CORROSION OF ALUMINIUM ALLOYS IN STATIC AND RECIRCULATING MINE WATERS

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Johannesburg, 1988.

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Signed.

TWENTY NINTHday of SEPTEMBER 1988

ABSTRACT

Little information is available on the corrosion behaviour of aluminium alloys in static and flowing mine water. To gain a basic understanding in this area, a flow loop was designed and constructed. This provided facilities for both electrochemical and total immersion testing, under controlled hydrodynamic conditions. Purpose designed and built controlled temperature baths were used in similar tests in static water.

Aluminium alloys 1200, Alclad 3004, 3004, 5251, 6063TB, 6063TF and 7017 were used in the tests, along with type 316L stainless steel, 3CR12 and mild steel for comparative purposes. Waters from ERPM and Freddies mines were used, with chloride levels of 111 and 1600ppm respectively. Other than 7017, the alloys exhibited some passivity in the two mine waters used. Flow increased corrosion rates in proportion to the square of the velocity and pitting was most severe under flow conditions. In the more aggressive water (1600ppm Cl^-), even type 316L stainless steel showed fairly limited resistance to pitting under flow conditions. Limited tests showed that for alloy 5251 corrosion rates increased with the square of temperature.

Overall, aluminium alloys are susceptible to severe pitting in these mine waters, especially under flow conditions and some form of extra protection would be required for any long term use.

TO MY WIFE

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TABLE OF CONTENTS

1.0 INTRODUCTION 1
1.1 General 1
1.2 Problem Statement 2
1.3 Aim 2
1.4 Justification 2
1.5 Scope 3
1.6 Limitations 4
1.7 Preview of the Report 5

2.0 LITERATURE REVIEW 6
2.1 Introduction 6
2.2 Pitting Corrosion 6
2.3 The Electrochemistry of Corrosion Processes 8
  2.3.1 Polarisation 9
    2.3.1.1 Activation polarisation 9
    2.3.1.2 Concentration polarisation 10
2.4 Passivity 11
2.5 Measurement of Corrosion Rates 13
  2.5.1 Linear polarisation resistance 15
2.6 The Corrosion of Aluminium 16
  2.6.1 The oxide film on aluminium 18
    2.6.1.1 Chemical composition (7) 18
    2.6.1.2 Physical properties 19
    2.6.1.3 The oxide film in water 20
  2.6.2 General corrosion behaviour 20
    2.6.2.1 Environmental effects 21
  2.6.3 Pitting behaviour of aluminium 23
    2.6.3.1 Pit initiation 24
    2.6.3.2 Pit propagation 25
    2.6.3.3 Pitting rates 27
    2.6.3.4 Summary of pitting 27
  2.6.4 Effects of alloying on corrosion behaviour 28
  2.6.5 Effects of heat treatment and processing 30

2.7 Hydrodynamic Effects On Corrosion 31
  2.7.1 Hydrodynamic concepts 32
    2.7.1.1 Fully developed tube flow 36
  2.7.2 Hydrodynamic effects on pitting 36
2.8 Mining Conditions 38
  2.8.1 Water composition 39
  2.8.2 Water temperatures 41
  2.8.3 Flow velocities 41
  2.8.4 Galvanic corrosion 41
  2.8.5 Aluminium in the mining industry 42

3.0 DESIGN AND CONSTRUCTION OF FLOW LOOP AND CONTROLLED TEMPERATURE WATER BATH 44
3.1 Introduction 44
3.2 Definition of Problem 44
  3.2.1 Problem statement 44
  3.2.2 Aim 45
  3.2.3 Requirements 45
3.3 Solution Specification - Flow Loop 46
  3.3.1 Total immersion test section 46
  3.3.2 Electrochemical test section 47
  3.3.3 Piping 49
  3.3.4 Pump 49
  3.3.5 Flow control and metering 49
  3.3.6 Heating 50
  3.3.7 Layout of the flow loop 50
  3.3.8 Tank 51
  3.3.9 Electrical circuits 52
  3.3.10 Construction 52
  3.3.11 Overall dimensions 53
  3.3.12 Performance 54
3.4 Solution Specification - Controlled Temperature Bath 54
  3.4.1 Tank 54
  3.4.2 Heating 54
  3.4.3 Specimens 55
  3.4.4 Specimen mounting 55
  3.4.5 Insulation 55

3.5 Concept Formation 55
  3.5.1 Overall design 55
  3.5.2 Tank 57
  3.5.3 Immersion test section 58
  3.5.4 Electrochemical test section 60
  3.5.5 Piping 62
  3.5.6 Pump selection 62
  3.5.7 Flow control and metering 62
  3.5.8 Heating 64
    3.5.8.1 Flow loop 64
    3.5.8.2 Water bath 64
  3.5.9 Cooling 65
  3.5.10 Supports for piping and test sections 65
  3.5.11 Drip trays 66

4.0 APPARATUS SPECIFICATIONS 67
4.1 Flow Loop 67
4.2 Controlled Temperature Bath - Immersion Testing 70
4.3 Controlled Temperature Bath - Electrochemical Testing 71
4.4 Corrosion Cell 73
4.5 Potentiostat 74
4.6 Computer 75
4.7 Printer 76
4.8 Software 76
4.9 Reference Electrodes 76
4.10 Tensile Test Machine 77
4.11 Chart Recorder 77
4.12 Scanning Electron Microscope 77

5.0 EXPERIMENTAL PROCEDURE 78
5.1 Overall Approach 78
5.2 Test Materials 78
5.3 Electrochemical Corrosion Testing 80
  5.3.1 Specimen preparation 80
  5.3.2 Potentiodynamic scans 81
  5.3.3 Cyclic polarisation scans 82
  5.3.4 Aeration and de-aeration 83

5.3.5 Temperature control 84
5.4 Total Immersion Testing 84
5.4.1 Specimen preparation 84
5.4.2 Specimen exposure 86
5.4.3 Specimen cleaning 86
5.4.4 Specimen examination 87
5.4.5 Corrosion product analysis 88
5.4.6 Tensile testing 88
5.5 Microbial Control 89
5.6 Water Collection 89

6.0 RESULTS AND DISCUSSION 90
6.1 Tests Conducted In ERPM, Hercules Shaft Water 90
6.1.1 Potentiodynamic scans - flow conditions, Hercules water . 91
6.1.2 Cyclic polarisation scans - flowing Hercules water 93
6.1.3 Potentiodynamic scans - static Hercules water 94
6.1.4 Cyclic polarisation scans - static Hercules water 97
6.1.5 Total immersion tests - flow conditions. 99
6.1.5.1 Pit depth results 105
6.1.5.2 Corrosion rate results - flowing water 106
6.1.6 Total immersion tests - static conditions 108
6.1.6.1 Pit depth results 113
6.1.6.2 Corrosion rate results - static conditions. 115
6.1.7 Tensile tests 117
6.2 Tests Conducted in Freddies No. 5 Shaft Water 119
6.2.1 Potentiodynamic corrosion scans - flow conditions 120
6.2.2 Cyclic polarisation scans - flow conditions 124
6.2.3 Potentiodynamic scans in Freddies Water - static conditions. 130
6.2.3.1 Aerated conditions 131
6.2.3.2 De-aerated conditions 132
6.2.4 Cyclic polarisation scans in Freddies Water, static conditions. 134
6.2.4.1 Aerated water 134
6.2.4.2 De-aerated water 136
6.2.5 Total immersion tests - flow conditions. 137
6.2.5.1 Pit depths 145
6.2.5.2 Corrosion rate results 147

