wedge type grips were used for flat specimens and threaded grips for round specimens.

2.6. Stress Corrosion Tests

Three types of stress corrosion tests were employed to determine the stress corrosion susceptibility (SCC) of alloys.

Constant Load Tests

A modified creep stand shown in fig. (3) was used. Vise type grips were used for flat specimens and threaded grips for the round specimens. The failure time was measured with an hourmeter which could be switched off by the falling weight. The stress corrosion cell fig. (2) consisted of a glass tube with teflon or rubber bungs fitted around the specimen. The cell was sealed with wax or silicone grease.
Figure (3). Modified creep stand for constant load tests (After Tiesenhausen and Lund (103)).
The failure time could be measured with an accuracy of ± 1 minute on the hourmeter. A stopwatch was used for short failure times.

2.7. **Load Relaxation Tests**

The major part of stress corrosion testing was carried out on notched cylindrical specimens in the Instron. The load relaxation curve consisted of three parts,

1. Initial load relaxation
2. Period of constant load
3. Period of crack propagation resulting in relaxation of the load, followed by rapid mechanical fracture.

Tests of this type are an improvement over the constant load test for several reasons.

1. The crack can be localized near the root of the notch.
2. Initiation and propagation times can be determined with fair accuracy.
3. Very high stresses can be applied to the notched specimen because of the triaxial stress state existing at the root of the notch. As a result, the stress corrosion failure times can be shortened.

2.8. **Strain Rate Tests**

Tensile tests were carried out on a quenched and averaged Al-2.6Mg-6.3Zn, in deionized water, 3.5% NaCl + 2% K₂CrO₄ and silica gel. The effect of strain rate on total elongation and uniform elongation was determined.
2.9. **Hydrogen Charging Experiments**

These experiments were conducted to determine whether hydrogen played any part in the stress corrosion process. Using 3.5% NaCl + 2% $K_2CrO_4$ as the environment, the notched specimen was made the cathode and a platinum wire loop placed around it, acted as the anode. A potential of 4.5 volts was applied for 30 minutes and vigorous hydrogen evolution took place at the specimen surface. The charging was continued until the specimen had been subjected to the required applied stress. Then the current was switched off, so as to prevent the application of a cathodically protective potential.

A dark film was formed on the specimen surface. The possibility that such a film may be contributing to stress corrosion was checked by hydrogen charging two specimens for thirty minutes, and holding them for 8 days at 0°C to allow the hydrogen to escape from the notch. These specimens were retested in 3.5% NaCl + 2.0% $K_2CrO_4$.

Charging tests were conducted on Al-21.5Zn and Al-2.6Mg-6.3Zn.

2.10. **Optical Microscopy**

Optical microscopy was used for grain size determination and for studying whether crack propagation was intercrystalline or transcrystalline.

All fracture surfaces were first examined under an optical microscope at low magnification before a replica was taken.
2.11. **Electron Microscopy**

1. Precipitate distribution for different aging treatments was studied to a limited extent, using thin film and replica techniques.

2. Slip line distribution was studied in peak aged Al-9Mg.

3. Extensive fractography was carried out on tensile and stress corroded specimens. The extent of the stress corroded area could be controlled by varying the initial stress level in the load relaxation test. From the nature of the load relaxation curve it was possible to determine the extent of stress corrosion compared to mechanical fracture.

Low magnification (300x) electron probe pictures of the fracture surface were used to locate areas of the specimen being observed on the replica.
3. RESULTS AND OBSERVATIONS

The isothermal precipitation hardening curves for Al-9Mg, Al-3Mg-6Zn and Mg-8.6Al are shown in figures (4-6). The first two alloys were tested in the rolled condition and the last in the extruded form.

3.1. Al-9Mg

The alloy was solution heat treated at 450°C for 15 minutes in air, water quenched and aged at 200°C. The grain size was 90 μ.

In figure (4) the 0.2% yield stress is plotted against the aging time. The peak yield strength is reached at an aging time of 7 hours. The uniform plastic elongation decreases with increasing aging times attaining a minimum value in seven hours.

3.2. Al-3Mg-6Zn

The rolled alloy was solution heat treated at 460°C for 4 hours in air, water-quenched and aged at 160°C for times ranging from a few hours to 120 hours. The specimens were water quenched after the aging treatment. From figure (5) it is seen that the maximum yield stress is reached in times between 8 and 10 hours at 160°C. The uniform elongation reaches a minimum at the same time and increases again on overaging.
Figure (4). Precipitation hardening of Al-9Wg, aged at 200°C.

0.2% Yield stress, $10^3$ psi

- Soln. treated, Y.S.
- Soln. treated, Eln.
- 0.2% Yield stress
- % elongation
Figure (5). Precipitation hardening of Al-3Mg-6Zn, aged at 160°C.
Figure (6). Precipitation hardening of Mg-8.6Al, aged at 200°C.
3.3. Mg-8.5Al

Cylindrical tensile specimens were solution treated at 420°C for 70 hours, water quenched and aged at 200°C. In figure (6) the 0.2% yield stress is plotted against ageing time. The strength reaches a maximum value after aging for 24 hours and stays constant up to 50 hours after which it starts to fall off. The uniform elongation decreases to a minimum value in 16 hours and then rises on further aging.

3.4. Stress Corrosion Testing Techniques

Both constant load and load relaxation type of tests were employed.

Constant load tests are used to evaluate the stress corrosion susceptibility at different stress levels and different heat treatments. The drawback of these types of tests is that once a crack is initiated, the stress increases at a very rapid rate and the area of stress corrosion crack propagation is therefore much smaller than the area of mechanical fracture due to overload. This makes it very difficult to get representative fractographs of the stress corroded area. In addition it is impossible to distinguish between crack initiation and crack propagation stages. Another drawback of constant load tests is that failure may occur on account of general corrosion more easily than in load relaxation tests. However, since most specimens tested failed in times less than a day, general corrosion was not a problem.

The drawbacks of the constant load tests were overcome by using load relaxation tests on notched specimens. The notch helped the stress to be localised so that a single crack was initiated. The extension
### Table (3)

**SUMMARY OF STRESS CORROSION TESTS AND TESTING CONDITIONS**

<table>
<thead>
<tr>
<th>Type of Alloy</th>
<th>Type of Test</th>
<th>Purpose of Study</th>
<th>Environment</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-9Mg Strip</td>
<td>Constant Loading</td>
<td>1. Aging time vs failure time at constant stress</td>
<td>3.5% NaCl +</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Aging time vs failure time at constant fraction of yield stress</td>
<td>2.0% K₂CrO₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Applied stress via failure time at peak strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-9Mg Round notched</td>
<td>Load relaxation test</td>
<td>1. Crack initiation and propagation times</td>
<td>3.5% NaCl +</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Nature of load propagation times</td>
<td>2.0% K₂CrO₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Activation energy analysis on peak aged specimens</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-3Mg-6Zn Strip</td>
<td>Constant load</td>
<td>1. Applied stress vs failure time at peak strength</td>
<td>3.5% NaCl +</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Aging time vs failure time at constant stress</td>
<td>2.0% K₂CrO₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Aging time vs failure time at constant fraction of yield stress</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-2.6Mg-6.32 Round notched</td>
<td>Load relaxation test</td>
<td>1. Initiation and propagation times</td>
<td>3.5% NaCl +</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Nature of load relaxation</td>
<td>2.0% K₂CrO₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ambient air,</td>
<td></td>
</tr>
<tr>
<td>Type of Alloy</td>
<td>Type of Test</td>
<td>Purpose of Study</td>
<td>Environment</td>
<td>Temperature °C</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------</td>
<td>----------------------------------------------------------------------------------</td>
<td>--------------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Al.2.6Mg-6.32</td>
<td>Tensile tests</td>
<td>Strain rate vs &amp; elongation in different media, for as quenched and overaged conditions</td>
<td>D. water, 3.5% NaCl + 2.9% K₂CrO₄, silica gel</td>
<td>20°C</td>
</tr>
<tr>
<td>(continued)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-2.6Mg-6.32Zn</td>
<td>Load relaxation test</td>
<td>Crack initiation and propagation times at constant stress in different media</td>
<td>D. water, silica gel Na dried Kerosene, Mg(OC₁₄)₂, ethanol</td>
<td>-20 to 20°C</td>
</tr>
<tr>
<td>Round, tensile</td>
<td></td>
<td></td>
<td></td>
<td>-30 to 20°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-65 to 20°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-70 to 20°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-21.5Zn</td>
<td>Load relaxation test</td>
<td>Crack initiation and propagation times</td>
<td>3.0% NaCl + 2.0% K₂CrO₄, D. water, silica gel</td>
<td>20°C</td>
</tr>
<tr>
<td>Round, notched</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-8.5Al</td>
<td>Constant load</td>
<td>Aging time vs failure time at a constant fraction of yield stress</td>
<td>3.5% NaCl + 2.0% K₂CrO₄</td>
<td>20°C</td>
</tr>
<tr>
<td>Round, unnotched</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Round, notched</td>
<td>Load relaxation test</td>
<td>Crack initiation and propagation times</td>
<td>3.5% NaCl + 2.0% K₂CrO₄</td>
<td>20°C</td>
</tr>
</tbody>
</table>
caused by this crack was registered on the Instron, as a load drop. In the absence of a stress raising notch, several cracks can be initiated in the specimen. This can result in a 'spring like' accommodation of the extension with no visible load drop at the moment of initiation. Other advantages of these types of tests are:

1. The applied load and the time to failure can be measured very accurately on the Instron.

2. Both crack initiation and crack propagation times can be measured. It is possible to know whether load relaxation is continuous or discontinuous.

3. Very high stresses can be applied at the root of the notch. In general, the notch tensile strength is at least two times the ultimate strength of the smooth specimen. The times of stress corrosion initiation can therefore be shortened drastically anywhere from a factor of 3 to 10.

4. Because of the high triaxial stress state at the root of the notch it is possible to use very dilute environments and still obtain failures in short times.

5. The stress corrosion test can be stopped and the notched specimen sectioned longitudinally to observe the mode of crack propagation.

6. A notched specimen approaches the service conditions better than an unnotched specimen because it takes into account the effect of stress raisers such as screwthreads, sharp fillets, fatigue and weld cracks and pits developed during exposure to a corrosive environment.

For the above reasons, notched wires were used in all four systems studied.
Tensile tests at different strain rates were conducted to evaluate the effect of environment on mechanical properties, particularly ductility.

3.4.1. Stress Corrosion Susceptibility

Susceptibility to stress corrosion was defined as the inverse of total failure time in the constant load test and the inverse of crack initiation time in the load relaxation test. The susceptibilities of two specimens having different yield strengths can be compared either at a constant fraction of the yield stress or at a constant stress. Both methods were used. From figures (7) and (9) it appears that both methods give similar variations in failure time vs aging time curve. A common environment namely 3.5 wt.% NaCl + 2.0 wt.% K₂CrO₇ solution in deionized water was prepared from reagent grade chemicals. This solution facilitated an evaluation of the relative susceptibilities of different alloy systems. The failure times were short compared to those in alternate immersion tests in NaCl/H₂O₂ solutions. They varied from a few seconds in Al-9Mg and Al21.5Zn to a few hundred hours in Al-3Mg-6Zn. If a specimen did not fail in 200 hours the test was discontinued. Certain specimens were tested for 600 hours before discontinuing the test.

3.4.2. Constant Load Tests

3.4.2.1. Al-9Mg

Strip specimens of 2 3/4 inches length and 0.8" gage length were tested by total immersion in the NaCl/K₂CrO₇ solution under a constant load.
In figure (7) the failure time is plotted against the time for isothermal aging at 200°C. It is found that the solution treated and water quenched specimens are immune to stress corrosion. As aging proceeds, the stress corrosion susceptibility increases rapidly. At peak hardness the failure time is only 15 seconds. Overaging leads to an improvement in the stress corrosion resistance.

The minimum in failure time occurs close to 7 hours aging at both stress levels used, namely 20,000 psi and 40% of the respective yield strengths.

There is a five orders of magnitude decrease in failure time, produced by peak-aging the solution treated specimen.

In figure (8) the applied stress is plotted against failure time on a log scale. It is obvious that the failure time $t$ is not related to the applied stress $\sigma$ by an exponential relationship of the form

$$t_f = A e^{-K \cdot \sigma}$$

as suggested by some workers (73). As the threshold stress of 5800 psi is approached. The failure time changes at a remarkable rate.

At high stress levels the failure times did not fluctuate by more than a factor of two and at lower stress levels variations of up to a factor of 4 were observed. For every stress level, specimens were tested in duplicate and in some cases in triplicate.

The purpose of the constant load tests was to arrive at the most susceptible heat treatment. This heat treatment was subsequently used in the stress corrosion tests on the notched specimens.
Figure (7). Failure time vs aging time for Al-9Mg aged at 200°C.
Figure (8). Applied stress vs failure time for Al-9Mg aged for 7 hours at 200°C.
3.4.2.2. Al-3Mg-6Zn

In figure (9) fracture time is plotted against aging time at a constant applied stress of 22,100 psi. The curve shows a minima at an aging time of 3 hours at 160°C which corresponds to an underaged condition.

When the stress level is changed to 40% of the 0.2% offset yield stress for that particular condition and the fracture time plotted against the aging time, the curve once again has a minima for an aging time of 3 hours at 160°C.

In this system the difference in cracking times, between the as-quenched and peak-hardened conditions is insignificant compared to the vast differences between the two conditions in Al-9Mg.

In fig. (10) the applied stress is plotted against fracture time for the peak-aged condition of 8 hours at 160°C. The curve drops rapidly at high stresses, and then more slowly as the applied stress is decreased. A similar trend is shown by the overaged specimens.

Once again the points do not lie on a straight line suggesting that there is no simple exponential relationship between the rate of cracking and the applied stress as suggested by Gruhl (73). Helfrich (72) observed a curve at lower stress levels and a straight line at high stresses.

3.4.2.3. Mg-8.6Al

This alloy was used in the form of a wire because it was not feasible to roll it. Cylindrical tensile specimens of this alloy were stress corroded at a constant load. The applies stress was 70% of the
Figure (9). Effect of aging time at 160°C on the failure time of Al-3Mg-6Zn in NaCl/K$_2$CrO$_4$. 

Failure time, hours

Aging time, hours

- 35 -
Figure (10). Applied stress vs failure time for the aged Al-3Mg-6Zn alloy.
Figure (11). Failure time vs aging time for Mg-8.6Al aged at 200°C.
Figure 12. Effect of applied stress on the failure time of solution treated and quenched Mg-8.6Al.
yield stress for a given aging time. The result is shown in figure (11) in which the failure time is plotted against the isothermal aging time at 200°C. The unaged alloy is the least susceptible and aging results in a progressive increase in the stress corrosion susceptibility. Unlike the previous two systems there is no observed minimum in the failure time before or at the peak strength. The minimum failure time is observed for an aging time of 76 hours when considerable overaging has occurred.

The applied stress vs failure time is plotted in fig. (12) and the points approximately lie about a straight line. The mode of stress corrosion cracking is transgranular in the Mg-8.6Al alloy.

Susceptibility tests as a function of aging time were not conducted on Al-22Zn, because it ages at room temperature and in such conditions is very susceptible to stress corrosion cracking.

3.4.3. Strain Rate Tests

3.4.3.1. Al-2.6Mg-6.3Zn

Strain rate tests were carried out over 6 different strain rates in two different media consisting of deionized water and 3.5% NaCl + 2.0% K$_2$CrO$_4$ for both the as-quenched condition and the overaged conditions. Specimens were also deformed at the lowest strain rate in dessicant dried air.

The results are shown in fig. (13) and fig. (14). In both cases there is a significant decrease in uniform elongation with a decreasing strain rate in both deionized water and NaCl/K$_2$CrO$_4$ solution. Changing the environment to dessicant dried air leads to a seven fold increase in ductility at the lowest strain rate in figure (13).
Figure (13). Strain rate vs uniform and total elongation for solution treated and quenched Al-2.6Mg-6.3Zn Alloy.
Figure (14). Strain rate vs uniform and total elongations for an overaged Al-2.6Mg-6.3Zn alloy.
3.4.3.2. Al-21.5Zn

Table (4)

EFFECT OF STRAIN RATE ON DUCTILITY AND YIELD STRENGTH IN DRY AIR AND DEIONIZED WATER

<table>
<thead>
<tr>
<th>Strain rate</th>
<th>Environment</th>
<th>0.05 psi</th>
<th>0.2 psi</th>
<th>UTS psi</th>
<th>Eln Max</th>
<th>Eln Fract.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0x10^-6/sec</td>
<td>silica gel</td>
<td>38,000</td>
<td>42,300</td>
<td>44,000</td>
<td>0.9</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>silica gel</td>
<td>38,600</td>
<td>41,400</td>
<td>43,200</td>
<td>0.8</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>deionized water</td>
<td>14,250</td>
<td>14,250</td>
<td>14,250</td>
<td>0.062</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>deionized water</td>
<td>14,250</td>
<td>14,250</td>
<td>14,250</td>
<td>0.045</td>
<td>1.1</td>
</tr>
<tr>
<td>2.7x10^3/sec</td>
<td>silica gel</td>
<td>39,400</td>
<td>42,200</td>
<td>49,200</td>
<td>3.23</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>deionized water</td>
<td>38,500</td>
<td>41,000</td>
<td>43,800</td>
<td>1.17</td>
<td>3.14</td>
</tr>
</tbody>
</table>

3.4.4. Load Relaxation Tests for Different Alloy-Environment Systems.

The crack initiation and propagation times as determined from load relaxation tests are listed in Tables (5-9) and figures (15-16).
Table (5)

CRACK INITIATION AND PROPAGATION TIMES FOR Al-3Mg-6Zn IN 3.5% NaCl + 2% $K_2CrO_4$

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Applied stress</th>
<th>In. time</th>
<th>Prop. time</th>
<th>Total time</th>
<th>Nature of load relaxation min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>460°, 4 hours, water quenched, N.T.S. = 74,500 ± 2000</td>
<td>48,000</td>
<td>208</td>
<td>28</td>
<td>236</td>
<td>discontinuous, down to zero load</td>
</tr>
<tr>
<td></td>
<td>50,000</td>
<td>46</td>
<td>49</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>460°, 4 hours, water quenched, 160°C, 24 hours N.T.S. = 124,000 ± 5000</td>
<td>55,000</td>
<td>117</td>
<td>6</td>
<td>123</td>
<td>discontinuous, followed by rapid mechanical fracture</td>
</tr>
<tr>
<td></td>
<td>69,000</td>
<td>50</td>
<td>2</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>69,000</td>
<td>93</td>
<td>4</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>460°C, 22 hours, water quenched, N.T.S. = 62,000</td>
<td>46,000</td>
<td>7</td>
<td>16</td>
<td>23</td>
<td>discontinuous, followed by rapid mechanical fracture</td>
</tr>
<tr>
<td></td>
<td>46,000</td>
<td>10</td>
<td>14</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

N.T.S. = Notch tensile strength in psi.

Grain size

The grain size of Al-3Mg-6Zn solution treated for 4 hours at 460°C was 265 microns, while for times of 22 hours it was 570 microns.

The grain size for Al-2.6Mg-6.3Zn solution treated for 4 hours at 460°C was 300 microns. In other words, there were approximately six grains across the notch.
<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Applied Stress</th>
<th>In. time</th>
<th>Prop. time</th>
<th>Total time</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>460°C, 4 hours, water quenched</td>
<td>57,600</td>
<td>1.6</td>
<td>0.6</td>
<td>2.2</td>
<td>3.5NaCl + 2.0K₂CrO₄</td>
</tr>
<tr>
<td>N.T.S.=72,000</td>
<td>57,600</td>
<td>10</td>
<td>3.5</td>
<td>13.5</td>
<td>Ambient air</td>
</tr>
<tr>
<td></td>
<td>57,600</td>
<td>11</td>
<td>7.5</td>
<td>18.5</td>
<td>Ambient air</td>
</tr>
<tr>
<td>460°C, 4 hours, water quenched</td>
<td>57,600</td>
<td>20</td>
<td>6</td>
<td>26.0</td>
<td>Ambient air</td>
</tr>
<tr>
<td>N.T.S.=104,000</td>
<td>83,000</td>
<td>14</td>
<td>480</td>
<td>494</td>
<td>Ambient air</td>
</tr>
<tr>
<td>160°C, 24 hours, water quenched</td>
<td>83,000</td>
<td>37.4</td>
<td>5.6</td>
<td>43</td>
<td>Deionized water</td>
</tr>
<tr>
<td>N.T.S.=104,000</td>
<td>83,000</td>
<td>89</td>
<td>16.0</td>
<td>105</td>
<td>Deionized water</td>
</tr>
</tbody>
</table>
Figure (15). Effect of different media on crack initiation and propagation times in Al-2.6Mg-6.3Zn alloy in solution treated and overaged conditions.
Table (7)

CRACK INITIATION AND PROPAGATION TIMES FOR Al-8.6Mg in 3.5% NaCl + 2% K$_2$CrO$_4$

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Applied stress</th>
<th>In. time</th>
<th>Prop. time</th>
<th>Total time</th>
<th>Nature of load relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C, 30 min., water quenched</td>
<td>12,500 psi</td>
<td>18.4 min.</td>
<td>1 min.</td>
<td>19.4 min.</td>
<td>Discontinuous, followed by rapid fracture</td>
</tr>
<tr>
<td>200°C, 7 hours, water quenched</td>
<td>31,200 psi</td>
<td>8.5 min.</td>
<td>0.5 min.</td>
<td>9.0 min.</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 62,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450°C, 30 min., water quenched</td>
<td>40,800 psi</td>
<td>0.16 min.</td>
<td>20 min.</td>
<td>20.16 min.</td>
<td>Discontinuous, followed by rapid fracture</td>
</tr>
<tr>
<td>200°C, 3 hours, water quenched</td>
<td>38,200 psi</td>
<td>0.75 min.</td>
<td>131.2 min.</td>
<td>132.0 min.</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 71,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450°C, 22 hours, water quenched</td>
<td>31,000 psi</td>
<td>3 min.</td>
<td>114 min.</td>
<td>117 min.</td>
<td>slow crack propagation to zero load</td>
</tr>
<tr>
<td>200°C, 7 hours, N.T.S. = 48,000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The grain size was 90 μ for the first two heat treatments and 250 μ for the third.
### Table (8)

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Applied stress psi</th>
<th>In. time min.</th>
<th>Prop. time min.</th>
<th>Total time min.</th>
<th>Type of solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>420°C, 70 hours water quenched</td>
<td>26,000</td>
<td>0.4</td>
<td>1.6</td>
<td>2.0</td>
<td>3.5%NaCl + 2.0% K₂CrO₄</td>
</tr>
<tr>
<td>N.T.S. = 32,000</td>
<td>26,000</td>
<td>0.2</td>
<td>1</td>
<td>1.2</td>
<td>3.5%NaCl + 2.0% K₂CrO₄</td>
</tr>
<tr>
<td></td>
<td>26,000</td>
<td>1.4</td>
<td>11.0</td>
<td>11.4</td>
<td>0.35%NaCl + 0.2% K₂CrO₄ no steps</td>
</tr>
<tr>
<td></td>
<td>26,000</td>
<td>0.7</td>
<td>10.0</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26,000</td>
<td></td>
<td></td>
<td>95 hrs. 0+</td>
<td>0.035%NaCl + 0.02% K₂CrO₄ no failure</td>
</tr>
<tr>
<td>420°C, 70 hours water quenched</td>
<td>30,000</td>
<td>0.2</td>
<td>0.8</td>
<td>1.0</td>
<td>3.5%NaCl + 2.0% K₂CrO₄</td>
</tr>
<tr>
<td></td>
<td>30,000</td>
<td>0.2</td>
<td>0.9</td>
<td>1.1</td>
<td>3.5%NaCl + 2.0% K₂CrO₄</td>
</tr>
<tr>
<td>200°C, 1 hour water quenched</td>
<td>30,000</td>
<td>0.7</td>
<td>2.0</td>
<td>2.7</td>
<td>0.35%NaCl + 2.0% K₂CrO₄</td>
</tr>
<tr>
<td>N.T.S. = 36,000</td>
<td>26,000</td>
<td></td>
<td></td>
<td>70.5 hrs. 0+</td>
<td>0.35%NaCl + 2.0% K₂CrO₄ no failure</td>
</tr>
</tbody>
</table>

The grain size was 120 μ for both the solution treated and the aged alloys.
Al-21.5Zn

Table (9)
EFFECT OF DIFFERENT MEDIA ON THE INITIATION AND PROPAGATION TIMES FOR Al-21.5Zn ALLOY

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Applied stress psi</th>
<th>In. time min.</th>
<th>Prop. time min.</th>
<th>Total time min.</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C, 1 hour, step quenched to 300°C, 1/2 hour water quenched</td>
<td>64,600</td>
<td>--</td>
<td>0.2</td>
<td>0.2</td>
<td>Deionized water</td>
</tr>
<tr>
<td>Aged at 20°C 1.5 hours</td>
<td>6.2</td>
<td>3.0</td>
<td>9.2</td>
<td>silica gel</td>
<td></td>
</tr>
<tr>
<td>N.T.S.=81,000 (20°C)</td>
<td>3.8</td>
<td>1.0</td>
<td>4.8</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>N.T.S.=84,000 (-60°C)</td>
<td>12.5</td>
<td>1.5</td>
<td>14</td>
<td>Mg(OCl_4)_2</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 84,000 (20°C)</td>
<td>14.2</td>
<td>1.5</td>
<td>15.7</td>
<td>Kerosene + Na</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 81,000 (20°C)</td>
<td>9</td>
<td>3</td>
<td>12.0</td>
<td>Mg(OCl_4)_2</td>
<td></td>
</tr>
<tr>
<td>500°C, 1 hour, step quenched to 300°C, 1/2 hour water quenched</td>
<td>64,600</td>
<td>--</td>
<td>0.2</td>
<td>0.2</td>
<td>Deionized water</td>
</tr>
<tr>
<td>Aged at 20°C 1.5 hours</td>
<td>6.2</td>
<td>3.0</td>
<td>9.2</td>
<td>silica gel</td>
<td></td>
</tr>
<tr>
<td>N.T.S.=81,000 (20°C)</td>
<td>3.8</td>
<td>1.0</td>
<td>4.8</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>N.T.S.=84,000 (-60°C)</td>
<td>12.5</td>
<td>1.5</td>
<td>14</td>
<td>Mg(OCl_4)_2</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 84,000 (20°C)</td>
<td>14.2</td>
<td>1.5</td>
<td>15.7</td>
<td>Kerosene + Na</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 81,000 (20°C)</td>
<td>9</td>
<td>3</td>
<td>12.0</td>
<td>Mg(OCl_4)_2</td>
<td></td>
</tr>
<tr>
<td>500°C, 1 hour, step quenched to 300°C, 1/2 hour water quenched</td>
<td>64,600</td>
<td>--</td>
<td>0.2</td>
<td>0.2</td>
<td>Deionized water</td>
</tr>
<tr>
<td>Aged at 20°C 1.5 hours</td>
<td>6.2</td>
<td>3.0</td>
<td>9.2</td>
<td>silica gel</td>
<td></td>
</tr>
<tr>
<td>N.T.S.=81,000 (20°C)</td>
<td>3.8</td>
<td>1.0</td>
<td>4.8</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>N.T.S.=84,000 (-60°C)</td>
<td>12.5</td>
<td>1.5</td>
<td>14</td>
<td>Mg(OCl_4)_2</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 84,000 (20°C)</td>
<td>14.2</td>
<td>1.5</td>
<td>15.7</td>
<td>Kerosene + Na</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 81,000 (20°C)</td>
<td>9</td>
<td>3</td>
<td>12.0</td>
<td>Mg(OCl_4)_2</td>
<td></td>
</tr>
<tr>
<td>500°C, 1 hour, step quenched to 300°C, 1/2 hour water quenched</td>
<td>64,600</td>
<td>--</td>
<td>0.2</td>
<td>0.2</td>
<td>Deionized water</td>
</tr>
<tr>
<td>Aged at 20°C 1.5 hours</td>
<td>6.2</td>
<td>3.0</td>
<td>9.2</td>
<td>silica gel</td>
<td></td>
</tr>
<tr>
<td>N.T.S.=81,000 (20°C)</td>
<td>3.8</td>
<td>1.0</td>
<td>4.8</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>N.T.S.=84,000 (-60°C)</td>
<td>12.5</td>
<td>1.5</td>
<td>14</td>
<td>Mg(OCl_4)_2</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 84,000 (20°C)</td>
<td>14.2</td>
<td>1.5</td>
<td>15.7</td>
<td>Kerosene + Na</td>
<td></td>
</tr>
<tr>
<td>N.T.S. = 81,000 (20°C)</td>
<td>9</td>
<td>3</td>
<td>12.0</td>
<td>Mg(OCl_4)_2</td>
<td></td>
</tr>
</tbody>
</table>

The grain size was 105 microns.
Figure (16). Effect of different media on initiation and propagation times in Al-21.5Zn alloy.
3.5. The pH of the \( \text{NaCl/K}_2\text{CrO}_4 \) Solution

The pH of the solution was 8.6 at room temperature and did not change significantly during the test. The dilute solutions used in Mg-8.6Al were adjusted to this pH. Dilute solutions were used in this system, because failure times in the normal solution were extremely short. The failure times could not be prolonged by using low stress levels, because the threshold stress was high (72% yield stress).

3.6. Activation Energy Analysis

The stress corrosion process is both stress and thermally activated. Data is scarcely available on the kinetics of the stress corrosion process in aluminum alloys. Of the data that is available, no distinction is made between the initiation and propagation times.

This study was undertaken with a view to determine the apparent activation energy of the rate controlling process in the stress corrosion of aluminum alloys. The effect of temperature on the rate of initiation and propagation was studied in a common environment namely ethyl alcohol. This environment was selected for two reasons.

1. It was possible to study the crack initiation and propagation rates of extremely susceptible alloys, such as Al-21.5Zn at sub-zero temperatures. The failure times in the salt solution were too short for a meaningful analysis. Low temperatures also reduced the tendency to overage during the test and extended the range of the Arrhenius plot.

2. With ethyl alcohol, high stress levels could be used. It was found that the separation of initiation and propagation times was more accurate at high stresses than at low stresses.
Generally the initiation times varied from a few minutes to a maximum of 66 hours. Temperature was regulated within \( \pm 1^\circ C \) by periodic addition of liquid nitrogen to the ethyl alcohol bath around the cell.

For the Al-Mg-Zn alloy, distilled water, and NaCl/K\(_2\)CrO\(_4\) solutions were also used in the temperature range of 0-85\(^\circ\)C. Generally duplicate specimens were tested at extreme temperatures and single specimens at intermediate temperatures.

Before testing, the specimens were electropolished, degreased in chloroethane and carefully examined for any pre-existing cracks in the notch. According to the Arrhenius rate law

\[
\text{Rate} = A e^{-\frac{Q}{RT}}
\]  

(1)

where \( A \) = Frequency factor

\( Q \) = Apparent activation energy of the rate controlling process.

In the present case, rates of cracking were defined as the inverse of initiation and propagation times in seconds. The logarithm of the rate was plotted against the reciprocal of absolute temperature.

It is assumed that the crack initiation and propagation distances remain constant at a given stress. Therefore the rates of initiation and propagation can be defined as the inverse of initiation and propagation times, respectively. However, as initial applied stress decreases, the crack propagation distance increases and the above assumption is no longer valid.
In all cases, the Arrhenius plots were straight lines. The apparent activation energy was calculated from the slopes of the lines. The lines were the best fits as calculated from regression analysis. In addition, the error in the slope for a 95% confidence limit was calculated for each set of data.

The results are described in more detail below.

3.6.1. Al-21.5Zn

This alloy was exposed to 99.9% ethyl alcohol as well as 95% ethyl alcohol, the remainder was water. The temperature ranged from 20° to 70°C and the applied stress from 58,000 psi to 72,000 psi. The Arrhenius plot is shown in fig. (17). The lines are parallel to each other within the experimental error.

The apparent activation energies are summarised in the following table.

Table (10)

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Applied stress psi</th>
<th>Environment</th>
<th>Temperature range, °C</th>
<th>Apparent Activation energy kcals/gm.mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-21.5Zn</td>
<td>64,600</td>
<td>95% C₂H₅OH</td>
<td>20-70</td>
<td>11.1 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>58,000</td>
<td>95% C₂H₅OH + 5% water</td>
<td>20-45</td>
<td>11.0 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>72,000</td>
<td>99.9% C₂H₅OH + 0.1% water</td>
<td>20-30</td>
<td>11.0 ± 3.9</td>
</tr>
<tr>
<td></td>
<td>58,000</td>
<td>99.9% C₂H₅OH + 0.1% water</td>
<td>20-20</td>
<td>12.0 ± 2.3</td>
</tr>
</tbody>
</table>
Figure (17). Logarithm of crack initiation rate vs 1/T for Al-21.5Zn in ethyl alcohol.
Figure (18). Logarithm of crack initiation rate/T vs 1/T for Al-21.5Zn in ethyl alcohol.
When the rate of the crack initiation was divided by the absolute temperature and the logarithm of this number plotted against the inverse of absolute temperature, the plot was once again a straight line in all four cases. The apparent activation energies as calculated from the slopes were slightly different from the values shown in the last table (10). From fig. (18) it is seen that

\[ \text{Rate} = T \cdot A e^{-\frac{Q}{RT}} \]  

(2)

This equation incorporates the effect of temperature on the strain induced diffusion of hydrogen in the lattice (90).

Table (11)

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Applied stress</th>
<th>Environment</th>
<th>Temperature range</th>
<th>Activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt % Zn</td>
<td>psi</td>
<td></td>
<td></td>
<td>kcal/gmmole</td>
</tr>
<tr>
<td>Al-21.5Zn</td>
<td>64,000</td>
<td>95%C_2H_5OH + 5% water</td>
<td>20 to -70</td>
<td>10.4 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>58,000</td>
<td>95%C_2H_5OH + 5% water</td>
<td>20 to -45</td>
<td>9.4 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>72,000</td>
<td>99.9%C_2H_5OH + 0.1%H_2O</td>
<td>20 to -30</td>
<td>10.5 ± 3.7</td>
</tr>
<tr>
<td></td>
<td>58,000</td>
<td>99.9%C_2H_5OH + 0.1%H_2O</td>
<td>20 to -20</td>
<td>11.6 ± 2.2</td>
</tr>
</tbody>
</table>

Therefore the given data fit both equations 1 and 2.

3.6.2. Applied Stress vs. Failure Time

In fig. (19) the applied stress is plotted against logarithm of failure time for notched Al-21.5Zn in 99.9% ethyl alcohol. A straight line fit is obtained which means that for constant temperature failure time is related to the exponential of the applied stress as follows:
Figure (19). The effect of applied stress on log failure time of Al-21.5Zn alloy in 99.9% ethyl alcohol.
\[ t_f = K_1 e^{-K_2 \sigma} \]  

(3)

where \( t_f \) = failure time  
\( \sigma \) = applied stress  
\( K_1, K_2 \) = constants

It will be shown in the discussion that failure time \( t_f \) can also be related to the applied stress \( \sigma \) by a power law of the form

\[ t_f = K_f \sigma^n \]  

(4)

3.6.3. \text{Al-2.6Mg-6.3Zn}

This alloy was stress corroded in three environments.

1. 99.9% ethyl alcohol + 0.1% water  
2. 3.5% NaCl + 2.0% \( K_2\text{CrO}_4 \)  
3. Double distilled water.

The alloy was used in the overaged condition. In fig. (20) the logarithm of crack initiation rate is plotted against the inverse of absolute temperature for 99.9% ethyl alcohol environment. The apparent activation energy of the rate controlling process is 14.7 kcals/gm-mole.

When a similar analysis is carried out in 3.5% NaCl + 2.0% \( K_2\text{CrO}_4 \) solution, a straight line is obtained. But the apparent activation energy is now 26 kcals/gm-mole, as shown in fig. (21a).

The activation energy is 26 ± 6 kcals/gm mole in double distilled water. The large deviation results from the fewer data points. Since double distilled water and salt solution were studied at the same applied
Figure (20). Logarithm of crack initiation rate vs $1/T$ for an averaged Al-2.6Mg-6.3Zn alloy in ethyl alcohol

Al-2.6Mg-6.3Zn
Ethanol
$Q = 14.7 \text{ kcaI/mol}$
Figure (21). Logarithm of crack initiation rate vs 1/T for Al-2.6Mg-6.3Zn in NaCl/K₂CrO₄ solution and water.

Al-2.6Mg-6.3Zn
76,000 psi

△ NaCl/K₂CrO₄
O Double distilled water

Q = 26 kcal/gm mole
Figure (22). Logarithm of crack initiation rate vs 1/T for aged Al-8.6Mg alloy in ethyl alcohol.
stress, the temperature range giving reasonable initiation times (less than 24 hours) was narrower in water. Consequently, fewer points were obtained in double distilled water.

Therefore, the same process seems to operate during stress corrosion of Al-2.6Mg-6.3Zn in distilled water and NaCl/K₂CrO₄, whereas a different process appears to be rate controlling in the ethyl alcohol.

3.6.4. Al-9Mg

In fig. (22) the log initiation rate is plotted against 10³/T in 99.9% ethyl alcohol-0.1% water, environment.

The apparent activation energy as calculated from the slope is 9.6 kcals/gm mole. The temperature range used was between 39°C and -11°C. The error in activation energy is ± 2.9 kcals/gm mole.

3.6.5. Apparent Activation Energy During Propagation

The propagation rate was assumed to be constant during cracking and was defined as the inverse of propagation time as measured from the load relaxation curve. According to Kraft and Mulherin (77), during crack propagation the stress intensity factor Kᵢ increases to a limiting value KᵢC when mechanical fracture takes place at an indefinitely fast crack velocity.