6.2.6 Total immersion tests - static conditions. 148
6.2.6.1 Pit depths. 151
6.2.6.2 Corrosion rates 152
6.2.7 Tensile tests 153
6.3 Optical Microscopy 155
6.4 Scanning Electron Microscopy 156
6.4.1 Alclad 156
6.4.2 Alloy 1200 158
6.4.3 Alloy 3004 159
6.4.4 Alloy 5251 159
6.4.5 Alloys 6063TB and 6063TF 162
6.4.6 Alloy 7017 163
6.4.7 General Comments 164
6.5 Corrosion Product Analysis 165
6.6 Electrochemical vs Total Immersion Testing 167
6.6.1 Corrosion rates for flow conditions 168
6.7 Comparison of Flow and Static Conditions 170
6.8 Temperature Effects 173
6.9 Flow Velocity Effects 175
6.9.1 Corrosion rates and velocity 175
6.10 Performance Rating of the Aluminium Alloys 177
6.11 The Effect of Composition and Microstructure 180

7.0 CONCLUSIONS AND RECOMMENDATIONS 183
7.1 Conclusions 183
7.1.1 ERPM Hercules' Shaft water 183
7.1.1.1 Electrochemical tests 183
7.1.1.2 Total immersion testing 184
7.1.1.3 Tensile strength 185
7.1.2 Freddies No. 5 Shaft water 185
7.1.2.1 Electrochemical corrosion testing 185
7.1.2.2 Total immersion tests 186
7.1.2.3 Microscopy 186
7.1.2.4 EDAX analysis 187
7.1.2.5 Electrochemical vs Total Immersion testing 187
7.1.2.6 Flow vs static conditions 187
7.1.2.7 Temperature effects 188

7.1.2.8 Rating of alloys 188
7.1.2.9 Suitability of alloys for use 189
7.2 Recommendations 189

8.0 REFERENCES AND BIBLIOGRAPHY 190
8.1 References 190
8.2 Bibliography 195

LIST OF ILLUSTRATIONS

Figure 1. Generalised process occurring at a pit site. 8
Figure 2. Corrosion rate vs oxidising power or potential 12
Figure 3. Schematic polarisation curve 13
Figure 4. Tafel slope extrapolation. 15
Figure 5. Linear polarisation resistance method. 16
Figure 6. Influence of pH on the solubility of the oxide film on aluminium. 23
Figure 7. Multiple reactions that may occur in an aluminium pit. 26
Figure 8. The effect of alloying on corrosion resistance. 28
Figure 9. The effect of increased mass transport on corrosion. . 33
Figure 10 The effect of flow on pitting current. 37
Figure 11. Total immersion coupon holder for flow loop. 46
Figure 12. Schematic of electrochemical corrosion test section. . 48
Figure 13. Schematic of layout of flow loop. 51
Figure 14. Concept 1 for flow loop layout. 56
Figure 15. Concept 2 for flow loop. 57
Figure 16. Concept 1 for immersion specimens for flow loop 58
Figure 17. Concept 2 for immersion specimens for flow loop 59
Figure 18. Concept 3 for immersion specimens for flow loop 59
Figure 19. Concept 1 electrochemical section 60
Figure 20. Concept 2 electrochemical section 61
Figure 21. Concept 3 electrochemical section 61
Figure 22. General view of flow loop. 68
Figure 23. General view of flow loop. 69
Figure 24. A portion of the electrochemical test section. 70
Figure 25. Control temperature water bath. 71
Figure 26. Controlled temperature bath for electrochemical testing. 72
Figure 27. Corrosion cell as set up for testing. 73
Figure 28. Specimens for flow and static tests mounted in resin. . 74
Figure 29. Potentionstat, computer and printer. 75
Figure 30. Alloy 7017 in flowing ERPM water 92
Figure 31. Alloy 3004 in flowing ERPM water 92
Figure 32. Alloy 6063TB in static ERPM water 96

LIST OF ILLUSTRATIONS

Figure 1. Generalised process occurring at a pit site. 8
Figure 2. Corrosion rate vs oxidising power or potential 12
Figure 3. Schematic polarisation curve 13
Figure 4. Tafel slope extrapolation. 15
Figure 5. Linear polarisation resistance method. 16
Figure 6. Influence of pH on the solubility of the oxide film on aluminium. 23
Figure 7. Multiple reactions that may occur in an aluminium pit. 26
Figure 8. The effect of alloying on corrosion resistance. 28
Figure 9. The effect of increased mass transport on corrosion. . 33
Figure 10. The effect of flow on pitting current. 37
Figure 11. Total immersion coupon holder for flow loop. 46
Figure 12. Schematic of electrochemical corrosion test section. . 48
Figure 13. Schematic of layout of flow loop. 51
Figure 14. Concept 1 for flow loop layout. 56
Figure 15. Concept 2 for flow loop. 57
Figure 16. Concept 1 for immersion specimens for flow loop 58
Figure 17. Concept 2 for immersion specimens for flow loop 59
Figure 18. Concept 3 for immersion specimens for flow loop 59
Figure 19. Concept 1 electrochemical section 60
Figure 20. Concept 2 electrochemical section 61
Figure 21. Concept 3 electrochemical section 61
Figure 22. General view of flow loop. 68
Figure 23. General view of flow loop. 69
Figure 24. A portion of the electrochemical test section. 70
Figure 25. Control temperature water bath. 71
Figure 26. Controlled temperature bath for electrochemical testing. 72
Figure 27. Corrosion cell as set up for testing. 73
Figure 28. Specimens for flow and static tests mounted in resin. . 74
Figure 29. Potentionstat, computer and printer. 75
Figure 30. Alloy 7017 in flowing ERPM water 92
Figure 31. Alloy 3004 in flowing ERPM water 92
Figure 32. Alloy 6063TB in static ERPM water 96

Figure 33. Alloy 316L in static ERPM water 96
Figure 34. Alloy 7017 in static ERPM water 97
Figure 35. Alloy 316L in flowing ERPM water 98
Figure 36. Upper surfaces of immersion specimens-flowing ERPM water 100
Figure 37. Immersion specimens-"Mill Finish"-Flowing ERPM water 101
Figure 38. Immersion specimens-"polished finish"-Flowing ERPM water 102
Figure 39. Non clad surface of Alclad specimen exposed in flowing ERPM water 103
Figure 40. "Tails" of corrosion product on specimens 104
Figure 41. Immersion specimens from flowing ERPM water 105
Figure 42. Front surfaces of specimens immersed in static ERPM water 109
Figure 43. Rear surfaces of specimens immersed in static ERPM water 110
Figure 44. Specimens immersed in static ERPM water 111
Figure 45. "Mill Finish" specimens exposed in static ERPM water 112
Figure 46. "Polished finish" specimens exposed in static ERPM water 113
Figure 47. Comparison of maximum pit depths 115
Figure 48. Loss in U.T.S. due to corrosion. 117
Figure 49. Alloy 1200 in flowing Freddies water 120
Figure 50. Alloy 7017 in flowing Freddies water 121
Figure 51. 3CR12 in flowing Freddies water 122
Figure 52. 316L stainless steel in flowing Freddies water . . . 123
Figure 53. Corrosion rates of alloys in Freddies Mine Water . . 124
Figure 54. Alloy 7017 flowing Freddies water 125
Figure 55. Alloy 6063TB in flowing Freddies water 126
Figure 56. Alloy 5251 in flowing Freddies water 127
Figure 57. 316L stainless steel in flowing Freddies water . . . 128
Figure 58. Passive and perfectly passive ranges for the range of alloys 129
Figure 59. Comparison of corrosion potentials 133
Figure 60. Comparison of corrosion rates 133
Figure 61. 316L stainless steel in static Freddies mine water . 135
Figure 62. Alloy 1200 in static Freddies mine water 136
Figure 63. Upper surface of Alclad specimen after immersion in flowing water 138
Figure 64. Upper surface of 5251 specimen after immersion . . . 139
Figure 65. Upper surface of alloy 6063TB after immersion 140
Figure 66. Upper surfaces of specimens after immersion 141