Because the propagation rate is measured under an unsteady state condition, the Arrhenius plot is difficult to interpret. Wei (82) obtained apparent activation energies for corrosion fatigue al aluminum alloys under constant stress intensity factor and found them to be inversely proportional to Kᵢ.
The Arrhenius plots for propagation rates are presented in figures (23-16). Only two systems show a significant correlation between log rate and 1/T. They are Al-2.6Mg-6.3Zn in NaCl/K₂CrO₄ solution, fig. (23) and Al-21.5Zn in 99.9% ethanol fig. (26) which yield apparent activation energies of 14.7 and 3.8 respectively. The plots in figures (24,25) show considerable scatter and cannot yield a meaningful activation energy. However, it appears that crack propagation in aluminum alloys in alcohol is relatively temperature insensitive. There are several reasons for the wide scatter in propagation rates.

1. At the stress levels used, the propagation times constituted only 5% of the total time. Small errors in separation of initiation and propagation stages caused large errors in propagation time.

2. The stress intensity factor was constantly increasing during propagation and this caused errors in the measured rate.

The value of Q lies in the range of 14 kcals/mole for Al-Mg-Zn in double distilled water and in the range 1-4 kcal/mole for aluminum alloys in alcohol.

3.7. **Hydrogen Charging Experiments**

The following tables (12,13) list the type of charging and the failure time of Al-21.5Zn and Al-2.6Mg-6.3Zn in NaCl/K₂CrO₄ solution. Notched specimens were tested at a constant stress of 10,000 psi in Al-21.5Zn and 76,500 psi in Al-2.6Mg-6.3Zn. Hydrogen charging was carried until the moment of load application. It was not possible to separate initiation and propagation times in the Al-Zn alloy. The charging time in table (12) was 30 minutes at 4.5 volts, 0.5 amps with a current
Figure (23). Logarithm of propagation rate vs 1/T for Al-2.6Mg-6.3Zn in NaCl/K$_2$CrO$_4$ and D. water
Figure (24). Logarithm of propagation rate vs $1/T$ for Al-Mg-Zn and Al-Mg alloys in ethyl alcohol.
Figure (25). Logarithm of propagation rate vs $1/T$ for Al-21.5Zn in 95% ethyl alcohol.

Al-21.5Zn  95% ethanol

$Q = 1.2$ kcals/gm mole

Poor Correlation
Figure (26). Logarithm of propagation rate vs $1/T$ for Al-21.5Zn in 99% ethyl alcohol

Al-21.5Zn
99.9% Ethanol

$Q = 3.86$ kcals/gm mole
density of 0.6 amps/cm$^2$.

The failure times were shortened by a factor of three by prior hydrogen charging of the specimen.

Table (12)

HYDROGEN CHARGING EXPERIMENTS ON Al-21.5Zn IN 3.5% NaCl + 2.0% K$_2$CrO$_4$

AT 10,000 psi

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>Avg. time</th>
<th>Total time</th>
<th>Voltage &amp; current</th>
<th>Current density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen charged</td>
<td>37.2</td>
<td>37.2</td>
<td>0.5A, 4.5 Volt</td>
<td>0.6 Amp/cm$^2$</td>
</tr>
<tr>
<td>Hydrogen charged</td>
<td>37.4</td>
<td>33.0</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Hydrogen charged</td>
<td>41.9</td>
<td>41.9</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Uncharged</td>
<td>126</td>
<td>126</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Uncharged</td>
<td>103</td>
<td>123</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Uncharged</td>
<td>60</td>
<td>60</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Hydrogen charged held 8 days</td>
<td>110</td>
<td>110</td>
<td>0.5A, 4.5 Volt</td>
<td>0.6 Amp/cm$^2$</td>
</tr>
<tr>
<td>tested uncharged</td>
<td></td>
<td>121.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen charged held 8 days</td>
<td>133.1</td>
<td>133.1</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>tested uncharged</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathodic protection</td>
<td>228.6</td>
<td>228.6</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Table (13)

HYDROGEN CHARGING EXPERIMENTS ON AGED Al-2.6Mg-6.3Zn ALLOY IN 3.5% NaCl + 2.0% K$_2$CrO$_4$ AT 76,500 psi

<table>
<thead>
<tr>
<th>Experimental condition</th>
<th>Failure time minutes</th>
<th>Avg. Voltage</th>
<th>Current density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen charged</td>
<td>3.5</td>
<td>4.5V, 1.5 A</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>11.6</td>
<td>4.5V, 2 A</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>4.1</td>
<td>4.5V, 2 A</td>
<td>2.4</td>
</tr>
<tr>
<td>Uncharged</td>
<td>48.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.5</td>
<td>37</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>35.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathodic protection</td>
<td>No failure</td>
<td>4.5V, 2 Amp.</td>
<td></td>
</tr>
<tr>
<td>removed</td>
<td>151 min.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathodic protection removed</td>
<td>Failure in 1 min.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.8. Electron Microscopy

3.8.1. Precipitate Distribution After Aging

The precipitate distribution was studied by taking indirect carbon replicas from etched specimens. The replicas were shadowed with chromium. Thin foils were also studied for certain alloy systems. The microstructure of aged Al-9Mg as revealed by thin foil and replica technique is shown in figures (27-31). The microstructure is characterised by an almost continuous network of grain boundary precipitates surrounded by a precipitate free zone having a width between 2 to 10 μ depending on
the aging time. The grain interior consists of rod like precipitates believed to be the partially coherent phase $\beta'$ (31,32,33).

The interparticle spacing as well as the width of the precipitate free zone decreases with increasing time of aging at 200°C until it reaches a minimum after aging for 7 hours. The minimum spacing of precipitates as determined by the method of Kocks (68) is $\sqrt{A/N} = 1 \mu$ Overaging leads to an increase in the spacing to $\sim 4 \mu$. The grain boundary precipitate has been shown to be the phase $\beta'$ by different workers (32,46).

The microstructure of the aged Al-3Mg-6Zn alloy is shown in figure (32,33). Once again grain boundary precipitates, a precipitate free zone and matrix precipitates are present. The grain boundary precipitate is presumably MgZn$_2$ while the precipitate in the grain interior is either the h.c.p. transition phase $\eta$ (52) or the phase $x$ (53).

Both the interparticle spacing and the width of the precipitate free zone are smaller in the aged Al-3Mg-6Zn alloy compared to the aged Al-9Mg alloy.

The present results agree with the electron microscopy of Al-3Mg-6Zn and Al-9Mg alloys carried out by other workers (31-39,52,53). Extensive information is available on the electron microscopy and X-ray diffraction study of these two systems as well as Mg-8Al and Al-22Zn alloys (41-45). For this reason, only a limited amount of electron microscopic study of these alloys was attempted in the present work.
Figure (27). Al-9Mg aged 7 hours at 200°C. Matrix precipitate distribution 10,000 x.

Figure (28). Al-9Mg aged 7 hours at 200°C. g.b.ppt. 10,000 x.
Figure 29. Al-9Mg, aged 5 hours at 200°C.  
g.b.ppt. and dislocations, 20,000 x.

Figure 30. Al-9Mg, aged at 200°C. Showing the precipitate free zone.  
(a) Aged 4 hours  (b) Aged 5 hours.
Figure (31). Al-9Mg aged at 200°C. Precipitate distribution.
(a) aged 6 hours, (b) 7 hours, (c) 24 hours, (d) 48 hours.
Figure 32. Shows the difference in precipitate size between the aged Al-9Mg and Al-3Mg-6Zn.
(a) Al-9Mg aged for 7 hours at 200°C.
(b) Al-3Mg-6Zn aged for 30 minutes at 160°C.
Figure 33. Al-3Mg-6Zn aged at 160°C for (a) 1 hour, (b) 3 hours.
Figure 34. Al-9Mg aged 5 hours at 200°C.
Strained (a) 1.3% (b) 4% (c) 4%.
(c) 2000 x
Figure (35). Mg-8.6Al aged for 1 hour at 200°C. Transgranular stress corrosion crack 40 x

Figure (36). Mg-8.6Al, solution treated and water quenched. Transgranular stress corrosion crack 80 x
Slip Line Study

Age hardened specimens of Al-9Mg were deformed 0.7%, 1.3%, 2%, 3%, and 4% in an Instron. Single stage silicon monoxide replicas were taken from the surface of the tensile specimens which were etched before deformation. The results are shown in figure (34). No slip was observed up to 2% strain. Some slip was visible at 3% strain while extensive slip and cross-slip were seen at 4% strain. The slip lines were present throughout the grain and not just confined to the precipitate free zone as reported by Thomas (32).

Stress Corrosion Crack Path

The aluminum base alloys exhibited intergranular stress corrosion cracking. The intergranular nature of the cracking is evident from fractographs shown in figures (37-41).

The crack path in Mg-8.5Al was transcrystalline as shown in figures (35,36). It follows a direction perpendicular to the direction of the applied stress.

3.8.2. Fractography

A detailed fractographic study was carried out using the electron microscope and the electron microprobe analyzer. The latter, used as a low magnification scanning microscope was useful in locating the area of the fracture surface from which the replica was taken. The microprobe pictures were of two types:

a) topography image
b) absorbed electron image
For each specimen, the replica micrographs are shown after the scanning electron micrographs. The fractographs shown in figures (37-40) are taken from specimens which exhibited complete stress corrosion failure. The criteria for this type of failure was that the load should gradually decrease to zero in the Instron load relaxation test. In other words, there was no tensile overload component resulting in an abrupt load drop. Therefore, the features shown in figures (37-40) can be considered part of a 'typical' stress corrosion surface.

Fractographs of notched specimens pulled to fracture were also studied in order to distinguish the stress corrosion surface from the tensile overload fracture surface. These are discussed in appendix (1).

The partially stress corroded specimens showed the most complex fracture features because they contained the stress corroded as well as the mechanically failed areas. In such cases it was very difficult to distinguish between the two types of areas, particularly on a replica. An example is shown in figure (41). Stress corrosion area in this specimen was present near the edge while the mechanically failed area was near the centre. However, part of the edge showed transcrystalline mechanical fracture.

A typical 'dry' tensile fracture of the notch showed the following features.

1. Dimples of cusps were present on the intergranular facets.
2. Slip steps were seen on intergranular facets.
3. Elongated dimples were present on the grain facets in some cases.
4. A narrow band of transgranular fracture containing 'rim lines' was present at the edge in Al-Zn and Al-Mg-Zn alloys.

5. The 'dry' fracture was predominantly intergranular.

All the above features were rarely observed together in the completely stress corroded specimen. Slip steps were present in such specimens and a small fraction of the edge showed rim lines but most of the surface appeared smooth and bright at low magnification. At high magnification the grain facets appeared to have a rough surface. The edge could be identified from the machine marks. Similar to those seen in figure(37a,b).

The stress corroded surface can be seen in figure (37). The intergranular cracking has occurred over 95% of the edge shown in figure (37a,b). Only 5% is covered by transgranular rim lines. Near the centre, slip steps can be seen in figure (37c). The rough nature of the surface is evident from figures (37d,e). The specimen was an Al-22Zn alloy, stress corroded in NaCl/K$_2$CrO$_4$ at low stress.

The same alloy was hydrogen charged and stress corroded at a low stress. Again 95% of the edge showed intergranular cracking while 5% had transgranular rim lines as seen in figure (38a,b). Corrosion product can also be seen. The facets shown in figure (38c) appeared to have surfaces shown in figures (38d-h) when examined at high magnifications. While corrosion product is present in figures (38e,f) the roughness of the surface can be seen in areas free of corrosion product such as fig. (38d,f,g,h). In figure (38h) the surface appears to consist of steps.
Figure (37). Aged Al-22Zn alloy, stress corroded in NaCl/K₂CrO₄ at 10,000 psi. Complete stress corrosion fracture.

(37a). Stress corrosion surface near the edge of the notch with machine marks.

(37b). Transgranular fracture near the end.

(37c). Slip lines near the centre showing plastic deformation during stress corrosion.

(37d,e) Stress corrosion surface.
38 (e) 6000 x

38 (f) 6000 x

38 (g) 7000 x

38 (h) 20,000 x
Figure 38. Al-22Zn, hydrogen charged for 30 minutes and stress corroded in NaCl/K₂CrO₄, at 10,000 psi.

38(a) Edge, showing rimlines and corrosion product.
38(b) Edge, stress corrosion surface and slip lines.
38(c) Centre, stress corrosion surface, inter granular fracture.
38(d) Typical stress corrosion surface with a rough texture.
38(e,f) Corrosion product in the stress corroded area. Dark lines in 38(f) are folds in the replica.
38(g,h) Another type of stress corrosion surface at two different magnifications. The rough area appears to consist of steps.
When Al-2.6Mg-6.3Zn is stress corroded in NaCl/K$_2$CrO$_4$, the grain facets show slip steps, fig. (39a,b). Intergranular cracking is observed over the fracture surface. Intergranular cracks can be seen branching off in fig. (39b). The rough texture of the facets is shown in fig. (39c-e). Some evidence of ductility is shown by the presence of corroded dimples in fig. (39e). This specimen showed a stepwise load relaxation.

When Al-9Mg is stress corroded in NaCl/K$_2$CrO$_4$ solution, the fracture is completely intergranular with no evidence of rim lines or slip steps as seen in fig. (40a). The surface has a corroded appearance when viewed at higher magnification, figs. (40b-d). The lower right area is probably caused by the tearing of replica.

The complex nature of the fracture surface of a partially stress corroded specimen is best illustrated by fig. (41). The specimen was stress corroded in alcohol at 30,000 psi. The area of stress corrosion was a small fraction of the total area. More than half the edge showed a transgranular fracture with rim lines, while the tensile fracture near the centre was intergranular. Rim lines and slip steps are present in fig. (41a,b). A magnified view of the transgranular fracture surface with rim lines is shown in fig. (41c). Fig. (41d) is the small area of stress corrosion surface near the edge. Dimples, shear dimples and slip lines associated with ductile fracture are present in fig. (41e,f). The dimples in Fig. (41f) have been attacked by the environment.
Figure (39). Al-2.6Mg-6.3Zn, solution treated and water quenched, stress corroded in NaCl/K$_2$CrO$_4$ at 55,000 psi. Predominantly stress corrosion surface.

39(a). Edge, intergranular fracture surface with extensive slip during stress corrosion.

39(b) Centre, intergranular facets, deformation in stress corroded area.

39(c,d). Characteristic stress corrosion surface with corrosion product or tear marks.

39(e). Dimples with rough surface in the stress corrosion region.
Figure 40. Aged Al-9Mg, stress corroded in NaCl/K$_2$CrO$_4$ at 7000 psi.
Predominantly stress corrosion surface.

40(a) Edge, intergranular facets with a bright appearance.

40(b,c) Stress corrosion surface showing a rough texture.

40(d) Stress corrosion surface, the bottom right area is presumably an artifact caused by the tearing of replica.
Figure (41). Al-22Zn stress corroded in 99.9% ethyl alcohol at 30,000 psi. Stress corrosion and tensile overload modes of failure.

(41a). Near edge, transgranular mechanical fracture showing rim lines.

(41b). Near centre, deformation on grain facets during tensile overload failure.

(41c). Near edge, magnified view of rim lines shown in (41a).

(41d). Near edge, stress corrosion surface.

(41e,f). Near centre, tensile overload region with dimples and slip lines. Note the roughening of the dimples by alcohol.
Figure (42). Phase diagrams of Al-Mg and Al-Zn systems. The Composition and heat treatment temperatures of the binary alloys used are indicated (112).
4. DISCUSSION

4.1. Precipitation Hardening and Mechanical Properties

In this section the precipitation hardening reactions and the nature of resulting precipitates is considered. The microstructure is then correlated to mechanical properties such as yield strength and ductility. The phase diagrams Al-Mg and Al-Zn systems are shown in figure 42.

4.1.1. Al-9Mg aged at 200°C

The aging sequence of this alloy can be represented as

supersaturated solid solution → β' → β(Mg2Al3)

Geissler, Barret and Mehl (46) have established that the transition structure β' is a partially coherent phase which forms as platelets on [120] of the matrix and that β phase is incoherent with the matrix. The structure of β' is uncertain but β phase is complex f.c.c. with 1168 atoms per unit cell (62).

Precipitation at grain boundaries can be observed microscopically before aging has progressed far enough to change yield strength and elongation measureably. Changes in yield strength and elongation are approximately coincident with appearance of precipitation within the
Grains (31). Grain boundary precipitates do not contribute to the increase in strength. The precipitate free zone observed in figs. (27-31) is denuded of solute and vacancies.

Nicholson and Embury (47) have shown that nucleation of $\beta'$ requires vacancies because it has a larger atomic volume than the matrix. Apparently the vacancy deficiency cannot be relieved by the grain boundary acting as vacancy source. Therefore the rod like $\beta'$ precipitates cannot nucleate in the zone adjacent to the grain boundary. On the other hand ppt. nucleation at the grain boundary is favoured because of a lowering in the value of free energy change. The grain boundary precipitate is then in a lower energy state than the intermediate precipitate formed within the grain and it will tend to increase in size during aging at the expense of intragranular precipitates. In addition the grain boundary precipitate is frequently nucleated before the intragranular precipitate and is able to draw solute atoms from within the grains.

The nucleation of precipitates is difficult in Al-9Mg alloy and occurs heterogeneously. A comparison of fig. (27) with fig. (33) indicates that the precipitates in Al-9Mg are coarse and the density of precipitation is low. This is the explanation of the poor age-hardening characteristics of binary Al-Mg alloys compared to ternary Al-Mg-Zn alloys.

Most of the precipitating phase at aging times employed in this work is the transition precipitate $\beta'$ (31). Fink and Smith obtained only $\beta'$ up to 136 hours at 200°C for an Al-10Mg alloy (31). On overaging the precipitate becomes coarser. Results of Perryman and Brooks (67) as well as Thomas and Nutting (32) show that the equilibrium precipitate
on aging at 200°C does not appear on peak aging but appears well into the overaging stage.

4.1.2. Al-3Mg-6Zn Aged at 160°C

The aging sequence in this alloy has been generally accepted as (51).

Solid solution $\rightarrow$ Spherical G.P. Zones $\rightarrow$ $\eta'$ $\rightarrow$ $\eta$(MgZn$_2$). It has been suggested by Mondolfo et al (52) that $\eta'$ is a h.c.p. transition phase which forms with the following orientation relationship with the matrix:

$$(001) \eta' II (111)Al$$

Further it is proposed that as aging progresses the $\eta'$ phase gradually transforms into $\eta$ phase by a steady change in lattice parameters.

The $\eta$ phase is also hexagonal and occurs with at least six different orientation relationships with the matrix (53). The paths which are most frequent have an orientation relationship:

$$(0001) \eta II (110)Al$$

According to Thackery (53), specimens aged at 165°C for 1, 5, 16, and 120 hours after a cold water quench from 465°C did not show any sign of $\eta'$. The precipitate consisted of a hitherto unreported phase X and equilibrium phase $\eta$. The crystal structure of X phase is uncertain, though probably hexagonal, with Zn as the predominant element.

The aging treatment in the present work was very close to that
used by Thackery and therefore the structure probably consists of dispersion of X and \( \eta \) phases, along with spherical G.P. zones.

The probable aging sequence is:

Spherical G.P. zones \( \rightarrow \eta (\text{MgZn}_2) \)

From fig. (32-33) it is evident that the precipitate size and interparticle spacings in Al-Mg-Zn alloys are considerably less than in Al-9Mg alloy. The precipitate free zone varies from 0.2 to 0.5 \( \mu \) in width compared to 2-10 \( \mu \) for Al-9Mg. The precipitate in fig. (27) is at least an order of magnitude larger than the precipitate in figs. (32-33). The width of the precipitate free zone obtained here agrees well, with that obtained by Embury and Nicholson under comparably aging conditions (54). However, these authors contend that the predominant phase after aging at 180\(^\circ\)C for 3 hours is \( \eta' \).

Thackery (53) suggests that the so-called \( \eta' \) plates may actually be a type of \( \eta \) precipitate. It is also possible that \( \eta' \) may in fact be the X phase.

4.1.3. **Al-21.5Zn Aged at Room Temperature**

Garwood and Davies (55) have plotted aging curves for 'step-quenched' Al-Zn alloys containing 17\% and 25\% Zn aged at room temperatures. From their data it is possible to calculate the time required for an Al-21.5Zn alloy to attain maximum hardness at room temperature. This time was approximately 1.5 hours. The maximum hardness was maintained for at least 11 days.
The aging sequence at elevated temperatures as proposed by Carpenter and Garwood (56) is:

Supersaturated solid solution → spherical G.P. zones →
coherent platelets of rhombohedral α → fccα' → hcp zinc rich
solid solution of equilibrium composition.

According to Niklewski (57) et al the coherent precipitates
are stable below 110°C.

In a specimen aged to peak hardness at room temperature there
is a mixed structure of spherical G.P. zones ~ 35 Å in diameter and
platelets of α' conjugate solid solution containing approximately 80%
Zn (57). These platelets are 100 Å in dia and ~ 20 Å thick. They form
on [111] habit planes of the matrix. The increase in hardness on aging
at room temperature can be attributed to these two coherent phases.

4.1.4. Mg-8.5Al aged at 200°C

The precipitation reaction in Mg-8.5Al alloy is (58-61):

Supersaturated solid solution → Equilibrium Mg17Al12 phase has a complex cubic structure.

No indication of a transition lattice form of Mg17Al12 or
G.P. zone formation were observed even at low temperatures during early
stages of precipitation (58-61).

It has been shown (61) that the Mg17Al12 plates form parallel
to the basal plane and are elongated in three close packed directions of
the matrix. Under optimum hardening conditions the interplate spacing
was relatively large about 2000 Å and no coherency strains were observed
around the precipitate.
Both intragranular and intergranular precipitation occurs competitively. Cellular precipitation takes place at a high angle or disordered grain boundaries. Cellular precipitation in this Mg-8.5Al alloy is believed to occur by the mechanism proposed by Smith (61) i.e. a grain boundary migrates into the adjacent grain with lamellae of precipitate and depleted matrix forming behind the advancing grain boundary.

4.1.5. Age Hardening Mechanism of Mg-Al

According to Clark (61), the results of trace analysis on large grained specimens of Mg-9Al show that different modes of deformation are operative in the solution treated and fully age hardened condition.

Basal slip and [10\(\bar{1}\)2] twins are the principal deformation modes in the solution treated condition. In the fully aged condition, basal slip and prismatic slip predominate. [10\(\bar{1}\)2] twins are almost completely absent. Fine basal slip in a solution treated specimen is replaced by wavy slip in a fully hardened specimen.

Transmission microscopy shows that as aging proceeds, planar arrays of basal dislocation decrease and areas of complex tangles increase. These tangles are responsible for hardening the alloy.

The [10\(\bar{1}\)2] twins in Mg-Al alloy do not shear the Mg\(_{17}\)Al\(_{12}\) plates and as the size and number of Mg\(_{17}\)Al\(_{12}\) plates increase the amount of [10\(\bar{1}\)2] twinning proportionately decreases.

In view of the simple precipitation process in Mg-Al it is not surprising that the agehardening response is small. The 0.2% offset yield stress increases from 27,000 psi to 40,000 psi e.g. 50%. The uniform plastic elongation drops from 4.5% to 1% and rises slightly on
Figure (43). Plates of equilibrium $\text{Mg}_{17}\text{Al}_{12}$ phase with basal plane habit. Arrows denote [1120] directions. Mg-9Al aged 8 hours at 260°C. After Clark (61).
overaging as shown in fig. (6).

The interplate spacing in Mg-Al alloys is not small enough to require shearing of the precipitate for dislocation motion and result in a large increase in strength. The role of Mg\textsubscript{17}Al\textsubscript{12} precipitates is to break up basal glide, cause cross slip and thus produce dislocation tangles which in effect strainhardens the matrix. However, the increased strength produced by strain hardening is not as large as in systems such as Al-Cu and Al-Mg-Zn.

4.1.6. **Effect of Aging on Mechanical Properties of Aluminum Alloys**

The increase of nearly 200% in the yield strength of aged Al-Mg-Zn is remarkable when compared with a mere 30% increase in Al-Mg alloys. On the other hand the uniform elongation on aging, decreases by a factor of 4 in Al-Mg-Zn compared to a decrease by a factor of 24 in Al-Mg, figs. (4,5).

In Al-21.5Zn alloy the increase in hardness for the given heat treatment is about 100% (55). The strength should increase by a proportional amount (48). The following qualitative description can be given of the variation in strength of age hardening aluminum alloys (63). Initially the strength of the alloy is that of the supersaturated matrix. If the initial particles are very small in at least one dimension, the strength is also very temperature dependent. The yield stress at this stage is governed by the stress necessary to force dislocation through the precipitates. The work done in forcing dislocations through the precipitates may be governed by factors like coherency stresses, internal order of precipitate and interface effects.
As the precipitate particles increase in size and possibly change their internal structure or the nature of their interface with the matrix, the work done in cutting each particle increases. Dislocations are eventually force between the particles, instead of through them. According to Thomas et al (32) the partially coherent precipitates such as $\beta'$ in Al-Mg deform with matrix.

Further increase in particle spacing then leads to a decrease in strength, the yield strength varying as $1/d$ where $d$ is the mean planar interparticle spacing, or according to the equation:

$$\tau = \tau_s + \frac{Gb}{4\pi} \phi \ln \left\{\frac{d-2r}{2b}\right\} \frac{1}{(d-2r)/2} \quad (1)$$

if Orowan criterion is met (102)

In this equation: $\tau$ = initial yield stress (shear) of the hardened alloy.

$\tau_s$ = yield stress of the matrix material

d = interparticle spacing

$r$ = radius of particles

$G$ = shear modulus

$\phi = 1/2(1 + \frac{1}{1-v})$

$v$ = Poisson's ratio

This sequence is illustrated schematically in fig. (44). At short aging times the applied stress $\tau_o$ necessary to force dislocation between the particles is much greater than the measured yield stress. The variation of $\tau_o$ with aging time is denoted by the dotted curve in Fig. (44).

After longer aging times $\tau_o$ controls the yield stress. If the particles
Figure (44). Schematic variation of yield stress with aging time for an age-hardening system. (After Kelly and Nicholson (63)).
are sufficiently strong, the flow becomes very turbulent since either dislocation loops with matrix Burger's vector or interface dislocations are left around particles. This produces a high density of dislocations which resists further slip.

In polycrystalline alloys of aluminum the grain boundary precipitate exerts little influence on yield strength. Usually the ductility of the alloys is decreased by the presence of grain boundary precipitate.

The poor age hardening response of Al-Mg alloy compared to Al-Mg-Zn and Al-Zn alloys can be explained by the following reasons:

1. A requirement of high strength in an aged alloy is that the precipitate dispersion should be fine (49-50). In Al-Mg alloy the dispersion is coarse compared to Al-Mg-Zn and Al-Zn alloys.

   In Al-Mg-Zn and Al-Zn the dispersion is finer by at least an order of magnitude and hence the strengthening is more pronounced figs. (27-33).

2. The nucleation of precipitates is difficult in the Al-Mg system owing to the large unit cell of the equilibrium precipitate $Mg_2Al_3$. This precipitate exhibits an $\alpha$-Mn complex f.c.c. structure with 1168 atoms per unit cell. The nucleation of intermediate precipitate $n'$ in Al-Mg-Zn and G.P. zones in Al-Zn is relatively easy.

   Further evidence of this fact can be seen in the age hardening response of these alloys at room temperature. Both Al-Mg-Zn and Al-Zn show precipitation within a few hours of solution treatment (55,66).
Al-9Mg alloys on the other hand can retain nearly all magnesium in the supersaturated solid solution and microscopically visible precipitate may take years to form (64). The decrease in uniform elongation on aging in Al-Mg, Al-Zn and Al-Mg-Zn alloys can be attributed to the presence of grain boundary precipitates. From figures in Appendix I, it appears that the tensile fracture is predominantly intercrystalline. Intergranular precipitates can adversely affect ductility by nucleating voids. Extensive void formation can be observed in figures shown in Appendix I. Interfacial energy would appear to be an important parameter and the stress concentrating effect of the precipitates may be of special importance (65).

In the circumferentially notched rods the voids are nucleated on the intergranular precipitates. The crack travels towards the surface. The initial mode of fracture is intergranular. When it reaches near the surface the stresses may be high enough for it to proceed in a transgranular manner. The mode can then be mixed inter- and transgranular as in Al-3Mg-6Zn. In Al-21.5Zn and Al-9Mg it is predominantly intergranular. In certain cases the final transgranular fracture is accompanied by the presence of rim lines shown in figs. (37-41). These linear features on the edge are found in notched and unnotched Al-Mg-Zn alloys and notched Al-Zn alloys. They are absent in unnotched Al-Zn and Al-Mg alloys.

It appears that the predominance of intergranular fracture is associated with the ease of void nucleation as well as the availability of suitably oriented grain boundary paths. In notched specimens, the final
fracture has to pass through the root of the notch even if no suitably oriented grain boundary is present. Therefore the crack goes through the grain and leaves linear markings or rim lines on the edge of the notch.

4.2. Parameters Affecting Stress Corrosion Cracking in Aluminum Alloys

4.2.1. Stress Corrosion Susceptibility and Microstructure in Al-9Mg Alloy

Stress corrosion susceptibility increases remarkably on isothermal aging at 200°C as seen in figure (7). The as quenched alloy did not fail even in 600 hours whereas the peak aged alloy failed in just 15 seconds. On comparing figures (7) and (4) it is seen that the stress corrosion susceptibility varies in the same fashion as the 0.2% offset yield stress. Since the yield stress is largely determined by the nature of precipitates and their distribution it is reasonable to believe that these factors influence the times to failure. The as quenched Al-9Mg alloy can retain magnesium in the solid solution for a long time (66). Isothermal aging results in precipitation of rod like β' phase in the grains and grain boundaries. β' phase corrodes in NaCl/K₂CrO₄ solution even when it is not coupled to a cathodic phase (69).

The maximum susceptibility to stress corrosion occurs close to peak hardness in Al-9Mg. During pre-aging and over-aging stages the failure time changes rapidly. The corresponding variations in yield strength, interparticle spacing and width of the PFZ are modest. A satisfactory stress corrosion theory must explain:
1. The reason for the maximum stress corrosion susceptibility close to peak hardness in Al-9Mg alloys.

2. The several orders of magnitude increase in stress corrosion susceptibility corresponding to relatively minor changes in yield strength, precipitate distribution and the width of the PFZ.

The Al-9Mg alloy is subject to intercrystalline corrosion in salt solution due to the presence of the grain boundary precipitate $\beta$ or $\beta'$ (69). Perryman found that if an Al-7Mg alloy was slowly cooled from the solution treatment temperature, it contained a discontinuous grain boundary precipitate and was resistant to stress corrosion cracking. Edeleanu (70) stated that stress corrosion occurred even when no second phase was observed at the grain boundary and that hydrogen was evolved from the cracks prior to failure. Farmery and Evans (14) attributed cracking to an anodic reaction at the crack tip that required the maintenance of an acid condition there. Erdmann-Jesnitzer and Hotzsch (69) reported that stress corrosion cracks in Al-7Mg followed grain boundaries of large mis-orientation which were normal to the direction of the applied stress. This is in agreement with present results in which the direction of crack propagation was along grain boundaries perpendicular to the applied stress.

4.2.2. **Applied Stress and Stress Corrosion Susceptibility**

A threshold stress equal to 20% of the yield stress was obtained for peak aged Al-9Mg alloy, fig. (8). It is seen that a change in stress level from 20% to 30% of the yield stress results in the specimen failing in one hour. This go-no-go type of test, with the
specimen failing in one hour or not failing in 200 hours is believed to be a feature of the chloride/chromate environment (71). Stress level has very little influence up to 75% of the yield stress. Thereafter large differences in failure times result from small variations on the applied stress. The shape of this curve is very similar to that obtained in tests of susceptible, wrought Al-Mg-Zn alloys (69).

4.2.3. **Nature of Slip and Stress Corrosion Susceptibility**

Thomas and Nutting (32) observed preferential slip in the denuded zone in Al-7Mg alloy overaged at 200°C. To test this observation, flat underaged and peak aged specimens were strained different amounts in tension and both carbon-chromium replicas and single stage silicon monoxide replicas were taken from their surfaces.

No slip could be observed in the peak aged specimen up to its fracture strain of 1%. Certainly no preferential slip in the denuded zone was visible. Similarly, there was no preferential slip in the underaged specimen up to a strain of 2%, fig. (34).

Transgranular slip could be observed in the underaged specimen at 3% strain. Slip bands and slip lines were present in the interior of the grain, fig. (34b). At the fracture strain of 4% extensive slip lines and bands were seen. Cross slip was also present, fig. (34c).

Similar results have been obtained on Al-Mg-Cu-Zn by Jacobs (20), Speidel (22) and other workers. They indicate that no preferential plastic deformation occurs in the precipitate free zone as postulated by Pugh (13) and Thomas (17). Transmission microscopy work of Speidel (22)
reveals no evidence for a large density of dislocations in the precipitate free zone. However Sedriks et al (87) have observed dislocation tangles in the PFZ. They postulate that dislocations are generated at precipitate particles and move across the soft solid solution in the PFZ until they are stopped by fine particles at PFZ-grain interface. At higher stresses the dislocations overcome the barriers and move into the grains resulting in the formation of bands.

4.2.4. Stress Corrosion Susceptibility and Microstructure in Al-3Mg-6Zn Alloy

The maximum susceptibility occurs at an aging time of 3 hours at 160°C. This time corresponds to a yield strength of about 80% of the peak yield strength. The occurrence of maximum susceptibility well before peak aging in Al-Mg-Zn alloys has been observed by other workers (22). This is in contrast to the behaviour of Al-Mg alloys, which are most susceptible at peak strength. The structure consists of a fine dispersion of partially coherent η' or X phase (53). The grain boundary precipitates, presumably equilibrium phase MgZn₂ are coarser than the matrix precipitates and about 0.1 μ long. The PFZ is approximately 0.25 μ in width (26). The interparticle spacing appears to be about 0.1 μ.

Another difference from Al-Mg system, is the fact that the as-quenched alloy is susceptible to stress corrosion. This can be explained in terms of the ease of nucleation of G.P. zones and subsequent phases even at room temperature. Speidel (22) observed grain boundary and matrix precipitation in Al-Mg-Zn-Cu alloy at room temperature
after aging for several hours.

The width of PFZ does not vary much at the same aging temperature, (38) yet the failure times between 3 hours and 24 hours at 160°C, vary by a factor of 10. The two heat treatments produce similar yield strengths and % elongations. Sedriks et al (26) working with a similar alloy, obtained three different sizes of PFZ at the same strength level, by varying the aging times and temperature. They observed an increase in failure time or a decrease in susceptibility with increasing width of PFZ. The present results indicate that the width of PFZ alone cannot account for the large differences in susceptibilities between underaged and overaged specimens. The specimens used by Pugh et al (26) were in different stages of precipitation hardening which means that there were differences, in the types of precipitates, interparticle spacings, as well as PFZ.

Not only do structures with similar PFZ show very different susceptibilities, but also specimens with same yield strength and ductility can have widely different susceptibilities to stress corrosion. This can be seen from figures (5,9).

It appears that the phases formed during the early stages of aging, such as G.P. zones and intermediate precipitates have a marked influence on the stress corrosion susceptibility of Al-3Mg-6Zn alloys. As aging proceeds, the proportion of intermediate precipitates decreases and that of equilibrium phase MgZn₂ increases. As a result, the susceptibility to stress corrosion decreases. Gruhl (19) observed that heat treatments which caused the metastable coherent phases to be replaced by stable MgZn₂ phase also resulted in improved resistance to
stress corrosion. Speidel (22) proposed that coherent precipitates are sheared by dislocations which therefore pile up adjacent to the grain boundary and cause high stress concentrations. Such precipitates also result in coarse slip because shearing of obstacles leads to a reduction of the flow stress in the activated slip plane. The following dislocations tend to remain and to move in the same plane, thus reducing the cross section of the particles even more and further slip in the same plane is facilitated.

Jacobs (20) and other workers have observed that susceptible alloys tend to show coarse slip and non-susceptible alloys show fine slip.

When aging is continued, the volume fraction of precipitates which cannot be sheared by dislocations increases. Such precipitates are by-passed by dislocations and loops are left around them which interact with mobile dislocations and increase the friction stress. Very overaged alloys show bands of high dislocation loop density (22). Stress concentration at the tip of such bands and the associated slip step is very small. Such alloys are very resistant to SCC as seen from fig. (9).

According to Speidel (22) the most susceptible alloys are those which can sustain high stress concentration at the grain boundary because of dislocation pile ups, exhibit coarse slip and thereby expose fresh metal surface to the environments. These conditions are met by Al-Mg-Zn alloys before peak strength. Other important factors are the potential difference between grain boundaries and interior of the grain, nature of the grain boundary precipitate and the rate of chemical
and electrochemical dissolution of the grain boundary and localized plastic deformation in the vicinity of the crack.

4.2.5. **Applied Stress and Stress Corrosion Susceptibility**

When the applied stress is decreased from 90% of the yield stress to 60% the failure time increases by a factor of two. A further decrease in the stress to 30% of the yield stress increases the failure time by a factor of 5 as seen in Fig. (10). Thus, Al-3Mg-6Zn in the peak aged condition shows a change in failure time with applied stress which is very similar to that observed in Al-9Mg in peak aged condition. However, below 60% of the yield stress, the rate of increase of failure time is much slower in Al-3Mg-6Zn than in Al-9Mg. For example, a change in stress level from 60% to 30% produces a five-fold increase in failure time in Al-3Mg-6Zn and a 170 fold increase in Al-9Mg.

Therefore, the susceptibility of peak aged Al-9Mg is highly stress sensitive compared to that of the peak aged Al-3Mg-6Zn.