Figure 67. Lower surfaces of specimens after immersion 142
Figure 68. Cleaned Alclad specimen after immersion 143
Figure 69. Upper surfaces of cleaned specimens after immersion . 144
Figure 70. Cleaned surface of alloy 6063TB after immersion . . . 145
Figure 71. Alloy 1200 after immersion in static Freddies water . 149
Figure 72. Specimens after immersion in static Freddies water . 150
Figure 73. Cleaned static Freddies water immersion specimens. . 151
Figure 74. Decrease in UTS due to corrosion 154
Figure 75. Decrease in UTS due to corrosion 154
Figure 76. Pitted cladding layer on Alclad specimen 157
Figure 77. Cross section of specimen showing breakdown of cladding layer 157
Figure 78. Pitting initiated by a surface scratch in an Alclad specimen 158
Figure 79. Pit in Alloy 1200 with surface breakdown around pit . 159
Figure 80. SEM micrograph of pitting of Alloy 5251 160
Figure 81. Semi-enclosed pit in Alloy 5251 161
Figure 82. SEM micrograph showing interlinked pits in Alloy 5251 161
Figure 83. SEM micrograph of pits in Alloy 6063TB 162
Figure 84. SEM micrograph of Alloy 6063TB 163
Figure 85. SEM micrograph of a section through Alloy 7017 164
Figure 86. Summarised EDAX results for Alloy 5251 166
Figure 87. Comparisons of EDAX results for Alloy 6063TB 166
Figure 88. Ratios of corrosion rates 168
Figure 89. Ratios of corrosion rates 169
Figure 90. Ratios of corrosion rates 170
Figure 91. Ratios of corrosion rates 171
Figure 92. Ratios of maximum pit depths between flow and static conditions. 172
Figure 93. Pits elongated in the direction of flow. 173
Figure 94. Variation of corrosion rate with temperature for Alloy 5251 174
Figure 95. Corrosion rate vs velocity for Alloy 5251 in Freddies water. 176
Figure 96. Corrosion rate vs velocity for Alloy 6063TF in Freddies water. 177

LIST OF TABLES

Table **Page**

2.1 EMF series 17

5.1 Aluminium alloy compositions 79

6.1 Analysis of ERPM Hercules Shaft water 90
6.2 Potentiodynamic scan results - flowing Hercules shaft water 91
6.3 Results of cyclic polarisation scans in flowing Hercules water 94
6.4 Results of potentiodynamic scans in static Hercules water 95
6.5 Results of cyclic polarisation scans in static Hercules water 98
6.6 Pit depths from immersion specimens in flowing Hercules Shaft water 106
6.7 Corrosion rates from total immersion tests in flowing Hercules Shaft water 107
6.8 Pit depths on specimens immersed in static Hercules Shaft water 114
6.9 Corrosion rates from total immersion tests in static Hercules Shaft water 116
6.10 Analysis of Freddies No. 5 Shaft water 119
6.11 Average data from cyclic polarisation scans - Freddies water flow conditions 130
6.12 Corrosion rates and Ecorr values for static conditions in Freddies mine water 131
6.13 Ecorr and corrosion rate values for Freddies mine water under de-aerated conditions 132
6.14 Data from cyclic polarisation scans in static, aerated Freddies water 134
6.15 Data from cyclic polarisation scans in static, de-aerated Freddies mine water 137
6.16 Pit depths in specimens exposed under flow conditions in Freddies mine water 146
6.17 Corrosion rates for immersion coupons in flowing Freddies mine water 147
6.18 Pit depths in specimens exposed in static Freddies mine water 152
6.19 Corrosion rates from immersion specimens in static Freddies mine

water 153
6.20 Performance positions in each test in ERPM water 178
6.21 Performance positions in each test in Freddies water 179
6.22 Performance totals and overall ratings of aluminium alloys .. 180

LIST OF SYMBOLS AND ABBREVIATIONS

η_a - activation polarisation resistance.
β - Tafel constant.
i - rate of reaction as current density.
i_0 - exchange current density.
i_L - limiting diffusion current density.
D - diffusion coefficient.
n - number.
F - Faraday constant.
C_B - concentration of reacting ions in the bulk solution.
x - thickness of the diffusion layer.
η_T - total overvoltage.
η_c - concentration polarisation overvoltage.
T - temperature.
E_{corr} - free corrosion potential.
e - electrochemical equivalent.
ρ - density.
β_a - anodic Tafel slope.
β_c - cathodic Tafel slope.
Re - Reynold number.
V - fluid velocity.
d - characteristic dimension in the direction of flow.
μ - dynamic viscosity.
ν - kinematic viscosity.
Sc - Schmidt number.
δ_d - boundary layer thickness.
δ_h - laminar layer thickness.
K - mass transfer coefficient.
Sh - Sherwood number.
St - Stanton number.
LCD - limiting current density.
ppm - parts per million.
TDS - total dissolved solids.
i_g - galvanic current.
uPVC - unplasticised polyvinylchloride.
TB - solution heat-treated and naturally aged.

TF - solution heat-treated and artificially aged.

E_p - pitting potential.

E_{pp} - passivation potential.

UTS - ultimate tensile strength.

SEM - scanning electron microscope.

EDAX - energy dispersive analysis of X-rays.

C.R. - corrosion rate.

1 - Alclad 3004

2 - Alloy 1200

3 - Alloy 3004

4 - Alloy 5251

5 - Alloy 6063TB

6 - Alloy 6063TF

7 - Alloy 7017

1.0 INTRODUCTION

1.1 GENERAL

Corrosion has been, and still is a major problem in all sectors of industry worldwide. Those industries operating in especially aggressive environments such as mining, chemical and marine are the most adversely effected.

Many studies to evaluate the actual cost of corrosion to the economy as a whole have been made in various countries. Slabbert (1) summarised their findings and found that in most industrial countries the direct and indirect costs of corrosion amounted to 3 to 4% of the GNP. More importantly, estimates from Sweden, the USSR, the German Federal Republic and the USA claimed that between 15 and 35% of these costs can be regarded as avoidable. In 1975 the "avoidable" corrosion costs in the USA were put at $10,5 Billion.

South Africa suffers similarly in the industrial and mining sectors. Research is thus needed to determine the suitability of materials of construction and protective methods under local conditions. The mining industry has severe corrosion problems especially in gold mines because of the corrosivity of the water. Many possible new materials for piping systems are being examined, and the possibility of using aluminium alloys has been considered.

1.2 PROBLEM STATEMENT

Little information is available about the corrosion behaviour of aluminium alloys under static and flow conditions in natural mine waters.

1.3 AIM

This project was initiated to provide data on the corrosion behaviour of a range of aluminium alloys under both static and flow conditions in two typical mine waters. This was to be achieved by the design and construction and subsequent use of a flow loop, complemented by static corrosion testing.

1.4 JUSTIFICATION

Aluminium has an inherent corrosion resistance because of the protective oxide film that forms on its surface. Aluminium alloys have the benefits of a high strength to mass ratio, which allows easier and cheaper handling for aluminium alloy fabrications compared with most other materials. The costs of corrosion have already been examined and for South Africa it was calculated that at 4 - 5% of the GNP, the corrosion costs in 1983 would be between R3 400 million and R4 200 million. Thus it is of great importance to find suitable corrosion resistant materials for local conditions.

1.5 SCOPE

There are many parameters that need to be investigated for a full understanding of the corrosion behaviour of aluminium alloys in mine water, these are:-

- Alloy composition and temper condition
- Water composition
- pH
- Water temperature
- Water velocity
- Microbial effects
- Abrasion / erosion

To fully investigate these variables would be far beyond the scope of this research project, also taking note that a large portion of the project was the design and construction of equipment required for the research.

Microbial and abrasion/erosion effects were not considered. A biocide was used to try to eliminate microbial corrosion and the waters used were left to stand for a week before being placed in the test systems, to allow solids to settle out.

Two mine waters were used in the testing, both being typical of the areas they came from;-

a) the East Rand

b) the Orange Free State

A water temperature of 40°C was used for most of the testing as this gives a good indication of corrosion rates at the extreme temperatures typical in the mining industry and this temperature could be maintained in the flow loop without the addition of cooling equipment. Limited testing was also conducted at temperatures in the range of 5-55°C.