Gruhl (73) postulates that the rate of cracking is related to the applied stress as

\[ Z = K^* \exp (c) \]  \hspace{1cm} (2)

where \( Z = \text{rate of cracking - inverse of failure time} \)

\[ K^* = k \exp \left( - \frac{Q}{RT} \right) \]

\( c, k = \text{are constants} \)
Q = activation energy of the rate controlling process

Thus the rate of cracking is given by

\[ Z = K \exp(c\sigma - Q/RT) \]  \hspace{1cm} (3)

The present results indicate that a plot of log. failure time vs applied stress is not a straight line but rather a curve. Helfrich (72) obtained a straight line at higher stresses turning into a curve at lower stresses. Gruhl obtained a constant threshold stress at different temperatures, whereas Helfrich observed a decreasing threshold stress level with increasing temperature. These differences could be due to the different compositions of alloys as well as different stress corrosion testing techniques used in the above works. When log applied stress is plotted against log failure time for Al-9Mg and Al-3Mg-6Zn in salt solution and a least squares fit applied to the points, straight lines with correlation coefficients of 0.92 and 0.98 are obtained. They are shown in figures (45,46). This indicates that applied stress (\sigma) is related to the failure time (t_f) by an equation of the form

\[ t_f = A \cdot \sigma^{-n} \cdot \exp \left( \frac{Q}{RT} \right) \]  \hspace{1cm} (4)

where A is a constant for a system.

The values of n are 6.0 for Al-9Mg and 2.4 for Al-3Mg-6Zn. In other words \( t_f \) is more stress sensitive in the case of Al-9Mg alloy than in the Al-3Mg-6Zn alloy.

It is important to note that the above equation holds for
Figure (45). Log-log plot of applied stress vs failure time for Al-9Mg in NaCl/K₂CrO₄.
Figure (46). Log-log plot of applied stress vs failure time for Al-3Mg-Zn in NaCl/K$_2$CrO$_4$. 

$n = 2.4$
stresses considerably higher than the threshold stress. Near the threshold stress the failure times are longer than predicted by equation (4).

The power law relationship between applied stress and initiation time holds for notched Al-21.5Zn in 99.9% ethanol tested in the notched form. The value of n is 6.3 and the correlation coefficient is 0.90. The plot is shown in fig. (47). Thus for Al-21.5Zn in ethanol the values of $\sigma$ and $t_f$ can fit an exponential equation of the form

$$t_f = B \cdot \exp(-\beta \sigma) \cdot \exp\left(\frac{Q}{RT}\right)$$

(5)

It should be noted that the Al-21.5Zn in ethanol was tested in the notched form, while other alloys were tested in the constant load apparatus as unnotched strips. Both the equations are valid only at stress levels higher than the threshold. The exponential fit is marginally better in Al-Zn while the powerlaw fit is better in Al-Mg and Al-Mg-Zn. If Gruhl's (73) results are plotted on a log-log scale they can fit both equations (4) and (5) giving n values lying between 2 and 3 compared to value of 2.6 in the present work. The choice of an equation describing the stress dependence of failure times cannot be made solely on the basis of the least squares fit. Rather it should be compatible with a typical process taking place during stress corrosion.

The crack propagation rate for Al-Zn in ethanol is also stress sensitive and can fit either a log rate vs log $\sigma$ plot or a log rate vs $\sigma$ plot. The value of n obtained from a log-log plot shown in figure (48) is 4.5.
Figure (47). Log-log plot of applied stress vs initiation time for Al-22Zn in ethanol.
Figure (48): Log-log plot of applied stress vs propagation rate (mm/hr) for Al-22Zn in ethanol.
4.3. **Stress Corrosion Susceptibility of Mg-8.5Al**

This system was studied because unlike the Al base alloys, the second phase in aged Mg-8.5Al alloys is cathodic to the matrix by approximately 0.4 volts in aqueous salt solution. The crack path was transgranular and normal to the direction of the applied stress. This is evident from figures (35,36).

When susceptibility is plotted against aging time, there is a steady increase in stress corrosion susceptibility with aging, fig. (11). Unlike Al base alloys the resistance to stress corrosion does not improve on overaging. Between as-quenched and peak aged condition there is a 50% increase in yield strength and a 200 fold decrease in failure time. After the maximum strength is reached, overaging results in 10% drop in yield strength, while the failure time decreases by a factor of 4. Obviously, the precipitation of $\text{Mg}_{17}\text{Al}_{12}$ phase leads to the increased susceptibility to stress corrosion cracking.

According to Priest (74), cracking is transcrystalline if the specimens are water quenched and intercrystalline if they are furnace cooled. Logan (75) observed threshold stresses between 70 and 90% for annealed Mg-6.5Al-1Zn alloy. In the present work the threshold stress was not obtained although it was less than 50% of the yield stress. The higher susceptibility of this alloy is probably due to the higher aluminum content. Loose and Barbian (75) observed an improvement in stress corrosion resistance with a decrease in aluminum concentration.

According to Timanova (76) the nucleus of a microcrack is created in a Mg-8.5Al alloy as a result of the selective corrosion of the intermetallic phase or of the supersaturated solid solution. The
stresses destroy the protective film, at the crack tip, which then corrodes at a higher rate than the crack walls. It is difficult to see why selective corrosion should occur at the intermetallic phase which is cathodic to the surrounding matrix.

Heidenreich et al (75) propose that the matrix adjacent to the intermetallic anodic to the intermetallic and goes into solution by an electrochemical process.

Logan (75) observed an increase in potential in the more active direction when the stress was applied and associated it with the rupturing of the protective film. The specimen was seen to be strained at a diminishing rate after full load had been applied. If the average strain rate was above a critical value, the stress concentration at few sites were believed to deform the specimen surface at a sufficient rate to prevent the film from reforming. The specimen would then fail in a short time.

In the present work, a similar extension-time curve was observed when notched Mg-8.5Al alloy was stress corroded in the Instron. The extension was not discontinuous, as observed by Logan.

Logan further proposes that if the film free area is very small and is surrounded by a large film covered area, rapid corrosion of the anode will take place. Such corrosion will form a sharp trench preventing film from reforming at its apex and will lead to the initiation of stress corrosion crack. Cracking could be stopped by the application of cathodic current and reinitiated if the current was removed (74); suggesting that crack propagation was an electrochemical process. However, Logan calculated that a current density of 14 amps/cm² would be required
to produce cracking at the rate determined in a Mg-Al alloy. This is an excessively high current density and it is more probable that crack propagation is an electrochemical-mechanical process.

The fact that no discontinuous extension was observed in load relaxation tests in the present work, does not mean that the crack propagation is a continuous process. The series of steps constituting the fracture process may be too short in time to be resolved by this technique.

The increase in stress corrosion susceptibility with increasing aging time is due to the reduction in the area of the matrix solid solution relative to the intermetallic phase Mg$_{17}$Al$_{12}$. As a consequence, the anodic current density increases and dissolution takes place at an increased rate.

Clark (61) observed planar arrays of dislocation in the solution treated condition and dislocation tangles in the overaged condition. Planar arrays should lead to coarse slip and increased susceptibility, but such is not the case. It appears that the role of deformation is to build up stress concentration by dislocation pile ups at the barriers. As a result, slip occurs in grains that were previously undeformed. The protective film is ruptured and stress corrosion is initiated. The delayed strain in these relatively resistant grains could account for the initial decrease in the load relaxation curve.

4.4. Variation in Stress Corrosion Susceptibility with the Alloy System

In this section a comparison will be made between the stress corrosion susceptibilities of Al-9Mg, Al-3Mg-6Zn, and Mg-8.6Al alloys.
It is difficult to compare failure times in systems having widely different isothermal aging curves. The problem is further complicated by the fact that the maximum susceptibility to stress corrosion is reached before peak strength in Al-3Mg-6Zn, at peak strength in Al-9Mg and well after peak strength in Mg-8.6Al. The comparisons are made on the basis of failure times observed in constant load tests. In all cases, a 3.5% NaCl + 2.0% K2CrO4 solution was used.

At 40% of the yield stress the solution treated and quenched Al-9Mg is immune. From extrapolation of the line in fig. (12), it appears that Mg-8.6Al will also be immune at 40% of the yield stress. Only Al-3Mg-6Zn is susceptible and fails in 50 hours.

During preaging Al-9Mg is the most susceptible, Al-3Mg-6Zn is next and Mg-8.6Al is still immune.

In the peak aged condition Al-9Mg fails in 1/2000 of the failure time of Al-3Mg-6Zn. Mg-8.6Al is still immune.

In the overaged condition the order of susceptibility remains the same as before, but the differences in failure times are reduced. There is only a two-fold difference in susceptibility of Al-9Mg and Al-3Mg-6Zn, while Mg-8.6Al is expected to be immune.

If failure times are compared at 40% of the yield stress for the most susceptible condition of each system, it is found that Al-9Mg is 200 fold more susceptible than Al-3Mg-6Zn and nearly 7000 fold more susceptible than Mg-8.6Al alloy.

In figure (49), the stress vs log failure time for Al-9Mg, Al-3Mg-6Zn and Mg-8.6Al is plotted. It will be noticed that Mg-8.6Al and Al-9Mg show failure times which are highly stress sensitive while
Figure (49). Applied stress vs failure time for three systems studied under constant load, in NaCl/K₂CrO₄.
failure times in Al-3Mg-6Zn are comparatively insensitive to changes in the applied stress. The reason why Mg-8.6A1 appears to be immune at 40% of the yield stress, whereas Al-3Mg-6Zn is still subject to stress corrosion cracking, is that the stress level at 40% yield stress for Mg-8.6A1 lies below the cross over of the two curves. Therefore, the relative susceptibilities to stress corrosion depend on the fraction of the yield stress at which comparisons are made. For example at 90% of the yield stress Al-3Mg-6Zn is the least susceptible. If failure times are compared at the same absolute stress level, the stronger alloy would appear to have longer failure time above the cross over point, because that stress level would correspond to a relatively lower fraction of its yield stress. Then again, comparisons are difficult to make at stress levels between the yield stresses of two alloys. For instance at 30,000 psi, the yield stresses of Al-9Mg and Mg-8.6A1 are exceeded and their susceptibilities cannot be assessed relative to Al-3Mg-6Zn or to each other. Therefore it seems that the best approach is to make comparisons of stress corrosion behaviour at a constant fraction of the yield stress. In this work the fractions of yield stress were 40% for Al-9Mg and Al-3Mg-6Zn and 70% for Mg-8.6A1 in their aged conditions.

4.5.1. Initiation and Propagation of Stress Corrosion Cracks in NaCl/\(K_2CrO_4\) Solution

The initiation time was defined as the elapsed time between the application of full load and the first detectable drop in the load. It is possible that cracks could have been initiated before the load drop
was noticeable. However, specimens unloaded before the anticipated initiation time, failed to reveal any cracks. Allowing for a factor of two variations in the anticipated initiation time, it was observed that cracks were seen only after the drop in the load. Initiation times were generally reproducible within a factor of two.

Three types of load-relaxation curves were observed as shown in fig. (50). The solution heat treated Al-3Mg-6Zn exhibited the type of curve shown in fig. (50a) at stresses up to 55,000 psi. In this the load relaxation occurs in small steps down to zero load. This type of behaviour suggests that crack propagation may be a discontinuous process, so that each step represents an electrochemical-mechanical advance of the stress corrosion crack. However, aluminum alloys show Portevin-Le Chatelier effect due to the pinning and unpinning of dislocations by solute atoms, and this effect produces a discontinuous yielding. During the notch tensile tests the load falls in a discontinuous manner much like in stress corrosion tests. This gives rise to two possibilities.

1. Stress corrosion crack propagation is continuous but the plastic flow at the crack tip is discontinuous as a result of locking and unlocking of dislocations.

2. Both crack propagation and plastic flow are discontinuous, but only the discontinuity of the plastic flow is detectable by the present technique. The second type of curve is shown in fig. (50b); the stress corrosion crack propagates part of the way through the specimen showing steps. Then at D, the stress at the tip of the crack exceeds the ultimate strength of the alloy and mechanical fracture occurs. This type of behaviour was observed in most aged alloys of
Figure (50). Three types of load relaxation curves observed in the present work.
aluminum. A third type of load-relaxation curve is shown in fig. (49c). This behaviour was noticed in Mg-8.6Al alloys under all conditions. The crack propagation is entirely continuous and no steps are detected in the load-relaxation curve.

Thus, solution treated Al-3Mg-6Zn showed the first type of curve at low stresses, Al-2.6Mg-6.3Zn and Al-8.6Mg showed the second type of curve (49b) in the aged condition; Al-21.5Zn and Mg-8.6Al showed the third type of curve although the former alloy exhibited small discontinuities during the propagation of the stress corrosion crack.

The crack propagation velocities were calculated for alloys in which the stress corrosion crack propagated through the entire cross section. This was done by dividing the radius of the notch by the propagation time as measured on the load-relaxation curve. As mentioned earlier, through stress corrosion cracks were observed in relatively few specimens and therefore the propagation velocities are approximations at best. The propagation rate in salt solution for as-quenched Al-Mg-Zn is 1 mm/hr at 55,000 psi; for aged Al-Zn it is 0.8 mm/hr at 10,000 psi; for aged Al-Mg it is 4 mm/hr at 30,000 psi. The as-quenched Mg-Al showed a crack propagation rate of 4.8 mm/hr at 26,000 psi in a salt solution ten times more dilute than the one used for aluminum base alloys. Pugh observed a propagation rate of 0.35 mm/hr in an Al-Mg-Zn alloy tested in 3.5% NaCl solution at 40,000. The higher rate of crack propagation in the present work is probably caused by the high triaxial stress state at the root of the notch. The rate of crack propagation is influenced by the initial applied stress. In the Al-Zn alloy in alcohol at room temperature the rate of propagation is proportional
to the logarithm of applied stress according to expression of the form

\[ \text{rate} = \sigma^n \]

where \( n = 4.5 \)

These rates were calculated assuming that crack progresses a distance \( L \) over a circular front until the stress on the remaining area exceeds the notch tensile strength.

Therefore if \( R = \) radius of the notch \( P = \) load at fracture

then stress on the remaining area = \( \frac{P}{\pi(R-L)^2} \)

Equating this to the notch tensile strength \( \sigma_n \) we get

\[ \frac{P}{\pi(R-L)^2} = \sigma_n \]

Rearranging \( L = R - \sqrt{\frac{P}{\pi \sigma_n}} \) \hspace{1cm} (6)

knowing the cracklength and propagation time, the propagation rate can be calculated. Because the radius of curvature of the machined notch is considerably greater than that of the crack, the above expression would over estimate the crack length. During crack propagation, the load falls but the stress concentration at the crack tip increases because of a reduction in the load bearing area. The behaviour of sub-critical crack propagation is illustrated in figure (50) where the stress intensity factor \( K_I \) is plotted against crack velocity and fracture time (77).
Figure (51). Variation in stress intensity factor $K_I$ during subcritical crack propagation (77).
\[ K_I = \sigma \sqrt{c} \times \text{constant} \]

where \( \sigma = \text{applied stress} \)
\( c = \text{initial crack length} \)

Stress corrosion cracks can propagate above a minimum threshold of stress intensity factor = \( K_{\text{ISCC}} \). The velocity is nearly constant once \( K_{\text{ISCC}} \) is exceeded until near \( K_{\text{IC}} \) where it becomes indefinitely fast and mechanical fracture occurs. The shape of this curve resembles the load relaxation curves shown in fig. (49b,c). Both \( K_{\text{ISCC}} \) and \( K_{\text{IC}} \) are constant for a given metal-environment system. The level of crack velocity is several orders of magnitude higher than can be inferred from models in which the crack dissolves or is the site of alternate formation and rupture of the oxide film (78.79). According to Pugh, (26) crack velocities of 0.35 mm/hr observed in an Al-Mg-Zn alloy correspond to current densities of 0.3 amp/cm\(^2\) and these are not considered to be unreasonably high for a corrosion process.

4.5.2. The Relative Lengths of Initiation and Propagation Times in NaCl/K\(_2\)CrO\(_4\) Solution

In Al-Mg-Zn alloy initiation times is greater than propagation time except for the large grained alloy. From Table (17) it is seen that lowering the stress results in an increase in the fraction of propagation time for the same heat treatment. The heat treatment given to a specimen remarkably alters the fraction of propagation time relative to initiation time. Propagation time comprises the greater part of the total failure time in the large grained (570 \( \mu \)) specimens. In the
solution treated specimens of smaller grain size (256 μ) propagation time is 12 to 50% of the total time, whereas in the overaged specimens it constitutes only 3-5% of the total time. Therefore the duration of crack propagation is favored by low stress, large grain size and a lack of precipitate.

In Al-8.6Mg alloy the propagation time consists of 92-99% of the total time for underaged alloys and only 5-16% for peak aged alloys. The large grained specimens also show propagation times between 95-97% of the total time. In aged Al-21.5Zn alloy there is no definite effect of stress level on the propagation part of stress corrosion, although it constitutes the major part of the failure time. The propagation part varies from 65 to 95% of the total failure time.

In solution treated and quenched Mg-8.6Al alloy the propagation time accounts for 74 to 96% of the total time. Dilution of the solution results in an increase in the fraction of propagation time while varying the stress level does not have any effect. The alloy aged for a short time (1 hour at 200°C), shows a slight decrease in the proportion of propagation time to initiation time.

4.6. The Effect of Different Environments on the Stress Corrosion Behaviour of Aluminum Alloys

Aluminum alloys were found to stress corrode in a number of environments as seen in Table (9-10) and figures (15) and (16). The total failure time decreased as the amount of water in the environment increased. Both aqueous and organic liquids caused cracking provided the applied stresses were high enough. The purpose of this set of
<table>
<thead>
<tr>
<th>Alloy Heat Treatment</th>
<th>Applied Stress psi</th>
<th>% Initiation time</th>
<th>% Propagation time</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-3Mg-6Zn as-quenched</td>
<td>48,000</td>
<td>88</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>55,000</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>over-aged</td>
<td>55,000</td>
<td>95</td>
<td>5</td>
<td>Discontinuous load relaxation in Al-Mg-Zn system.</td>
</tr>
<tr>
<td></td>
<td>55,000</td>
<td>97.5</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>69,000</td>
<td>96</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>69,000</td>
<td>95.5</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>as-quenched, large grain size</td>
<td>46,000</td>
<td>33</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>46,000</td>
<td>41</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Al-1.26Mg-6.3Zn, as-quenched</td>
<td>57,600</td>
<td>71</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>57,600</td>
<td>67</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Al-8.6Mg, underaged</td>
<td>40,800</td>
<td>8</td>
<td>92</td>
<td>Discontinuous load relaxation in Al-8.6Mg system</td>
</tr>
<tr>
<td></td>
<td>38,200</td>
<td>0.6</td>
<td>99.4</td>
<td></td>
</tr>
<tr>
<td>peak aged</td>
<td>12,500</td>
<td>95</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31,200</td>
<td>94.5</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>Al-8.6Mg, peak aged, large grain size</td>
<td>31,000</td>
<td>2.6</td>
<td>97.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27,000</td>
<td>4.5</td>
<td>95.5</td>
<td></td>
</tr>
<tr>
<td>Al-21.5Zn, peak aged</td>
<td>40,000</td>
<td>5</td>
<td>95</td>
<td>Continuous load relaxation in Al-21.5Zn</td>
</tr>
<tr>
<td></td>
<td>26,000</td>
<td>17</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26,000</td>
<td>35</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10,000</td>
<td>30</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Mg-8.6Al, as-quenched</td>
<td>26,000</td>
<td>20</td>
<td>80</td>
<td>solution diluted by 10:1</td>
</tr>
<tr>
<td></td>
<td>26,000</td>
<td>17</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26,000</td>
<td>3.5</td>
<td>96.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26,000</td>
<td>6.5</td>
<td>93.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30,000</td>
<td>20</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30,000</td>
<td>18</td>
<td>82</td>
<td>Continuous load relaxation in Mg-8.6Al</td>
</tr>
<tr>
<td>Aged 200°C, 1 hour</td>
<td>30,000</td>
<td>26</td>
<td>74</td>
<td></td>
</tr>
</tbody>
</table>
Table (15)

RELATIVE LENGTHS OF INITIATION AND PROPAGATION TIMES IN VARIOUS ALLOY-ENVIRONMENT SYSTEMS

<table>
<thead>
<tr>
<th>Alloy, heat treatment</th>
<th>Environment</th>
<th>Applied stress psi</th>
<th>% Initiation time</th>
<th>% Propagation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-2.6Mg-6.3Zn</td>
<td>3.5% NaCl + 2.0% K₂CrO₄</td>
<td>57,600</td>
<td>71</td>
<td>29</td>
</tr>
<tr>
<td>Solution treat and quenched</td>
<td>D. water</td>
<td>57,600</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Ambient air</td>
<td>57,600</td>
<td>74</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Silica Gel</td>
<td>57,600</td>
<td>60</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Methyl alcohol</td>
<td>60,000</td>
<td>83</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>CCl₄ + D. water</td>
<td>60,000</td>
<td>42.5</td>
<td>47.5</td>
</tr>
<tr>
<td></td>
<td>CCl₄ + D. water</td>
<td>68,000</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>CCl₄</td>
<td>68,000</td>
<td>36</td>
<td>64</td>
</tr>
<tr>
<td>Overaged</td>
<td>Ambient air</td>
<td>83,000</td>
<td>3</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>D. water</td>
<td>83,000</td>
<td>87</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Ethyl alcohol</td>
<td>76,500</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>86,000</td>
<td>88.5</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>86,000</td>
<td>81</td>
<td>19</td>
</tr>
<tr>
<td>Al-9Mg</td>
<td>Ethyl alcohol</td>
<td>40,000</td>
<td>87.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Al-21.5Zn peak aged</td>
<td>D. water</td>
<td>64,600</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Ambient air</td>
<td>64,600</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Ambient air (760 mm)</td>
<td>64,600</td>
<td>69</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Ambient air (20 μm)</td>
<td>64,600</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Silica gel</td>
<td>64,600</td>
<td>67.5</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td>Mg(OCl₄)₂</td>
<td>64,600</td>
<td>85.5</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>Sodium dried, Kerosene, 1 M, NaOH</td>
<td>64,600</td>
<td>58</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Ethyl alcohol, 99.9%</td>
<td>58,000</td>
<td>87</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Ethyl alcohol 95%</td>
<td>58,000</td>
<td>95</td>
<td>5</td>
</tr>
</tbody>
</table>
experiments, was to establish the effect of different environments on the initiation and propagation of stress corrosion cracks. Preliminary tests were carried out on solution treated Al-2.6Mg-6.3Zn but later work was confined to the peak aged and overaged conditions. This was necessary in view of the fact that supersaturated aluminum alloys undergo precipitation during plastic deformation. Incipient precipitation at the tip of a stress corrosion crack is likely to change the rate of chemical or electrochemical attack as well as mechanical properties of the alloy. In the peak aged or overaged condition the above processes would not occur as most of the solute would be present as precipitate and not in the solid solution.

As the amount of water in the environment is reduced, the failure time increases significantly for Al-2.6Mg-6.3Zn alloy in both the solution treated and overaged conditions. This can be seen from figure (15). The failure times increase by factors of 6 to 8 when the environment is changed from deionized water to ambient air. A further 50 fold increase takes place when a dessicant such as silica gel is used. This effect shows the importance of water vapour in the stress corrosion of aluminum alloys provided a sufficient stress concentration exists at the root of the notch. The importance of water vapour is also illustrated by figures (13) and (14). A significant increase in elongation is observed when the regular environment is replaced by a dessicant.

In the as-quenched alloy, propagation times constitutes between 10 to 40% of the total failure time. In the overaged alloy, most of the failure time in ambient air is taken up by the propagation of the stress corrosion crack, whereas in deionized water, initiation
time seems to constitute the major part of the time to failure.

The load relaxation curve is discontinuous up to a certain point beyond which mechanical fracture takes place.

Organic liquids such as methyl alcohol, ethyl alcohol, and carbon tetrachloride also caused stress corrosion cracking in aluminum alloys. The cracking times were an order of magnitude longer in methyl alcohol than in water. The major part of stress corrosion failure was still taken up by the crack initiation stage. In carbon tetrachloride saturated with water, failure occurred in about the same time as in water free carbon tetrachloride. There are two possibilities.

1. The cracking was caused by the minute quantity of water present in the organic liquid and further increase in water concentration did not have a significant effect on the stress corrosion rate. Hence similar times were observed for water saturated and water free carbon tetrachloride.

2. Water played no part in the process and therefore no difference was detected in failure times.

A further experiment was carried out to resolve the role of water in the process. The cell containing carbon tetrachloride was surrounded by a polythene bag containing a desiccant. Therefore the organic liquid was in equilibrium with dry air rather than ambient air. The specimen did not fail in 100 hours whereas previously it failed in less than two hours. This demonstrates that water plays an important role in the process.

In ethyl alcohol the propagation time was less than twenty percent of the total time to failure both in the Al-Mg-Zn and Al-Mg alloy.
Al-21.5Zn alloy was extremely susceptible to stress corrosion and failed 350 times faster than aged Al-2.6Mg-6.3Zn in water; at the same fraction of their respective notch strengths. The failure time in silica gel was also 1000 times shorter. Different media were tried in an attempt to prolong the life of specimens. These included magnesium perchlorate, sodium dried kerosene, and sodium hydroxide and air at reduced pressure. However, the life times of specimens could not be prolonged beyond fifteen minutes. The failure times were increased 35 to 70 fold compared to deionized water, by using various dessicants. This compares with an increase of 80 times in the overaged Al-2.6Mg-6.3Zn alloy.

Except in deionized water, the major part of failure times consisted of the initiation of the stress corrosion crack. The initiation stage constituted between 65 to 95% of the total time for different dessicants and organic liquids. However, in water the initiation was almost instantaneous. This suggests that perhaps the crack was initiated during the loading of the specimen.

The load relaxation curve was continuous as in figure (46c). The load drop was 15 to 20% of the maximum load, followed by mechanical fracture. The stress corrosion as well as mechanical fracture was intercrystalline. The fracture surface was bright in aqueous mediums and dull in ethyl alcohol.

Aluminum alloys can react with alcohol and produce hydrogen once the protective oxide film is ruptured. This was demonstrated by the following experiment.

A piece of aluminum was rubbed on coarse emery paper and
immediately dipped in a mercurous chloride solution. A mercury-aluminum amalgam was formed wherever the oxide film was broken and prevented the repair of the film. Then the specimen was placed in ethyl alcohol. A combustible gas, presumably hydrogen, was seen to evolve from the specimen as a result of the action of fresh aluminum surface with the alcohol. A similar effect was noticed in carbon tetrachloride and water. The evolution of the gas was most rapid in water. This shows that without its protective oxide film, aluminum surface is highly reactive in aqueous and organic liquids. It is therefore not surprising that traces of water in the air, or in dessicants are sufficient to cause stress corrosion cracking in the aluminum alloys.

4.6.1. Stress Corrosion in Alcohols

Stress corrosion cracking in ethyl alcohol can be caused either by the trace of water present in it or by a reaction between the alloy and ethyl alcohol at points where the protective oxide film has been ruptured.

All three aluminum base alloys were susceptible to stress corrosion in 99.4% ethyl alcohol. Al-2.6Mg-6.3Zn alloy was also susceptible in methyl alcohol as well as in carbon tetrachloride as seen in fig. (15).

The importance of residual water in determining the rate of cracking is illustrated in fig. (16). For the same stress level, the rate of initiation is between 6 to 8 times faster in 95% ethyl alcohol than in 99.9% ethyl alcohol. However, the apparent activation energy of the process of stress corrosion cracking in alcohol containing small amounts of water, is substantially different from the apparent activation
energy of the process responsible for stress corrosion in distilled water. This is evident from figures (20) and (21). The activation energy in ethyl alcohol is 14.7 kcals/gm mole whereas in distilled water and NaCl/K₂CrO₄ solution, it is 26 kcals/gm mole. Therefore it appears that while addition of water enhances the rate of crack initiation it does not change the apparent activation energy of the process responsible for cracking in alcohol. Furthermore, the apparent activation energy of this process is between 9.6 and 14.7 kcals/gm mole in the three aluminum base alloys, compared to an apparent activation energy of 26 kcals/gm mole in distilled water and NaCl/K₂CrO₄. The nature of the possible processes consistent with the above activation energies will be considered later.

4.6.2. **Effect of Environment on the Mechanical Properties of Al-2.6Mg-6.3Zn**

Environments such as deionized water and NaCl/K₂CrO₄ solution affected the tensile ductility of the heat treated Al-Mg-Zn and Al-Zn alloys, but had no significant effect on the yield stress or ultimate tensile strength of the Al-Mg-Zn alloy. Both environments markedly reduced the uniform plastic elongation as shown in figs. (13,14) and table (7). D'Antonio et al (101) observed that the flow stress of Al-Mg-Zn alloys was strain rate insensitive at room temperature between strain rates employed in the present work. They concluded that discontinuous flow should be observed at slow strain rates at room temperature. Discontinuous flow was observed both in deionized water
and NaCl/K₂CrO₄ up to strain rates of 2 x 10⁻⁴ sec⁻¹ in the present work.

In the solution treated Al-2.6Mg-6.3Zn alloy the uniform plastic elongation increases with increasing strain rate in both deionized water and NaCl/K₂CrO₄. The elongation in deionized water is always greater than that in NaCl/K₂CrO₄. The elongation increases by a factor of 9 as the strain rate is increased from 4 x 10⁻⁶ sec⁻¹ to 2 x 10⁻³ sec⁻¹.

The low ductility at low strain rates is a result of long exposure to the environment. As the strain rate goes up, the time of exposure under stress goes down. Consequently, the embrittling effect of the environment is reduced and the ductility increases. At very high strain rates the environment is practically ineffective in reducing the ductility and the limit of elongation is set by the mechanical properties of the alloy. Therefore the elongation at the highest strain rate in both deionized water and NaCl/K₂CrO₄ is the same as elongation in air at a lower strain rate; which in turn is nearly the same as elongation in dessicant dried air at even a lower strain rate. Therefore more aggressive environments require high strain rates in order to produce the same elongation as in the less aggressive environments.

When a dry air (silica gel) environment is used at a strain rate of 2 x 10⁻⁶ sec⁻¹, the uniform elongation increases by more than a factor of 7 while the flow stress remains unchanged compared to their respective magnitudes in the more aggressive environments.

The change in elongation, due to the change in strain rate
alone, was about 20% of the total difference in elongation, between strain rates of \(2 \times 10^{-6}\) sec\(^{-1}\) and \(2 \times 10^{-3}\) sec\(^{-1}\). The environment was directly responsible for the remaining 80% increase or decrease in the uniform plastic elongation.

Similarly in the overaged Al-Mg-Zn alloy, both uniform elongation and ductility increase with increasing strain rate.

The uniform elongation in silica gel-dried air was 4 times that in NaCl/K\(_2\)CrO\(_4\) and deionized water at comparable strain rates for the overaged Al-Mg-Zn. In all environments at lower strain rates the load relaxation was discontinuous, or steplike. This suggests that the steps observed in stress corrosion tests were also probably the result of discontinuous yielding of the alloy at low strain rates, rather than caused by the arrest and propagation of the stress corrosion crack. Discontinuous yielding was observed up to strain rates of \(2 \times 10^{-4}\) sec\(^{-1}\). Therefore, it is reasonable to infer, that when steps are observed in a stress corrosion test, the crack propagates at a strain rate of not more than \(2 \times 10^{-4}\) sec\(^{-1}\), whereas when no steps are observed the crack propagation takes place at a higher strain rate.

In the overaged alloy discontinuous yielding took place at a lower strain rate \(10^{-5}\) sec\(^{-1}\). There are two reasons why steps are not observed in the stress corrosion test of overaged Al-2.6Mg-6.3Zn alloy under static load.

1. The uniform elongation or ductility of the overaged alloy is less than 50% of the ductility of the solution treated alloy. Consequently the region of crack propagation in solution treated alloy is larger than in the overaged alloy as is the probability of observing a stepwise decrease in the load. There is also less solute in the overaged alloy
2. Strain rates at which discontinuous yielding is observed are one order of magnitude less in the overaged alloys compared to the solution treated alloys. In the environments such as deionized water and NaCl/K_2CrO_4 the crack propagation results in a strain rate higher than $10^{-5}$ sec$^{-1}$ and no steps are observed.

The extent of step formation can be increased by changing from an aggressive environment to a less aggressive environment. This effect was noticed in solution treated Al-2.6Mg-6.3Zn alloy, when dessicant dried air was used instead of deionized water or ambient air. Stress corrosion crack propagated through the specimen and the load relaxation was discontinuous in dry air, while in other environments the crack propagated partially through the specimen before mechanical fracture due to tensile overload occurred.

4.6.3. Effect of Environment and Strain Rate on Mechanical Properties of Al-21.5Zn

Deionized water drastically reduces the ductility of aged Al-21.5Zn alloy. The uniform elongation can be increased 16 fold and the total elongation three times when deionized water is replaced by dessicant dried air, at strain rates of $6 \times 10^{-6}$ sec$^{-1}$. The yield stress is increased by a factor of 2.5, table (7).

At strain rates of $2.7 \times 10^{-3}$ sec$^{-1}$ there is a 3 fold increase in uniform elongation on using dry air in place of deionized water and no significant change in the yield stress.

On increasing the strain rate from $6 \times 10^{-6}$ sec$^{-1}$ to $2.7 \times 10^{-3}$ sec$^{-1}$ the elongation in deionized water increases 20 fold and that
in silica gel 4 fold.

Al-21.5Zn stress corrodes even in dessicant dried air and that is the reason for observing the latter increase in uniform elongation. The values of elongation and yield strength depend on the time the alloy has been exposed to the environment. These times are small at higher strain rates and therefore the yield strength or elongation is not affected significantly. At low strain rates the yield strength as well as elongation is reduced in the dessicant dried air and deionized water. This is so, because sufficient time is available for stress corrosion cracks to be nucleated when the strain rate is low. No truly inert environment was found for Al-21.5Zn.

4.6.4. Effect of Strain Rate on Serrated Yielding

Serrated yielding was most often observed in the solution treated Al-Mg-Zn alloy and was altogether absent in the Al-Zn alloy. In the solution treated alloy serrated yielding was observed up to a strain rate of $2 \times 10^{-4}$ sec$^{-1}$, whereas in the overaged alloy it was present only below a strain rate of $10^{-5}$ sec$^{-1}$.

The reason serrations are present only below a critical strain rate is that at low strain rates it is easier for solute atoms present in the solution to segregate to dislocations. In addition the concentration of solute atoms is higher in the supersaturated solid solution than in the overaged alloy. As a result longer diffusion times are required for a sufficient number of solute atoms to segregate to a dislocation and cause discontinuous yielding in the case of the overaged alloy. Therefore in an overaged alloy, discontinuous yielding can be observed
only at strain rates lower than in the solution treated alloys.

No serrations are observed in the overaged Al-21.5Zn alloy because it is highly brittle.

When pure aluminum (99.995) was tested in two different environments at strain rates of $2 \times 10^{-6} \text{ sec}^{-1}$ no significant difference was observed. The environments were silica gel and deionized water. Similarly at higher strain rates there was no change in yield strength or uniform elongation. This is so, because pure aluminum is not susceptible to stress corrosion. Thomas (81) reported that pure (five 9's) aluminum was susceptible to stress corrosion if quenched from an annealing temperature of 600°C. However, in the present work both smooth and notched specimens of 99.99% aluminum were found to be immune in deionized water and NaCl/K$_2$CrO$_4$ solution.

Tensile tests carried out using water as the heating medium, under the assumption that water is an inert medium can lead to erroneous results. This is particularly true in the case of aged Al-21.5Zn and Al-2.6Mg-6.3Zn alloys at strain rates less than $10^{-4} \text{ sec}^{-1}$. The same results are to be expected in the aged Al-8.6Mg and Mg-8.6Al alloys. Uniform and total elongations are the properties most affected by water and NaCl/K$_2$CrO$_4$. Yield strength and work hardening rate are not changed at different strain rates (80) except in the highly susceptible Al-21.5Zn alloy.

The change in uniform elongation for a given alloy, due to the change in environment depends on several factors. These are:

(i) The relative susceptibility of the alloy in the two environments. Higher the difference in the susceptibilities in the two
environments greater the difference in uniform elongation. For example, in the solution treated Al-2.6Mg-6.3Zn alloy, the stress corrosion susceptibility in deionized water and NaCl/K₂CrO₄ is almost the same and so is the uniform elongation. But the failure time in silica gel is 500 times that in NaCl/K₂CrO₄ and the uniform elongation is 7 fold. Similar results are observed for Al-21.5Zn alloy.

(ii) The aging treatment of the alloy. The absolute value of the uniform elongation is decreased in the overaged Al-2.6Mg-6.3Zn alloy. The strain rate at which environment induced embrittlement occurs is reduced by at least an order of magnitude relative to the solution treated alloy.

(iii) The value of the strain rate. Maximum embrittlement occurs at the lowest strain rate. Very low strain rate tests approximate a constant load stress corrosion test and therefore produce the maximum embrittlement or the minimum uniform elongation.

4.7. Temperature Dependence of the Stress Corrosion Process

The stress corrosion cracking of aluminum alloys tested in alcohol, distilled water and NaCl/K₂CrO₄ solution, is a thermally activated process. The apparent activation energy of the rate controlling process varies with the alloy-environment system. It also changes during initiation and propagation stages.

The temperature dependence of failure times of Al-Mg-Zn alloys in salt solutions has also been studied by Gruhl (73) and Helfrich (72). Gruhl obtains a value of 12.6 kcals/gm mole at 75% of the yield stress.
At a stress level close to the yield strength the Arrhenius plot is not a straight line, but the gradient increases between 50 and 70°C. The apparent activation energy between these two temperatures is 22.2 kcals/gm mole. At other stress levels there is no significant change in the activation energy. Helfrich (72) obtains activation energy values between 17 and 20 kcals/mole. The observed activation energy increases with decreasing applied stress and has a value of 20 kcals/mole in the absence of stress.

Before comparing the results of the present work with those of Gruhl and Helfrich, it should be remembered that their composition of alloys as well as testing techniques were different. In the present work Al-2.6Mg-6.3Zn was tested by continuous immersion of notched cylindrical specimens in 3.5NaCl/2.0K₂CrO₄ solution. Helfrich used C rings of Al-4.2Zn-5Mg immersed in aerated 5.8 %NaCl solution. Gruhl tested an Al-4.9Zn-3Mg alloy in a 3 %NaCl solution which was circulated around the specimen. A distinction was made between initiation and propagation times in the present work, whereas total times to failure were measured in the other two works. The criterion for failure in Helfrich's work (72) was the first visible evidence of cracking at five diameters magnification.