The water velocity for testing under flow conditions was maintained at $1,75ms^{-1}$ and limited testing was performed within the range 1,0 to $3,25ms^{-1}$.

1.6 LIMITATIONS

Total time for testing was limited to six months so immersion testing was limited and thus extrapolation for long term behaviour would have to be made.

Some conflict always exists between academic and industrial research. In this instance the use of "mill finish" specimens for all tests would probably have given a better approximation to mining conditions. However, this approach affords no control of surface finish and hence no reproducibility of surface finish. A compromise was made with limited tests being performed with specimens in the "mill finish" surface condition.

1.7 PREVIEW OF THE REPORT

Chapter 2 gives an overview of available present knowledge on the aqueous corrosion of aluminium alloys, mining conditions in South Africa and hydrodynamic fundamentals used in the design of the flow loop.

The following chapter summarises the design specifications of the equipment produced and the route taken in arriving at the final designs.

Apparatus specifications (Chapter 4) gives a brief summary of the specifications of major equipment used.

The methods and procedures used in the experimental work are detailed in Chapter 5.

Chapter 6 is the most voluminous, and includes the results obtained together with an analysis and discussion of them.

In the final chapter, the important conclusions are laid out with emphasis on recommendations for further work based on the results of this research.

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

Estimates from a number of industrial countries put the cost of corrosion in the region of 4% of the Gross National Product (1). In the United States, the cost of corrosion and corrosion protection was estimated at 8 Billion Dollars in 1983 (3). Hence corrosion control and the selection of the correct materials of construction to prevent corrosion failures is of great importance, both in terms of human safety and overall costs.

Aluminium has only been commercially produced for just over 100 years (2), but has become one of the most important materials available to industry. It is used in almost all spheres of life, from household goods and architectural finishes to the most demanding area of aerospace applications. Besides its properties of low density and relatively high strength in alloyed form, one of its most important properties is that of atmospheric corrosion resistance, especially in the anodised condition. Aluminium forms an insoluble oxide layer on its surface which protects the underlying metal from corrosion.

2.2 PITTING CORROSION

Pitting has been described as "one of the most destructive and insidious forms of corrosion" (3), mainly because it can lead to failure of equipment through perforation even though only limited mass loss has occurred. Pitting is a highly localised attack that usually results in the formation of small holes, with the surface diameter often being equal to or less than the depth. The mechanism is very similar to that of crevice corrosion, but requires something to initiate the localised attack. This initiation may be due to surface damage or discontinuities such as an emerging dislocation, an inclusion or a precipitate. This would give rise to a higher rate of metal dissolution, causing a net positive charge and hence chloride ions would migrate to this point. The process is summarised in Figure 1. Flow of corrosive medium may effect pit growth as higher velocities tend to remove any local concentrations of ions and hence may prevent or decrease pitting. Gravity has an effect on pitting and pits tend to grow fastest in the direction of gravity. Alloys that depend on a passive surface film for corrosion resistance such as stainless steels and aluminium alloys are the most susceptible to pitting.

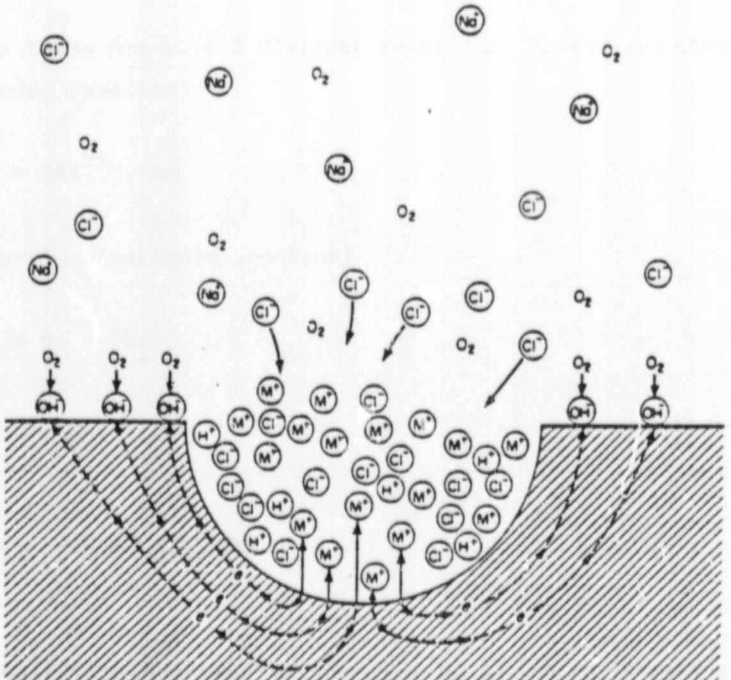

Figure 1. Generalised process occurring at a pit site.

Since the reduction of oxygen is taking place around the pit as the cathodic reaction, the surrounding area is protected, and so even with a large pit, it is often surrounded by an uncorroded area.

2.3 THE ELECTROCHEMISTRY OF CORROSION PROCESSES

All corrosion processes are electrochemical in nature and this may be illustrated by the corrosion of aluminium by hydrochloric acid:

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2 \qquad (2.1)$$

This takes place as 2 distinct reactions, anodic and cathodic. Oxidation (anodic reaction)

$$2Al \rightarrow 2Al^{3+} + 6e \qquad (2.2)$$

Reduction (cathodic reaction)

$$6H^{+} + 6e \rightarrow 3H_2 \qquad (2.3)$$

2.3.1 POLARISATION

Polarisation has been defined (3) as the displacement of electrode potential resulting from a net current. Electrochemical corrosion reaction rates are controlled by concentration and resistance polarisation. The magnitude of polarisation is referred to as overvoltage (η). This is the difference between the equilibrium potential i.e. at zero net current and the potential when a net current is flowing.

2.3.1.1 Activation polarisation

The overall rate of a sequence of chemical reactions is determined by the slowest step in that sequence. In a corrosion reaction there may be a number of steps involved at the metal - corrodent interface. If the overall reaction rate depends on a particular reaction, this is referred to as activation polarisation. The relationship between reaction rate and overvoltage in this case is given by:

$$\eta_a = \pm \beta \log \frac{i}{i_o} \qquad (2.4)$$

2.3.1.2 Concentration polarisation

This type of polarisation is due usually to the electrochemical reaction being controlled by the rate of diffusion of some ionic specie to or from the reacting surface. Changes in the environment, such as an increase in the velocity of the corrodent or its concentration will then affect the reaction, since there will be a change in the quantity of aggressive ions at the corroding surface and in the rate at which they reach the surface. The limiting rate can then be expressed as the limiting diffusion current density i_L. This represents the maximum rate of reduction possible for a given system. This rate is then expressed as :-

$$i_L = \frac{DnFC_B}{x} \qquad (2.5)$$

The diffusion layer thickness is decreased by agitation i.e. flow velocity of the corrodent over the metal surface and/or a build up of the cations produced in the corrosion reactions.

Both activation and concentration polarisation usually occur at an electrode surface, with activation polarisation dominating at low reaction rates and concentration polarisation predominant at higher reaction rates (3). The total polarisation of an electrode is thus the sum of the contributions made by both of the polarisation types.

i.e. $\eta_T = \eta_a + \eta_c$ (2.6)

This equation may then be applied to a process such as a reduction process. During anodic dissolution, where concentration polarisation is **NOT** a factor the kinetics of anodic dissolution are given by (3):

$$\eta_{diss} = \beta \log \frac{i}{i_o} \qquad (2.7)$$

Then as a reduction reaction reaches its limiting rate, concentration polarisation becomes the important factor. The equation for concentration polarisation is (from the Nernst Equation):

$$\eta_c = 2,3 \frac{RT}{nF} \log \left(1 - \frac{i}{i_L}\right) \qquad (2.8)$$

Then combining the two for the complete reduction process.

$$\eta_{red} = \beta \log \frac{i}{i_o} + 2,3 \frac{RT}{nF} \log \left(1 - \frac{i}{i_L}\right) \qquad (2.9)$$

This equation describes any reduction reaction and applies to almost all anodic dissolution reactions, except where a metal exhibits active-passive behaviour.