Not all the aluminium alloys are similarly affected by temperature. The stress corrosion failure times of agehardened 2024 aluminum alloy were found to be independent of testing temperature between 3 and 60° by Rostoker and Nicholas (84).
Wei (82) studied moisture enhanced fatigue crack propagation in a high strength aluminum alloy and "interpreted" it as a thermally activated process with apparent activation energies that depend strongly on the crack tip stress intensity factor and vary in magnitude from 1-4 kcals/gm mole.

It should be emphasized that the value of apparent activation energy determined by experiment can correspond to a number of rate controlling processes. Therefore additional information is necessary to eliminate some of the processes with overlapping activation energies. In addition the values of the apparent activation energies of some of the possible processes are not available. Several possible models will be discussed in the light of the above results. The values of apparent activation energies of some of the possible rate controlling processes are listed in table (16).

4.8. The Hydrogen Mechanism

The essential steps in the proposed hydrogen mechanism of stress corrosion are as follows:

1. The first step in the initiation of a stress corrosion crack is the electrochemical dissolution of the equilibrium grain boundary precipitate. The attack takes place at the partial-matrix interface because the protective oxide film is broken at the interface. Helfrich (83) observed dissolution at the constituent particle-matrix interface and Jacobs (20) observed dissolution of the equilibrium precipitate. However, Hunter (12) found that the MgZn$_2$ particles were
Table (16)

THE APPARENT ACTIVATION ENERGIES FOR CRACK INITIATION AND PROPAGATION
AND THE POSSIBLE RATE CONTROLLING PROCESSES

<table>
<thead>
<tr>
<th>Observed Q</th>
<th>Alloy-Env. system</th>
<th>Initiation or Propagation</th>
<th>Possible Mechanism</th>
</tr>
</thead>
</table>
| 26         | Al-Mg-Zn of salt solution | Initiation | 1. Electrochemical dissolution of MgZn$_2$ or aluminum. Q = up to 25 kcals/mole (85)
|            |                   |                           | 2. Creep process controlled by cross slip. Q = up to 27.5 kcals/mole (97) |
| 12         | 1. Al-Zn, Al-Mg, Al-Mg-Zn in alcohol | Initiation | 1. Diffusion of hydrogen through aluminum solid solution Q = 10.9 kcal/mole (97) |
| 12 (9.6-14.7) | 2. Al-Mg-Zn in salt solution | Propagation | 2. Creep process controlled by intersection of dislocations Q = 11 ± 8 kcals/mole (89) |
|            |                   |                           | 3. Movement of single vacancies through aluminum solid solution Q = 12 kcals/mole (73) |
|            |                   |                           | 4. Escape of dislocation from segregated atmosphere (108) |
| 1-4        | Al-Zn, Al-Mg,     |                           | 1. Transport processes in the liquid Q = 2-6 (101). |
left unattacked by an acidified NaCl/AlCl₃ solution whereas the grain boundary was attacked. It is possible that the nature of attack depends on the pH of the solution. In fact Helfrich (83) observed that when Al-Mg-Cu and Al-Cu alloys were stress corroded in an acid (pH = 0.5) salt-dichromate solution cracking initiated at the grain boundaries. But when these alloys were stress corroded in a solution of pH = 4 the electrochemical attack started at the constituent particles. Therefore, it appears that at acid pH's the protective oxide film is destroyed and fresh aluminum is exposed which is attacked in preference to MgZn₂.

From the potential -pH diagram of Al-H₂O system it is seen that the oxide is stable only between pH's of 4 to 8.8 (88) which is therefore the range of passivation of aluminum. In this range MgZn₂ is anodic to aluminum and is therefore corroded by the environment. Since the pH in the present work was 8.6 it is reasonable to suggest that corrosion initiated at the grain boundary precipitates in all the aluminum alloys.

2. While dissolution takes place at the anode, atomic hydrogen is liberated at the aluminum solid solution which acts as the cathode. The hydrogen atoms diffuse to the region of the notch. Dissolution assists in maintaining the notch while deformation at the tip tends to blunt it. Hydrogen probably diffuses to the blocked dislocation arrays at the region ahead of the notch (90). These arrays can be produced by the blocking of dislocations at grain boundaries and by formation of a shear stress field in the triaxial region beneath a notch (9). Alternatively, hydrogen can nucleate at the incoherent interface of the grain boundary precipitate. It has been shown (91) that the absence
of large voids and mobile dislocations in iron whiskers is related to their resistance to hydrogen embrittlement.

The hydrogen precipitates at the defects in the molecular form and an expansion due to the gas pressure takes place as proposed by Zapffe (92), Tetelman and Robertson (8) and others. The internal pressure P lowers the applied stress $\sigma_F$, necessary to cause crack growth. It is proposed that observable crack propagation takes place after the crack has grown to a critical length $2C_0$. During the initiation time, the crack grows to this critical length $2C_0$ by a linking up of microvoids formed by recombination of atomic hydrogen at incoherent interfaces. The hydrogen pressure is additive to the triaxial stress state and assists in the separation of the matrix from incoherent particles.

Once a crack of a critical length is initiated slow crack growth occurs. This process consists of void formation ahead of the crack by the action of triaxial stress state and hydrogen pressure and ductile linking up to the voids in the presence of applied stress.

When the crack reaches a critical length $2C_F$ it satisfies the criteria for unstable fracture.

From Griffith's criteria, the fracture stress, for plane strain condition in an elastic solid is given by

$$\sigma_F = \left( \frac{2Ey}{(1-\nu^2)}\pi C_F \right)^2$$

(7)

$2C_F = \text{internal crack length}$
From Orowan's correction (102)

\[
\sigma_F = \left( \frac{2EP}{(1-v^2)\pi C_F} \right)^{1/2}
\]

(8)

where \( P = \gamma + P_w \)

\( \gamma = \) surface energy

\( P_w = \) plastic work

Also \( G = 2P \)

where \( 2P = \) total energy associated with generation of two surfaces of unit areas.

\[(1-v^2) \rightarrow 1 \text{ for most metals} \]

\[
\sigma_F (\pi C_F^{1/2}) = (EG)^{1/2}
\]

(9)

or

\[
\sigma_F = \sqrt{\frac{EG}{\pi C_F}}
\]

The term \( \sigma_F C_F^{1/2} = K_{IC} \) is known as the stress intensity parameter at fracture stress

\[
K_{IC}^2 = EG
\]

(10)

It will be noticed that processes occurring during initiation are the same as those taking place during the propagation of the stress corrosion crack with one important difference. The difference lies in the value of the stress intensity factor \( K_I \). During initiation
the stress intensity factor remains essentially constant at a value of $K = K_{ISCC}$. Once crack propagation starts there is a sharp increase in the stress intensity factor even if the actual crack velocity remains rather constant (77). When $K_I$ increases to a value $K_{IC}$, unstable fracture takes place at an indefinitely fast crack velocity.

Thus, the propagation stage is marked by a rapidly increasing stress intensity factor and a relatively constant crack velocity until instability is reached. The high stress concentration influences the kinetics in such a way that a different process becomes rate controlling. Consequently, the activation energies of the initiation and propagation stages are significantly different in the same alloy-environment system.

Further support of the hydrogen hypothesis is furnished by the work of Ells and Evans (96). They observed hydrogen agglomerates at the grain boundaries in samples of proton irradiated aluminum at temperatures less than 100°C. Grain boundary cracking was observed at higher temperatures. According to them, the main driving force for nucleation and initial growth of hydrogen filled bubbles is due to a supersaturation of gas in the metal and bubbles can form at 100°C with gas concentrations as low as 1 ppm. Their work shows that microscopic cavities are not necessary for bubble-formation even though a cavity is a highly preferred point of nucleation of hydrogen bubbles. Bubble growth is possible when the pressure is $10^3$ atmospheres in a bubble of 0.1 μm radius. This is equivalent to a hydrogen concentration of $10^{-7}$ ppm at 100°C. The concentration is calculated from Sievert's law.
\[ S = K \cdot p^{1/2} \]

\[ S = 2 \times 10^3 \exp\left(\frac{-19400}{RT}\right) \cdot p^{1/2} \]  \hspace{1cm} (11)

The diffusivity of hydrogen at 100°C is \(8 \times 10^{-8}\) cm²/sec. Hydrogen charging experiments on Al-Mg-Zn and Al-Zn alloys in the present work showed that there is a significant reduction in the failure time if cathodic charging is continued up to the application of load and then stopped. This enables the dissolution to occur in the absence of a protective cathodic potential. Dissolution results in the formation of a notch. The hydrogen forms voids ahead of the crack which link up by ductile tearing.

In the Al-Zn alloy, the crack propagation started as soon as maximum load was applied and prior hydrogen charging significantly shortened the propagation time. In the Al-Mg-Zn alloy both crack initiation and propagation times were shortened significantly by hydrogen charging. In both the alloys if charging was continued after maximum load, failure times could be prolonged considerably. Therefore it may be surmised that anodic dissolution accompanied by the maintenance of a sharp notch is an essential step in the stress corrosion process. This step determines the flux of hydrogen available for diffusion as well as the stress concentration existing at the root of the notch. Hydrogen charging results in an increase in the flux of hydrogen and a decrease in time required for diffusion to form the microvoids. Consequently, both the initiation and propagation times should be reduced.
This is observed in the Al-Mg-Zn and Al-Zn alloys.

Haynie and Boyd (95) used an autoradiographic technique to determine whether hydrogen concentrates at the grain boundaries, using 1 N Na\textsubscript{2}SO\textsubscript{4} containing tritiated water. They found that hydrogen is present in higher concentrations at the grain boundaries of stressed Al-Mg-Zn alloy than in the unstressed material. They concluded that stress apparently increases the solubility of hydrogen at the grain boundaries. When a strip specimen is anodically polarised on one side and cathodically polarised on the other, immediate stress corrosion cracking takes place. There is no cracking when the specimen is polarised only anodically or cathodically.

Haynie and Boyd conclude that hydrogen may be involved in the stress corrosion process in two ways. It may increase localised attack at the grain boundaries by increasing the cation gradient through the strained oxide film. The relative distribution of protons in the oxide at the grain boundary and grains may cause preferential grain boundary attack. Both anodic potential and applied tensile stress increase the diffusivity of the aluminum ions through the oxide film.

It has also been shown (96) that alloys susceptible to stress corrosion show higher rates of hydrogen evolution than the non-susceptible alloys. In the present work, when pure aluminum samples were amalgamated to break up the oxide film and exposed to ethyl alcohol, carbon tetrachloride and salt solutions, evolution of hydrogen was observed. The rate of evolution was higher in the salt solution than in alcohol.

Normally, the distinction between stress corrosion cracking and hydrogen embrittlement is made by applying anodic and cathodic current.
If embrittlement is enhanced by an anodic current the process is stress corrosion cracking and if it is enhanced by a cathodic current then the process is considered hydrogen embrittlement. But this kind of distinction is inadequate if anodic dissolution is an essential step for hydrogen embrittlement as postulated in the present model. The function of anodic dissolution is not clear.

**Drawbacks of the hydrogen model**

1. If hydrogen diffusion was the rate controlling process cathodic charging during stress corrosion should lead to a reduction in stress corrosion lifetime. However, cathodic protection is possible in aluminum alloys.

2. Only the crack initiation in alcohol and crack propagation in salt solution have apparent activation energies equal to activation energy for diffusion of hydrogen. The initiation rate in salt solution and the propagation rate in alcohol have activation energies which are very different from that for hydrogen diffusion. A hydrogen diffusion mechanism cannot convincingly explain why

   (a) The apparent activation energy of propagation is less than that of initiation.

   (b) The differences in respective activation energies in salt solution and alcohol.

3. The application of anodic potential seems to be necessary for hydrogen to have any effect. The reason for this can not be explained by the present hydrogen model.
4. The diffusivity of hydrogen at -70°C in alcohol is too low to account for the observed propagation times.

5. A hydrogen model cannot explain why oxygen is necessary for stress corrosion.

4.9. The Requirements of a Satisfactory Model

A satisfactory stress corrosion model for aluminum alloys must explain the following observations:

1. The stress corrosion cracking is intergranular in both salt solution and ethanol. The stress corroded area appears to have a rough surface.

2. The presence of coherent precipitates enhances the susceptibility to cracking significantly. The presence of grain boundary precipitates and a narrow PFZ is also associated with high stress corrosion susceptibility. On the other hand, solution treated and precipitate free Al-Mg alloy as well as pure aluminum are immune to stress corrosion.

3. A change in environment, at a given stress level changes the crack initiation and crack propagation rates.

4. A change in the initial applied stress always changes the initiation and propagation rates for a given alloy-environment system.

5. The temperature sensitivities of crack initiation and propagation rates are different for a given alloy-environment system. The temperature sensitivity also changes with the environment.

Specifically the model should explain the apparent activation energies listed in the table (17).
Table (17)

APPARENT ACTIVATION ENERGIES OF CRACK INITIATION AND
PROPAGATION FOR ALUMINUM ALLOYS

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Environment</th>
<th>Average 'Q' in kcals/mole during Initiation</th>
<th>Propagation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-2.6Mg-6.3Zn</td>
<td>Salt solution</td>
<td>26</td>
<td>14</td>
</tr>
<tr>
<td>&quot;</td>
<td>D.D. water</td>
<td>26</td>
<td>--</td>
</tr>
<tr>
<td>&quot;</td>
<td>Ethanol</td>
<td>12</td>
<td>1-4</td>
</tr>
<tr>
<td>Al-8.6Mg</td>
<td>Ethanol</td>
<td>12</td>
<td>1-4</td>
</tr>
<tr>
<td>Al-22Zn</td>
<td>Ethanol</td>
<td>12</td>
<td>1-4</td>
</tr>
</tbody>
</table>

4.9.1. Models Involving Either Dissolution or Deformation and Their Drawbacks

(a) According to Helfrich (72) the rate controlling step in the stress corrosion of Al-Mg-Zn alloy in salt solution is the anodic dissolution of MgZn$_2$ particles at the grain boundary. The model is based on the equation of Hitlig and Charles (100), that activation free energy for a corrosion reaction under stress can be expressed as

\[ Q^*(s) = Q^*(o) + s \frac{\partial Q^*}{\partial s} + \ldots \]

\[ s = 0 \]

\[ Q^*(o) = \text{activation energy at zero stress} \]

\[ s = \text{stress} \]

\[ \left( \frac{\partial Q^*}{\partial s} \right) = V^* = \text{activation volume} \]
V* is equated to the molar volume of the phase MgZn$_2$.

Two types of anodic sites have been observed in Al-Mg-Zn alloys. Hunter (12) found that an acidified (pH = 1) NaCl/AlCl$_3$ solution attacked the grain boundaries but not the MgZn$_2$ precipitate. On the other hand Jacobs (20) and Helfrich (21) observed attack at the constituent particle interface. Pugh (26) observed that stress corrosion surface had a corroded appearance. In the present work the typical stress corrosion surface of figures (37-40) was observed. The surfaces exhibited a rough appearance in both salt solution and ethanol.

Helfrich (72) did not distinguish between initiation and propagation rates. His model postulates dissolution of grain boundary precipitates leading to brittle fracture between precipitates but the details of the mechanism are not clear. It does not explain why maximum susceptibility is associated with coherent precipitates and why the temperature sensitivity is different during initiation and propagation stages. It is difficult to explain the present results on the basis of Helfrich's model.

(b) Sodriks et al (26) believe that localized plastic deformation in the PFZ causes preferential anodic dissolution of the deforming metal within the PFZ. The crack propagation rate of 0.35 mm/hr is equivalent to a current density of 0.6 amp/cm$^2$ which is believed to be reasonable for a corrosion process (26).

This model again does not explain the role of coherent precipitates, the stress sensitivity and the temperature dependence of the stress corrosion process. It does not account for the initiation stage nor does it describe in detail mechanics of crack propagation.
(c) Jacobs (20) has proposed that both the precipitate and film free aluminum alternate as anodes with respect to the film covered crack walls. The interparticle distance is bridged by mechanical fracture. However no evidence of ductility has been found in the stress corroded area in the present work.

(d) Krafft and Mulherin (77) believe that microvoid coalescence takes place adjacent to a precipitate or an inclusion. The microvoids link up with the crack tip and the crack advances. The fractography in this work does not rule out the possibility that microvoid formation takes place which is subsequently obliterated by general corrosion. Once again this theory does not explain in detail the role of heat treatment, stress and temperature during initiation and propagation stages.

Models based on dissolution cannot explain some of the observations listed in section (4.8). In addition such models do not explain why pre-immersion in stress corroding solutions did not reduce the initiation or propagation times.

Similarly models based on deformation processes affecting the rate of slip step emergence, slip step height and spacing cannot account for the fact that a change in environment always changes the rate of initiation and propagation in the same alloy at the same stress level. Therefore while apparent activation energies of 26 kcals/mole and 12 kcals/mole are close to the apparent activation energies such deformation processes as cross-slip of dislocations and intersection of forest dislocations respectively; still the deformation process alone cannot explain all the results.
Therefore one can only conclude that both dissolution and deformation processes contribute to the rate of initiation and propagation of stress corrosion crack. A model based on this conclusion is now proposed.

4.10 The Proposed Model

The application of stress results in generation of dislocations at the grain boundary precipitates as proposed by Sedriks et al (26). The dislocations move across the precipitate free zone until their motion is impeded by the precipitates adjacent to the PFZ. The precipitates are sheared by dislocations and attacked by the environment as shown in fig. (52a). Corrosion ceases, when the precipitate is completely dissolved and the aluminum solid solution is covered by a thin film of its oxide. This position is shown in fig. (52a). Further advance of the crack must await the arrival of the next sheared precipitate. After a certain time the sheared precipitate arrives at the crack tip and is dissolved as before, fig. (52b). The process of cooperative dissolution and deformation continues and the crack advances along a slip plane until it reaches an intersecting slip plane. Then the crack changes direction turning towards the PFZ. This change of direction is favoured because the shearing is most pronounced adjacent to the PFZ. The position is shown in fig. (52c). The crack reaches the PFZ and then turns away from it and the sequence starting from fig. (52a) is repeated. The result is a zig-zag crack path confined close to the PFZ and produced by linking of tunnels.

During the initiation stage the crack reaches a critical length until $K_I > K_{ISCC}$. Then crack propagation starts with the same
Figure (52). Illustration of the proposed model.
sequence of events except that deformation takes place at an ever-increasing rate. Therefore, the rate of crack propagation is much greater than that of initiation. When the reduced cross section can no longer support the applied load, the stress intensity factor $K_I = K_{IC}$ and failure occurs. The mode of failure is generally intercrystalline and is accompanied by void formation.