2.4 PASSIVITY

Passivity refers to the loss of chemical reactivity of certain metals and alloys under particular environmental conditions. Figures 2 and 3 show corrosion rate versus oxidising power of the solution for an active metal and an active-passive metal respectively. For the active metal, the corrosion rate increases with an increase in the oxidising power of the solution. On the other hand, the active-passive metal exhibits a totally different behaviour. The corrosion rate increases at first and then suddenly decreases and remains constant (the passive region) up to the same point, where it starts increasing again (the transpassive region). The potential at the active-passive transition is referred to as the primary passivation potential (Epp). The current corresponding to the passive range is i_{pass} - the passive current density. The potential at which the corrosion current starts increasing is known as E_t - the threshold potential or more commonly E_p - pitting potential. In this transpassive region pitting takes place.

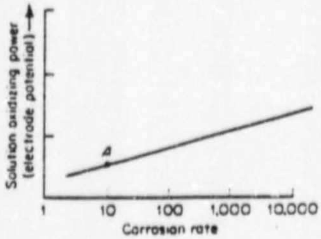

Figure 2. Corrosion rate vs oxidising power or potential: Active metal.

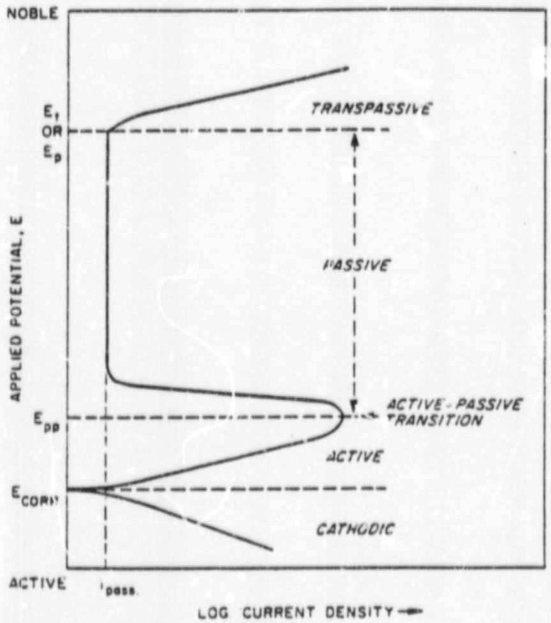
NOBLE
E_t
OR
E_p
TRANSPASSIVE
PASSIVE
APPLIED POTENTIAL, E
E_pp
ACTIVE-PASSIVE TRANSITION
ACTIVE
E_CORR
CATHODIC
ACTIVE
i_pass.
LOG CURRENT DENSITY

Figure 3. Schematic polarisation curve: Current density or corrosion rate vs potential.

2.5 MEASUREMENT OF CORROSION RATES

Since the corrosion rate of a metal or alloy is directly related to the number of electrons and hence the current, leaving its surface, electrochemical techniques involving current measurements can be used to calculate corrosion rates.

Mixed potential theory forms the basis of two electrochemical methods used in determining corrosion rates, Tafel Extrapolation and Linear Polarisation.

The corrosion current cannot be measured directly since it flows between the undifferentiated anodic and cathodic sites on the surface of a corroding metal. However it is possible to measure it indirectly. The technique involves using a potentiostat which applies a current to a specimen in such a way to enable the potential (measured against a reference electrode) to be controlled.

The basic method is as follows. The specimen is polarised from the cathodic into the anodic region through the rest potential and a plot of applied potential versus the log of current density is obtained. There are regions of linearity on this plot, on both the anodic and cathodic curves, known as the Tafel regions. By extrapolating the Tafel slopes back to where they intersect the value of E_{corr}, i_{corr} may be obtained (see Figure 4), which may then be converted into a corrosion rate using the relationship:-

$$R = 0,13\ i_{corr} \frac{e}{\rho} \qquad (2.10)$$

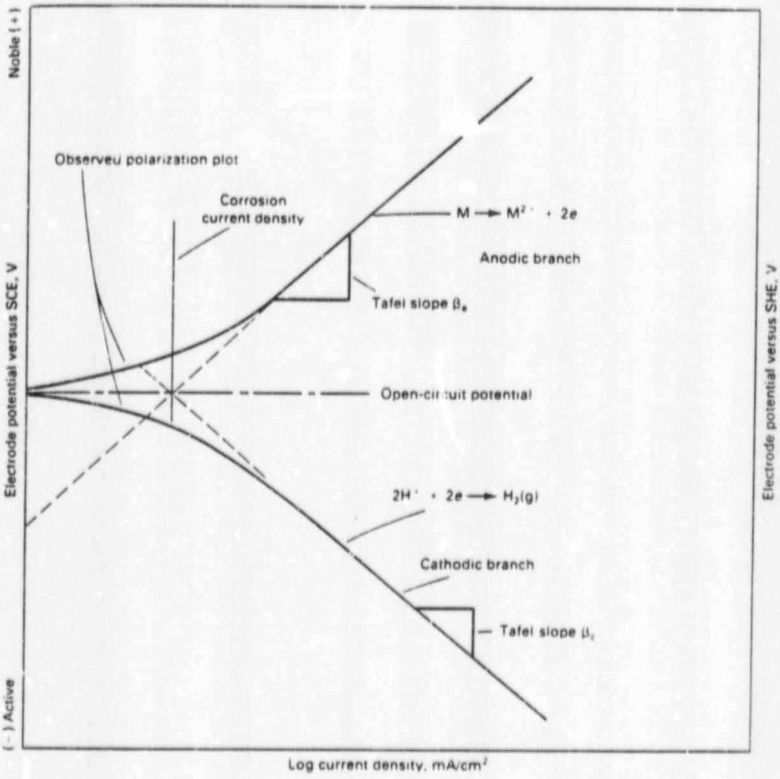
Noble (+)
Observed polarization plot
Corrosion current density
$M \rightarrow M^{2+} + 2e$
Anodic branch
Tafel slope β_a
Electrode potential versus SCE, V
Electrode potential versus SHE, V
Open-circuit potential
$2H^+ + 2e \rightarrow H_2(g)$
Cathodic branch
Tafel slope β_c
(−) Active
Log current density, mA/cm^2

Figure 4. Tafel slope extrapolation.

2.5.1 LINEAR POLARISATION RESISTANCE

At potentials very close to E_{corr} (i.e. ±10mV) the slope of the potential/current slope is approximately linear. This region is shown in Figure 5. The slope has units of resistance $\Delta E/\Delta i$ and it has been found that i_{corr} is inversely related to this slope by the equation:

$$i_{corr} = \left[\frac{\beta_a \beta_c}{2,3\,(\beta_a + \beta_c)}\right] \frac{\Delta i}{\Delta E} \qquad (2.11)$$

Where β_a and β_c are the anodic and cathodic Tafel slopes respectively.

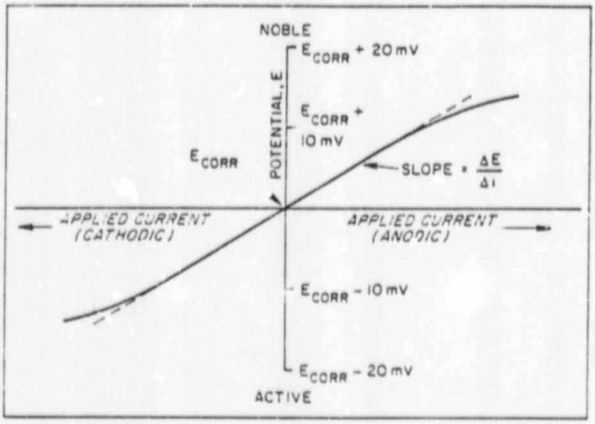

Figure 5. Linear polarisation resistance method.

2.6 THE CORROSION OF ALUMINIUM

Aluminium is low in the E.M.F. series (Table 2.1) and thus is an active metal. However, exposure to oxygen results in the formation of a compact, adherent, protective film of aluminium oxide, that resists further oxidation (8). This oxide film being relatively inert gives aluminium its corrosion resistance and reforms quickly on being dissolved or mechanically damaged. If the film is however removed, the underlying metal undergoes uniform corrosion (8).

In air the film developed is usually 50-100A° thick (6).

Table 2.1 EMF series for metals.

Metal-metal ion equilibrium (unit) activity		Electrode potential vs normal hydrogen electrode at 25°C (V)
	$Au-Au^{+3}$	+1,498
	$Pt-Pt^{+2}$	+1,2
Noble or	$Pd-Pd^{+2}$	+0,987
cathodic	$Ag-Ag^{+}$	+0,799
	$Hg-Hg^{+2}$	+0,788
	$Cu-Cu^{+2}$	+0,337
	H_2-H^{+}	0,000
	$Pb-Pb^{+2}$	-0,126
	$Sn-Sn^{+2}$	-0,136
	$Ni-Ni^{+2}$	-0,250
	$Co-Co^{+2}$	-0,277
	$Cd-Cd^{+2}$	-0,403
	$Fe-Fe^{+2}$	-0,440
	$Cr-Cr^{+3}$	-0,744
	$Zn-Zn^{+2}$	-0,763
Active or	$Al-Al^{+3}$	-1,662
anodic	$Mg-Mg^{+2}$	-2,363
	$Na-Na^{+}$	-2,714
	$K-K^{+}$	-2,925

2.6.1 THE OXIDE FILM ON ALUMINIUM

2.6.1.1 Chemical composition (8)

The naturally formed oxide film on aluminium comprises mainly amorphous alumina (Al_2O_3). It probably exists in various degrees of hydration depending on humidity and temperature during its formation. Aluminium alloy oxide films will also contain the alloying elements.

In humid or water immersed conditions this oxide film thickens, the growth rate increasing with temperature. Aluminium corrosion products tend also to be mainly Al_2O_3 but are produced at a distance from the metal-environment interface and are non-protective.

There are six common crystalline forms of aluminium oxide and the type depends on temperature and degree of hydration. The naturally occurring forms are:-

a) Gibbisite (α-$Al_2O_33H_2O$), which is the main constituent of many bauxite ores; however it has not been identified in any oxide films (8).

b) Bayerite (β-$Al_2O_33H_2O$) which is the usual corrosion product film that forms on aluminium in water at temperatures below 85°C. It is also the major component of nodules of corrosion product that form on aluminium undergoing pitting.

c) Boehmite (α-$Al_2O_3H_2O$ or AlO.OH) which is found in many bauxites and also in oxide films formed on aluminium in water at temperatures above 85°C. Troutner (10) reports that films produced on aluminium in water at 300°C consisted of amorphous alumina and Boehmite. This temperature of 85°C for the corrosion products is independent of pH and alloying elements (9). The boehmite film is protective below 200°C and above that temperature the boehmite crystals begin to grow rapidly and the film ceases to be protective and rapid oxidation takes place. Dillon (14) has shown that the oxides formed in flowing water are more porous, the reason being that the soluble constituents are leached out of the oxide film, which is thus less protective.

d) Diaspore (β-$Al_2O_3H_2O$) has been found in some bauxites, but not in surface films.

e) Gamma alumina (γ-Al_2O_3) may be performed at temperatures above 400°C by dehydrating boehmite.

f) Corundum (α-Al_2O_3) occurs in nature.

2.6.1.2 Physical properties

Hunter and Fowle (13) have shown that the oxide film is a duplex corrosion product. This consists of a thin, protective non-porous barrier film adjacent to the aluminium surface and a more permeable outer bulk film. The thickness of the barrier layer was found out by Troutner (10) to be dependent only on temperature, and that the barrier film formed in water was the same thickness as that formed in air. The only difference between the films formed in water and air is that the bulk film grows much thicker in water than it does in air.

In dry air, the barrier film controls the rate of oxidation, however in water the rate of film growth appears to be controlled by the thickness of the bulk film (8). Different corrosion rates in aqueous media seem to be caused by differing solubilities of the bulk film.

2.6.1.3 The oxide film in water

On immersion in water the oxide film thickens rapidly, at a rate dependent on temperature and time. The rate decreases with time until a limiting thickness is reached, depending on pH, oxygen content, ions present and temperature. Contaminants in water may reduce the thickness of the film e.g. even 1ppm silica reduces the film thickness by as much as 50%, and renders it more soluble in acid (8). Godard also suggests that thickened films developed in pure water give better corrosion resistance in other solutions than films formed in these other solutions.

Dillon (14) has put forward a corrosion mechanism in low temperature water (ambient) which requires diffusion of metal ions through the n-type (excess metal ions) oxide film. At higher temperatures, the rate determining process becomes the extent of the bulk film, even though per unit thickness it is much more permeable that the barrier film.

2.6.2 GENERAL CORROSION BEHAVIOUR

The corrosion behaviour of aluminium alloys is of greater practical interest than that of pure aluminium. These alloys are used in numerous applications in atmospheric, fresh water, sea water, chemical and underground environments. Aluminium alloys are being used on an increasing scale in the chemical industry especially for neutral or oxidising substances. Fabrications, from pipelines, to yachts, to space craft, have aluminium alloy components. The environment in which the alloy is used determines its behaviour, so that a knowledge of environmental effects is important before any preliminary alloy selection for an application may be made.

2.6.2.1 Environmental effects

Water

Other than during high temperature oxidation or gas-metal reactions, water together with oxygen must be present before the corrosion of aluminium will take place. In water aluminium corrodes mainly in three distinct ways: by pitting attack, uniform corrosion and intergranular attack. Pitting generally occurs below 85°C, a temperature range in which uniform attack usually occurs in conjunction with it, but is usually of minor importance. Between 85 and 250°C, uniform corrosion often becomes the principal form of attack, and above 250°C intergranular corrosion predominates.

The pH of the water is of great importance and aluminium is often regarded as being passive within a pH range of 4 to 8,5 (15). General corrosion will occur outside this range in both acidic and basic solutions. The attack is often more severe in stagnant (deoxygenated) solutions at elevated temperatures. Pitting can, and does occur at a neutral pH, especially in the presence of certain ions, such as Cl^- and Cu^{2+}.

Temperature

As previously mentioned there is usually an increase in the corrosion rate with temperature and the form of the corrosion may also vary with temperature. Mears and Brown (31) studied the influence of temperature on pitting probability in chloride solutions. They concluded that as the temperature rose, the density and probability of pitting increased, but the pitting penetration rate decreased (between 5 and 50°C). Godard et al (8) studied pitting in a type 1100 aluminium alloy in a mild water up to a temperature of 70°C. They found that the pitting rate/temperature curve had a maximum at about 40°C. The rate of pitting was up to 5 times as great as that at 25°C. Above 40°C the pitting rate dropped and the pitting probability increased.

A temperature increase can affect pitting in two ways: a) by reducing the solubility of oxygen in the solution and, b) by stimulating the initiation of pitting.

Water velocity

An increase in velocity of a corrosive gas or liquid in contact with aluminium usually increases the corrosion rate. However, the higher water velocities (in excess of 0,04ms^{-1}) can decrease or even eliminate pitting in some waters. Perkins et al (17) produced results indicating that the erosive (mechanical) component is insignificant relative to the electrochemical (mass transport) effect of velocity up to 3ms^{-1}. Above 7ms^{-1} cavitation and erosion begin to play a major role in removal of metal. These velocity values are highly dependent on the corrosive constituents in the water, so that no critical velocities can be defined.