The temperature and stress dependence during initiation and propagation stages can be expressed as

$$\text{Rate} = A_0 \sigma^n \exp\left(-\frac{Q}{RT}\right)$$  \hspace{1cm} (12)

or under certain conditions

$$\text{Rate} = B_0 e^{\delta_0} \exp\left(-\frac{Q}{RT}\right)$$  \hspace{1cm} (13)

where $A_0$ and $B_0$ are constants depending on the alloy-environment system, thermo-mechanical treatment, orientation of grains etc.

It is proposed that the apparent activation energy observed in the present work is composed of two terms, one for a deformation process and the other for a dissolution process. Transition from initiation to propagation is accompanied by a change in the rate controlling process of deformation, but no change in the process of dissolution.

So that

$$\text{Rate} = A_0 \sigma^n \exp\left(-\frac{Q_{\text{Def}}}{RT}\right)\left(\frac{Q_{\text{Diss}}}{RT}\right)$$  \hspace{1cm} (14)
The equations (12) and (13) are similar to creep equations (89). If creep alone was controlling the rate of cracking, then a change in environment from salt solution to ethanol, using the same alloy, should not affect the apparent activation energy. But the value of Q changes from 26 kcals/mole to 12 kcals/mole. Therefore dissolution as well as creep must be involved in the initiation of stress corrosion cracks. Similarly if dissolution alone was rate controlling, then it is difficult to explain the stress sensitivity of the cracking rates as well as the change in apparent activation energy between initiation and propagation.

The sum of apparent activation energies during crack initiation is given by

\[
\begin{align*}
Q_{\text{Def}} + Q_{\text{Diss}} &= 26 \text{ in salt solution} \quad (15) \\
Q_{\text{Def}} + Q_{\text{Diss}} &= 12 \text{ in ethanol} \quad (16)
\end{align*}
\]

Therefore \(Q_{\text{Def}}\) cannot exceed 11 12 kcals/mole.

During crack propagation the dissolution process is believed to remain the same, but since the observed apparent activation energy decreases the creep process must change. Therefore,

\[
\begin{align*}
Q'_{\text{Def}} + Q_{\text{Diss}} &= 14 \text{ in salt solution} \quad (17) \\
Q'_{\text{Def}} + Q_{\text{Diss}} &= 2 \text{ in ethanol} \quad (18)
\end{align*}
\]

If the creep process during initiation is controlled by escape of dislocations from segregated atmosphere as proposed by Congleton and Parkins (108) then \(Q_{\text{Def}} = 11 \text{ kcals/mole}\).

Substituting in equations (15) and (16) we obtain \(Q_{\text{Diss}}\) in salt solution = 14 kcals/mole, \(Q_{\text{Diss}}\) in ethanol = 1 kcal/mole.

Substituting these values in equations (17) and (18) we get \(Q'_{\text{Def}}\) during propagation \(= 0 \sim 1 \text{ kcal/mole}\).
Summarising:

\[ Q_{\text{Diss}} \text{ in salt solution and D.D. water} \quad 14 \text{ kcals/mole} \]
\[ Q_{\text{Diss}} \text{ in ethanol} \quad 1 \text{ kcals/mole} \]
\[ Q_{\text{Def}} \text{ during initiation} \quad 11 \text{ kcals/mole} \]
\[ Q_{\text{Def}} \text{ during propagation} \quad 1 \text{ kcals/mole} \]

Then the apparent activation energies can be added as follows:

Table (18)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Env.</th>
<th>Initiation</th>
<th>Propagation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( Q_{\text{Diss}} )</td>
<td>( Q_{\text{Def}} )</td>
</tr>
<tr>
<td>A1-Mg-Zn</td>
<td>Salt</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>D.D. water</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>A1-Mg</td>
<td>Ethanol</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>A1-Zn</td>
<td>Ethanol</td>
<td>1</td>
<td>11</td>
</tr>
</tbody>
</table>

The values of \( Q_{\text{Diss}} \) and \( Q_{\text{Def}} \) add up to the observed apparent activation energies listed in Table (17).

The activation energies of electrochemical dissolution of the coherent or partially coherent precipitates in salt solution or alcohol are not available in literature. It is not known whether dissolution is controlled by anodic or cathodic processes. According to West (85) metals can have apparent activation energies of electrochemical dissolution ranging from 5-25 kcals/mole which are strongly dependent on the anion present.
It is possible that the rate controlling step is desorption of hydrogen at the cathode by any of the following reactions:

a) \[ M-H + M-H \rightarrow H_2 \]  
(adsorbed hydrogen on the metal)

b) \[ (H_3O)^+ + M-H + e^{-} \rightarrow H_2 \]  
(solvated hydrogen)

c) Depolarisation in the presence of oxygen
\[ 4(M-H) + O_2 \rightarrow 2H_2O \]

If the last step was rate controlling, that would explain the observation of some workers (12) that oxygen is essential for stress corrosion.

The dissolution process in alcohol is assigned an activation energy of 1 kcal/mole. Such low values of Q are generally associated with transport processes in the liquid (101). Greenler (104) and Boreskov (105) have observed the formation of surface ethoxide on alumina by alcohol and postulate that hydrogen ions are evolved in the reaction. The rate controlling step could be the diffusion of reaction products in the crack.

The dissolution processes are believed to remain essentially unchanged during the transition from initiation to propagation.

The deformation process during crack initiation can be controlled by dislocation-solute interaction. The supersaturation of solute during pre-aging can cause pinning of dislocations. Congleton and
Parkins (108) have studied the substitutional strain aging in Al-Zn and Al-Mg alloys during creep. They determined that the apparent activation energy of escape of dislocations from the segregated atmosphere is between 10-11 kcals/mole. They arrived at an expression of the form

$$\frac{\dot{\varepsilon}}{\varepsilon} = 40 \exp \left(-\frac{U}{RT}\right)$$

(16)

where $\dot{\varepsilon}$ = strain rate
$\varepsilon$ = plastic strain
$U$ = apparent activation energy

During crack propagation the increasing stress at the crack tip causes the rate controlling process of deformation to change. Deformation during crack propagation appears to be temperature insensitive. The shearing of precipitates takes place at an increased rate limited not by the rate of escape of dislocations from a segregated atmosphere but rather by some other process. The limiting process could be the long range interaction of dislocations which is temperature insensitive.

The stress sensitivity of initiation and propagation rates could be explained by steady state creep. If the time dependent strain during strain aging is plotted against stress on a log-log plot, value of $n$ between 3 and 9 are obtained for two Al-Zn alloys used by Congleton and Parkins (108). The 'n' values of Al-Zn in alcohol based on equation (12) varies between 6 and 4.5 for initiation and propagation respectively.

The rate equations for stress corrosion initiation and propagation are similar in form to creep equations (89,109). But the parameters
are based on models involving dislocation climb and contain activation energy for self diffusion, which in aluminum is 34 kcals/mole. This value is too high to fit in the proposed stress corrosion model.

Although the assigned values of apparent activation energies are somewhat arbitrary they are not unreasonable for the processes believed to be taking place during stress corrosion. Further developments in the model must await better knowledge of the rate controlling processes involved in the dissolution of precipitates in salt solution and ethanol. Furthermore, more knowledge is required about the deformation process taking place during stress corrosion.

4.10.1. The Observations Explained by the Proposed Model

The model explains all the observation outlined earlier but the evidence for it is largely circumstantial. It explains the generation of a continuous path of chemical heterogeneity, by the action of synergetic processes of dissolution and deformation.

1. Cracking seems to be intergranular because the rate of link up of sheared precipitates will be high close to the PFZ. The finely roughened surface seen infractography is consistent with the model. It is also possible that the cracking is initiated at rim lines shown in figs. (37a, 38b, 41a) which have a zig-zag appearance. Although the 'dry' tensile fracture showed rim lines such specimens also stress corrosion cracked.

2. The model explains the high susceptibility of pre-aged alloys which have higher proportion of coherent or partially coherent
precipitate capable of being sheared. A narrow PFZ would increase the rate of shearing of precipitates by moving them closer to sources of dislocations. The grain boundary precipitates are essential as a source of dislocations, and to cross grain boundary by mechanism of Krafft et al (77). In highly overaged alloys with no precipitates that can be sheared, it is possible that the grain boundary precipitates constitute the path of stress corrosion by nucleating microvoids in the manner suggested by Krafft and Mulherin. The present model explains why stress corrosion does not occur in solution treated Al-Mg and pure aluminum. These two have no precipitates and therefore are immune to stress corrosion.

3. It explains why a change in environment or a change in stress level changes both the initiation and propagation rates. This is so because dissolution and deformation re-inforce each other during stress corrosion.

4. It explains the temperature dependence of initiation and propagation rates since temperature influences the dissolution as well as deformation rates.

5. It may account for the fact that oxygen is essential for stress corrosion since oxygen may assist in cathodic depolarisation of hydrogen and increase the rate of dissolution. It may also explain why NaCl is a more aggressive environment than NaBr and NaI. The desorption of Cl\textsuperscript{−} at the anode may be easier than that of Br\textsuperscript{−} or I\textsuperscript{−}.
4.11. Conclusions

1. Stress corrosion cracking in aged Al-9Mg, Al-3Mg-6Zn and Al-21.5Zn is intergranular in both aqueous and ethanol environments and is influenced by the magnitude of the applied tensile stress, composition, heat treatment and microstructure of the alloy, composition of the environment, geometry of the specimen, orientation of grain boundaries with respect to the tensile axis and temperature.

2. Stress corrosion cracking occurs by initiation of cracks at suitably oriented grain boundaries and propagation of the cracks with an increasing stress intensity factor, leading to mechanical fracture of the remaining material. The initiation time constitutes the major portion of the total time to failure. The relative lengths of initiation and propagation time as well as the relative areas of stress corrosion and tensile fracture can be varied by changing the stress level.

3. Initiation and propagation times in aqueous solutions and ethanol show an Arrhenius type of temperature dependence.

   The apparent activation energy during initiation and propagation is believed to consist of two terms one for dissolution of the sheared precipitates and the other for a deformation process responsible for linking up of the precipitates. Furthermore the rate controlling step in deformation is believed to change during the transition from initiation to propagation. The synergetic processes of dissolution and deformation are therefore responsible for stress corrosion cracking in aluminum alloys.

4. The fractography and other evidence is consistent with a model involving shearing and link up of precipitates adjacent to the grain boundary to form a path of chemical heterogeneity and subsequent dissolution
of this path in the environment.

5. The hydrogen embrittlement model is plausible, but suffers from a number of drawbacks. It is more likely that hydrogen plays an indirect role in dissolution by controlling the cathodic process.

4.12. Suggestions for Further Work

1. It would be useful to extend the study of initiation and propagation times to Al-Mg-Zn-Cu and Al-Cu alloys in aqueous and organic environments and compare the stress and temperature sensitivity with the present results.

2. The stress corrosion kinetics of notched specimens should be compared to that of smooth specimens, both during initiation and propagation stage to see if the same rate controlling process is operating in two types of specimens.

3. The kinetics of propagation should be studied at the same stress-intensity factor so that a meaningful activation energy can be derived.

4. More information is required on the dissolution kinetics of precipitates and aluminum solid solutions in different media. Only then the models postulating anodic or cathodic controlled dissolution reactions can be tested. However, the kinetics under zero stress condition may be significantly different from that under stress.
Appendix I

Tensile Fractography of Aluminum Alloys

The mode of fracture in aluminum alloys was predominantly intergranular in both smooth and notched tensile specimens. In notched specimens of Al-Mg-Zn and Al-Zn the mode of fracture was transgranular near the edge, resulting in a circular band with striated fractures referred to as "rim lines" in this work. The band width was \( \sim 40 \mu \) in Al-Zn and \( \sim 150-300 \mu \) in Al-Mg-Zn. The other features present on a typical tensile fracture surface were:

1. Dimples of cusps
2. Slip steps
3. Elongated dimples

The tensile fracture surface of Al-22Zn fractured in dessicant dried air at 20 in/min. and 0.01 in/min. is shown in figures (53a-h). The edge is shown in figures (53a-f). A circular band of rim lines is present on the edge of the notch. Near the centre, the mode of fracture is intergranular with dimples of elongated dimples and slip lines present on the grain facets. This is shown in figures (b-e, g,h). The presence of the rim lines can be explained by the fact, that the crack front is nucleated near the centre and then travels outwards. The crack is confined to the notch and the final fracture is transgranular even though the initial mode of fracture is intergranular.

In notched and aged Al-Mg-Zn, the fracture is intergranular near the centre and transgranular through the edge. The transgranular fracture is perpendicular to the tensile axis. The rim lines are shown
Figure (53). Tensile fracture surface of aged, notched Al-22Zn alloy fractured in dessicant dried air at crosshead speeds of 20 in/min (a-e) and 0.01 in/min (f-h).

(53a). Edge, encircling a band of rim lines.

(53b). Near centre, dimples.

(53c,d). Shear dimples with slip lines.

(53e). Dimples of a smaller size than seen in fig. 1a.

(53f). Edge, intergranular facets and transgranular rim lines.

(53g,h). Near centre, dimples at two different magnifications.
Figure (54). Notched aged Al-2.6Mg-6.3Zn alloy pulled to fracture in air at 0.01 in/min.

(54a). Edge, rim lines on a transgranular fracture surface.

(54b). Near centre, deformation on grain facets.

(54c,d). Magnified view of rim lines extending towards the centre.

(54e,f). Dimples near the centre with slip lines on their surface.
Figure (55). Aged Al-9Mg pulled to fracture in air at 0.01 in/min.

(55a). Intergranular fracture with bright facets.

(55b). Dimples on the facets.
in figures (54a,c,d). They seem to lie parallel to the direction of the crack propagation. Figure (54d) shows the junction of the inter and transgranular fracture surfaces. The intergranular fracture surface with accompanying dimples and slip steps is illustrated by figures (54b,e,f).

The aged Al-9Mg alloy exhibits a bright faceted surface without any evidence of rim lines. The absence of transgranular fracture can probably be attributed to the wide PFZ and large intergranular β precipitates in this alloy. According to Unwin and Smith (106) intergranular fracture is facored by wide PFZ and large grain boundary precipitates in Al-Mg-Zn alloys. Both features assist in the nucleation of voids ahead of an advancing grain boundary crack.

The grain facets showing dimples can be seen in figure (55b). No dimples can be seen under the microprobe as seen in figure (55a).

The fractographs of smooth tensile specimens, showed the same features as the notched specimens but without the presence of the transgranular band of rim lines. In the absence of a notch the crack presumably follows the usual intergranular mode of fracture.
Appendix II

The straight line fits were obtained by linear regression analysis using a suitable program in the Hewlitt Packard 9100A calculator. The program yielded the values of intercept b, slope m and correlation coefficient r. The significance of 'r' was determined by using the curves plotted by Thornhill (110). In these curves the value of r for different number of trials, is plotted against the probability of exceeding r when true value is zero. If the probability that the limited range of experiments might permit a value of r equal or greater than that actually obtained is less than 0.05, it is generally agreed that there is genuine correlation.

The correlation coefficients obtained during Arrhenius plots of initiation and propagation and their significance is indicated in table (19). The error in apparent activation energy ΔQ is also listed. This error was calculated for a 95% confidence limit as follows:

The equation of the straight line fit is

\[ y = mx + b \]

\[ y = \text{initiation or propagation rate} \]
\[ x = \text{reciprocal absolute temperature} \]

Then error in slope m is given by \( m \pm tR \) (111).

where \( tR = \text{confidence limit} \)

\[ R = \sqrt{\frac{\sum (y_i - y)^2 - m \Sigma (y_i - y)(x_i - x)}{\sum (x_i - x)^2 - \frac{n-1}{n-2}}} \]

where \( x \) and \( y \) are the means and \( n \) is the number of trials.

The \( t \) values were taken from a table for appropriate number
Table (19)

THE CORRELATION COEFFICIENT AND ERROR IN APPARENT ACTIVATION ENERGY
FROM THE ARRHENIUS PLOTS

<table>
<thead>
<tr>
<th>Crack Initiation</th>
<th>Alloy</th>
<th>Environment</th>
<th>Number of tests</th>
<th>r</th>
<th>Q ± ΔQ</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al-21.5Zn</td>
<td>99% C₂H₅OH</td>
<td>7</td>
<td>0.95</td>
<td>11</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99% C₂H₅OH</td>
<td>8</td>
<td>0.97</td>
<td>12</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95% C₂H₅OH</td>
<td>8</td>
<td>0.98</td>
<td>11</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95% C₂H₅OH</td>
<td>4</td>
<td>0.90</td>
<td>11</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>Al-2.6Mg-6.3Zn</td>
<td>99% C₂H₅OH</td>
<td>11</td>
<td>0.90</td>
<td>14.7</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaCl/K₂CrO₄</td>
<td>22</td>
<td>0.97</td>
<td>26</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D.D. water</td>
<td>6</td>
<td>0.89</td>
<td>26</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>Al-8.6Mg</td>
<td>99% C₂H₅OH</td>
<td>12</td>
<td>0.87</td>
<td>9.6</td>
<td>2.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crack Propagation</th>
<th>Alloy</th>
<th>Environment</th>
<th>Number of tests</th>
<th>r</th>
<th>Q ± ΔQ</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al-21.5Zn</td>
<td>99% C₂H₅OH</td>
<td>13</td>
<td>0.62</td>
<td>3.8</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95% C₂H₅OH</td>
<td>7</td>
<td>0.23</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Al-2.6Mg-6.3Zn</td>
<td>99% C₂H₅OH</td>
<td>8</td>
<td>0.34</td>
<td>3.4</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaCl/K₂CrO₄</td>
<td>22</td>
<td>0.86</td>
<td>14.2</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D.D. water</td>
<td>5</td>
<td>0.80</td>
<td>25</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>Al-8.6Mg</td>
<td>99% C₂H₅OH</td>
<td>9</td>
<td>0.25</td>
<td>3.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>

of experimental points and a probability value.

The log-log or semi-log plots were transposed to a linear scale before calculating the best fit.

In the hydrogen charging experiments on Al-Zn alloys it can be shown that the differences in time to fracture with and without prior
hydrogen charging are significant.

The appropriate t-function is given by

\[ t = \Delta \frac{N_1N_2(N_1+N_2-2)}{\Sigma x_1^2 + \Sigma x_2^2 + (N_1+N_2)} \]

In the present case

- \( N_1 \) = number of tests with prior hydrogen charging
- \( N_2 \) = number of tests without hydrogen charging
- \( \Delta \) = difference between the means of two sets of experiments.
- \( x_1 \) and \( x_2 \) are differences in mean value and individual values for the two sets of experiments.

Substituting the appropriate values we obtain

\[ t = 5.2 \]

From Thornhill's curves (110) it is seen that a t value of 5.2 for 6 experiments can be regarded as highly significant.

Similarly the difference in failure times between prior hydrogen charged specimens and those held for 8 days after hydrogen charging is also highly significant as it gives a t value of 21.4 for 5 experiments.
Bibliography


34. Schmalzried H., Gerold, V., Z. Metallkunde, 1958, 49, 64.


69. Logan, H.L., Ref. 2, 206.


75. Logan, H.L., Ref. 2, 228.

76. Timanova, M.A., Intergrystaline Corrosion and Corrosion of Metals under Stress, 263.


88. Pourbaix, M., Deltombe, E., Corrosion, 1958, 16, 496.