The increase in velocity of the water also has the effect of improving the mass transfer between the liquid and the metal. It may be beneficial in that it brings fresh oxygen to rapidly repair any damaged areas of the protective film, i.e. increasing the supply of oxygen to the anode, enabling passivation of local cells, or it may be detrimental in transporting away material from the bulk layer of the oxide film hence thinning it, i.e. reducing concentration polarisation. Movement probably also prevents the accumulation of acid at the anodic areas and alkali at the cathodic areas. The presence of solids in the water may increase material loss through erosion and erosion-corrosion. Mansfeld and Kenkel (18) found that corrosion rates tend to increase with the square root of velocity, whilst the pitting potential becomes more noble. Two general rules on the effect of velocity (3) state that:

a)Solution velocity influences the corrosion rate of a diffusion-controlled system, but has no effect on activation-controlled systems.

b)The corrosion rate of a metal in a diffusion controlled system becomes independent of solution velocity at very high velocities.

Rajagopalan et al (11) found a 5,5 times increase in the general corrosion rate of alloy 6061 at 40°C on increasing the flow velocity from 0,3ms^{-1} to 1,5ms^{-1}.

2.6.3 PITTING BEHAVIOUR OF ALUMINIUM

The major problem with pitting corrosion damage is that even though negligible thinning of metal due to uniform corrosion may have occurred, perforation of a vessel may have taken place. It is thus of importance to ascertain whether pitting will occur under a certain set of conditions and establish the rate of penetration.

Pitting of aluminium alloys occurs in the pH range of 4,5 to 9,0. Outside this range, corrosion is usually uniform attack, since the protective surface oxide film starts to dissolve as shown in Figure 6.

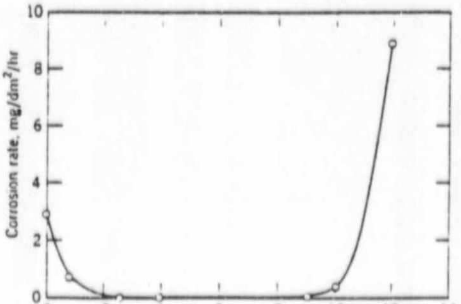

Figure 6. Influence of pH on the solubility of the oxide film on aluminium.

The shape of pits vary greatly, although the mouth of a pit tends to be roughly circular and the cross section to be roughly hemispherical. These are pits that are well developed. "New" pits, tend to be in the form of tiny tunnels of square cross section. Intergranular corrosion is sometimes associated with pitting, especially if associated with microbial corrosion. In this case intergranular damage proceeds from the pit cavity.

Pitting takes place in two stages; initiation and growth.

2.6.3.1 Pit initiation

As was mentioned in the general discussion on pitting, the origin of pits is controlled by the existence of weak points in the surface oxide layer. At these positions corrosion proceeds at a higher rate than on the remainder of the passive surface. The high corrosion current at these sites leads to a local increase in the surface salt concentration as a result of transport processes (migration and diffusion) and anion adsorption (14). This high surface concentration of anions displaces water molecules from the passive layer and suppresses the passivation reaction,

$$xM_2 + yH_2O \rightarrow M_xO_y + 2yH^+ \; +2ye \qquad (2.12)$$

and promotes oxide film dissolution. Thus the film thickness decreases and the current density increases. Under the action of this high electric field, aggressive anions will penetrate the oxide film. Then as the density of the lattice defects increases along with the high electric field, the ionic conductivity of the oxide layer increases. Finally the oxide layer loses its passivating properties and is transformed to a non-passivating oxide capable of sustaining high corrosion current densities.

The adsorption step

The adsorption of the anions that would promote pitting corrosion in a competitive step, viz. the chloride or other aggressive ions compete with hydroxyl or water ions, which if adsorbed, tend to promote passivation. Viden reported by Foley (20), stated that no pickup of the radioactive chlorine-36 isotope was detected on an aluminium surface before breakdown of the passive film had taken place. Similar work by Berzins et al (21) placed adsorbed $^{36}Cl^-$ primarily at corroding pit sites. Various studies reported by Foley (20) are in agreement that the chloride was found in the outer 15-20°A of the barrier film.

2.6.3.2 Pit propagation

This basically involves metal dissolution once the oxide film is sufficiently thin and permeable. Because of the high activity of aluminium and the small area involved in each pit attack is usually rapid. The growth of the pit proceeds with the direct interaction between aluminium and the environment, which varies as the reaction proceeds.

Some of the numerous reactions taking place in an aluminium pit are shown in Figure 7. Included in this set of reactions is the effect of the presence of Cu^{2+} ions in the electrolyte. At the metal/electrolyte boundary oxidation of the aluminium takes place.

$$Al \rightarrow Al^{3+} + 3e^- \qquad (2.13)$$

The aluminium ions may then be involved in numerous possible reactions. The compounds formed are generally hydrated salts and aluminium hydroxide. The composition of the solution within the pit differs substantially from that of the bulk solution. Saturated metal salt solutions may form, salt films may precipitate, the solution become more acid by hydrolysis of the metal salt, the potential become more active than outside, and hydrogen gas may be generated (20).

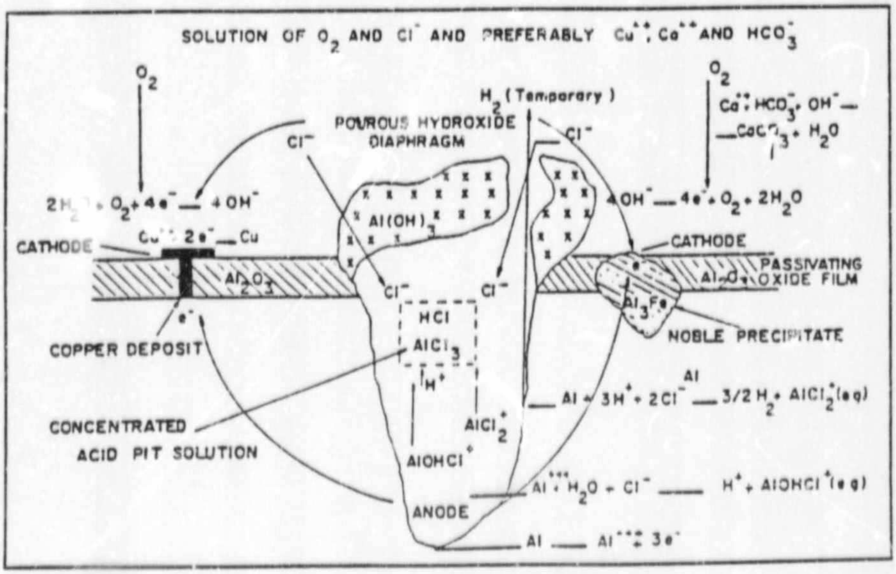
SOLUTION OF O2 AND Cl⁻ AND PREFERABLY Cu⁺⁺, Ca⁺⁺ AND HCO3⁻
O2
2H2O + O2 + 4e⁻ — 4OH⁻
Cu⁺⁺ + 2e⁻ — Cu
CATHODE
Al2O3
e⁻
COPPER DEPOSIT
CONCENTRATED ACID PIT SOLUTION
Cl⁻
POUROUS HYDROXIDE DIAPHRAGM
Al(OH)3
Cl⁻
HCl
AlCl3
H⁺
AlCl2⁺
AlOHCl⁺
ANODE
H2 (Temporary)
Cl⁻
Cl⁻
O2
Ca⁺⁺ + HCO3⁻ + OH⁻ — CaCO3 + H2O
4OH⁻ — 4e⁻ + O2 + 2H2O
CATHODE
e⁻
PASSIVATING OXIDE FILM
Al2O3
Al3Fe
NOBLE PRECIPITATE
Al + 3H⁺ + 2Cl⁻ — 3/2 H2 + AlCl2⁺(aq)
Al⁺⁺⁺ + H2O + Cl⁻ — H⁺ + AlOHCl⁺(aq)
Al — Al⁺⁺⁺ + 3e⁻

Figure 7. Multiple reactions that may occur in an aluminium pit.

Rosenfeld and Marshakov (23) measured corrosion currents and pH in artificially produced crevices in aluminium in NaCl solutions and found that the pH immediately became acid in the range 3,2 to 3,4. Similar results were obtained by Brown (24) who found a pH of 3,5 at the crack tip in aluminium in an NaCl solution. This results from the hydrolysis of the Al^{3+} ions to give $Al(OH)^{2+}$

i.e. $2AlCl_3 + 3H_2O \rightarrow Al_2O_3 + 3HCl$ (2.14)

Sotouhdeh et al (25) in studying the hydrolysis of $Al(OH)^{2+}$ showed that at a value of $1,4x10^{-5}$, the resultant pH would be 3,5. What was of great interest was their conclusion that the "autocatalytic" nature of aluminium pit propagation was due to the action of the highly basic $AlCl_3$ and not to any action from pH or Cl^- effects. Further work by the same authors supported this when they found, that in other solutions similar pH effects could be obtained, but aluminium sulphate solutions for example, were actually non-corrosive. Davis reported by Foley (20), found that pH at a crack tip changed only slightly when the pH of the bulk solution was varied in the pH range of 2 to 10. He also found that the pH at the crack tip was most acidic and increased towards the bulk solution.

2.6.3.3 Pitting rates

Pathak and Godard reported in the Corrosion Handbook (6) that the maximum pit depth of aluminium alloys exposed to various waters was found to vary as the cube route of time.

$$\text{i.e. } D = Kt^{1/3} \qquad (2.15)$$

Where K is a constant that is dependant on the composition of the water and the alloy.

2.6.3.4 Summary of pitting

The localised corrosion process thus appears to take place in four steps:-

a) Adsorption of the reactive anion on the oxide-covered aluminium surface.

b) Reaction of the adsorped anion with the aluminium ion in the aluminium oxide lattice or the precipitated aluminium hydroxide.

c) Thinning of the oxide film by dissolution.

d) Direct attack of the exposed metal by the anion, under the influence of the influence of the anodic conditions set up.

2.6.4 EFFECTS OF ALLOYING ON CORROSION BEHAVIOUR

Generally speaking, pure aluminium has the highest corrosion resistance and this decreases with alloying as can be seen in Figure 8.

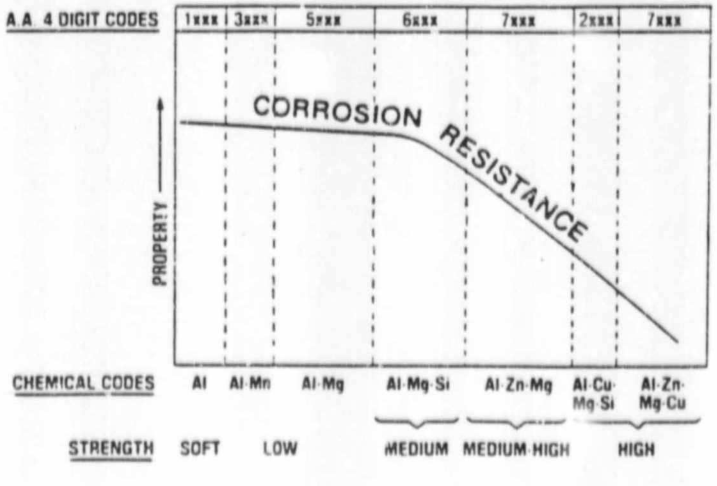

Figure 8. The effect of alloying on corrosion resistance.

It is not only the type and quantity of the alloying element that influences corrosion behaviour, but also the composition, location, quantity and continuity of mic[illegible]nstituents. These will be modified by processing methods and any h[illegible]ent applied to the alloy. The electrochemical potential of s[illegible]or precipitates relative to aluminium is of great impor[illegible]ilicon in commercially pure aluminium form constituents th[illegible] to aluminium (6). Since they form cathodic points over which the fi[illegible]eak, they may promote electrolytic action in the surrounding aluminium.

The aluminium-copper alloys have poor corrosion resistance and the amount of copper in the alloy has a strong influence on its electrode potential. The quantity of the alloying copper in solid solution is important, as this effects the electrode potential, rather than the total quantity of copper. In fact the amount of copper in solid solution can be determined by electrode potential measurements. Aluminium and manganese form intermetallic compounds having almost the same electrode potential as the aluminium itself, and hence these alloys have good corrosion resistance.

Chromium has little effect when in solid solution on the electrode potential of aluminium. Its main function is to increase resistance to stress corrosion cracking.

Likewise, silicon in solid solution has a minor influence on the electrode potential of aluminium and Al-Si alloys have good corrosion resistance. Silicon particles within the alloy promote severe galvanic corrosion.

The "3" series wrought aluminium alloys have a high resistance to corrosion. Manganese is present in solid solution, as submicroscopic precipitates and in larger particles of $Al_6(Mn,Fe)$ or $Al_{12}(Mn,Fe)_3Si$ phases, both of which have solution potentials close to that of the solid solution matrix (6).

Magnesium is an important alloying element for aluminium and the solid solution formed is anodic to aluminium. Excess magnesium forms a constituent that is anodic to the aluminium-magnesium solid solution. Under some conditions precipitation of this Al_8Mg_5 phase as semi-continuous zones at grain boundaries or along slip planes caused by plastic deformation may occur. In a corrosive environment this can result in highly selective attack on the anodic precipitate, and may cause exfoliation and SCC. Generally this is not problem since magnesium has a high solubility in aluminium and precipitation can be controlled to give a finely dispersed precipitate. Al-Mg alloys are as corrosion resistant as commercially pure aluminium, and even more resistant in salt water and some alkaline solutions.

The "6 series" alloys (Al-Mg-Si) often have a very similar electrode potential to pure aluminium as the silicon makes the solid solution more cathodic and in the ratio 2Mg:1S this balances out the anodic effect of the magnesium.

In the "7 series" alloys (Al-Zn+others), the zinc substantially decreases the electrode potential of aluminium. These Al-Zn alloys are frequently used in Alclad coatings and as sacrificial anodes in cathodic protection. These alloys are the most susceptible to SCC.

Nickel and aluminium form a strongly cathodic constituent that has a detrimental effect on corrosion resistance.

Titanium forms $TiAl_3$ which although cathodic, has little effect on corrosion resistance due to the small quantities added to aluminium alloys.

Tin, bismuth and lead do not form intermetallic compounds but are cathodic in aluminium alloys.

2.6.5 EFFECTS OF HEAT TREATMENT AND PROCESSING

Thermal treatment and cold working determine the quantity and distribution of constituents of aluminium alloys and the magnitude of residual stresses. Thus they may have a significant effect on corrosion properties. Welding may result in the formation of inhomogeneities in a component which are anodic, providing selective corrosion. As was discussed in the previous section, if poorly dispersed or even continuous precipitates are allowed to form, these may lead to severe localised attack.

Although variations in grain size and orientation have little effect on resistance to corrosion, they do play a major effect on SCC in thick sections. In some processing methods, such as die forging and extruding, components may be produced that have large recrystallised grains on the surface. These grains are usually slightly cathodic - 5 to 20mV, (6) to the underlying unrecrystallised grains. This can cause a preferential attack of the more anodic layer at machined surfaces or edges, resulting in exfoliation, with a loss of all the material above the interface between the two layers.

Cold working operations, such as shearing may render the metal more prone to corrosion. Edges of sheet or plate are often not only cold worked, but are also rough, resulting in a high surface area to volume ratio.

Edge attack is likely on coupon specimens. This edge attack also tends to prote ct the other surfaces. Some work has shown that where edges of coupons are not masked, there is a lower pitting rate on the other surfaces as the higher rate of corrosion on the edges tends to protect the other surfaces.

2.7 HYDRODYNAMIC EFFECTS ON CORROSION

Fluid flow can influence both the rate and type of corrosion. In order to understand the effects of flow, the system in which corrosion measurements are being made must be characterised in terms of flow conditions. Electrochemical measurements may be made in flowing conditions to give data on (26):

Author Buchan Andrew John
Name of thesis Corrosion Of Aluminium Alloys In Static And Recirculating Mine Waters. 1988

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