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A STUDY OF CORROSION FATIGUE CRACK PROPAGATION OF 403 STAINLESS STEEL IN AQUEOUS ENVIRONMENTS

The Ohio State University

PH.D.

1979

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A STUDY OF CORROSION FATIGUE CRACK
PROPAGATION OF 403 STAINLESS STEEL
IN AQUEOUS ENVIRONMENTS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Lillian Abrego, B.A., M.S.

*****

The Ohio State University
1979

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DEDICATION

To my Mom and Dad
ACKNOWLEDGEMENTS

I would like to express my deep appreciation to my advisor, Dr. James A. Begley for his guidance and aid during the course of this research work. I would also like to acknowledge the encouragement of Dr. Roger W. Staehle in the pursuit of my studies.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>VITA</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF PLATES</td>
<td>xvi</td>
</tr>
<tr>
<td>1.0 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2.0 LITERATURE SURVEY</td>
<td>3</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>3</td>
</tr>
<tr>
<td>2.2 Metallurgical Aspects of 12% Chromium Steels</td>
<td>4</td>
</tr>
<tr>
<td>2.3 Fracture Mechanics Aspects of Fatigue</td>
<td>9</td>
</tr>
<tr>
<td>2.3.1 Fracture Mechanics Methods</td>
<td>10</td>
</tr>
<tr>
<td>2.3.2 Fatigue Crack Growth</td>
<td>13</td>
</tr>
<tr>
<td>2.4 Environmental Aspects of Fatigue</td>
<td>25</td>
</tr>
<tr>
<td>2.4.1 Introduction</td>
<td>25</td>
</tr>
<tr>
<td>2.4.2 Stress Corrosion Cracking-Hydrogen Embrittlement of Martensitic Stainless Steels</td>
<td>26</td>
</tr>
<tr>
<td>2.4.3 General Corrosion and Pitting Behavior</td>
<td>29</td>
</tr>
<tr>
<td>2.4.4 Corrosion Fatigue</td>
<td>31</td>
</tr>
</tbody>
</table>
2.4.5 Corrosion Fatigue Crack Growth Mechanisms.......................... 46

2.5 Summary

3.0 EXPERIMENTAL PROCEDURE........................................... 50
3.1 Introduction............................................................... 50
3.2 Experimental Apparatus.................................................. 51
3.2.1 Material................................................................. 51
3.2.2 Specimen Geometry .................................................... 51
3.2.3 Closed Loop Servo-Hydraulic Fatigue Machine ...................... 55
3.2.4 Electrochemical Equipiment ........................................ 62
3.2.5 Electrolytes............................................................. 62
3.3 Experimental Techniques................................................. 65
3.3.1 Specimen Preparation.................................................. 65
3.3.2 Precracking Procedure............................................... 65
3.3.3 Measurement Techniques.............................................. 66
3.3.4 Fatigue Crack Growth Test Procedure............................... 71
3.3.5 Fatigue Crack Growth Data Reduction................................ 75
3.3.6 Fatigue Crack Threshold Determinations........................... 77
3.4 Fractography ..................................................................... 78

4.0 EXPERIMENTAL RESULTS ................................................. 80
4.1 Introduction................................................................. 80
4.2 Air ................................................................................. 80
4.2.1 Fatigue Crack Growth Rates in Air................................. 80
4.2.2 Fractographic Results.................................................... 84
4.3 Water ........................................... 92
  4.3.1 Fatigue Crack Growth Rates in Water ............... 92
  4.3.2 Fractographic Results ................................ 97
4.4 Sodium Chloride ...................................... 111
  4.4.1 Fatigue Crack Growth Rates in Sodium Chloride ....................... 111
  4.4.2 Fractographic Results ................................... 115
4.5 Sodium Sulfate ....................................... 130
  4.5.1 Fatigue Crack Growth Rates in Sodium Sulfate ....................... 130
  4.5.2 Fractographic Results ................................... 130
4.6 Sodium Phosphate and Sodium Silicate .................. 135
  4.6.1 Fatigue Crack Growth Rates in Sodium Phosphate and Sodium Silicate ....................... 135
  4.6.2 Fractographic Results ................................... 135
4.7 Open Circuit Potentials ................................ 140
5.0 DISCUSSION .......................................... 143
  5.1 Introduction ........................................... 143
  5.2 Effect of Environment .................................... 143
    5.2.1 Air ........................................... 143
    5.2.2 Water ........................................... 143
    5.2.3 Sodium Chloride and Sodium Sulfate ....... 145
    5.2.4 Effect of pH .................................... 149
    5.2.5 Sodium Phosphate and Sodium Silicate ....................... 155
  5.3 Effect of Test Frequency ................................ 158
5.4 Model for Dissolution Assisted Crack Growth................................. 161
5.4.1 Anodic Dissolution Approach .................. 161
5.4.2 Hydrogen Embrittlement Approach............. 175
6.0 CONCLUSIONS................................................. 179
BIBLIOGRAPHY .......................................................... 181
LIST OF TABLES

1. Fatigue Crack Laws for Several Steels ................. 17
2. Threshold Stress Intensity Data for Some Engineering Steels ........................................ 24
3. Summary of Fatigue Crack Growth Laws for the Various Environments Shown in Figure 18........................................ 40
4. Mill Chemistry of 403 Stainless Steel ............... 52
5. Heat Treatment of 403 Stainless Steel.............. 52
6. Mechanical Properties of 403 Stainless Steel ................................................................. 52
7. Test Matrix .................................................. 64
8. Power Law Expressions for Fatigue Crack Growth Rates in Water ........................................ 96
9. Power Law Expressions for Fatigue Crack Growth Rates in Sodium Chloride Solutions .................................................. 117
10. Power Law Expressions for Fatigue Crack Growth Rates in Sodium Sulfate Solutions .............................................. 132
11. Power Law Expressions for Fatigue Crack Growth Rates in Phosphate and Silicate Solutions ........................................ 137
12. Pitting Potentials in Sodium Chloride and Sodium Sulfate at 100C ............................................... 148
13. Calculation of $i_{ave}$ ........................................ 172
14. Hydrogen Penetration Distances ...................... 178
LIST OF FIGURES

1. The 0.1% carbon portion of the iron–chromium–carbon phase diagram ........................... 6
2. The effect of tempering temperature on the mechanical properties of 403 stainless steel .... 7
3. The effect of tempering temperature on strength and ductility ................................. 8
4. The effect of tempering temperature on fracture toughness ...................................... 8
5. Three basic modes of crack surface displacements and the equations that describe the elastic stress field in the vicinity of the crack tip in a body subjected to Mode I deformations........................................ 11
6. Schematic representation of fatigue crack propagation in steel.............................. 15
7. Summary of fatigue crack propagation rates for martensitic steels in air.................... 18
8. Schematic of monotonic and cyclic plastic zones.................................................. 20
9. Schematic of "plastic blunting process" of fatigue crack propagation..................... 22
10. Effect of tempering temperature and stress intensity of the velocity of SCC cracks....... 28
11. Effects of tempering temperature on toughness (K_{IC}) and crack velocity in water of a 12% chromium steel......................................................... 28
12. Effect of heat treatment on the corrosion rate of 410 stainless steel in a salt fog environment............................................................. 30
13. Effect of heat treatment on corrosion rate of 410 stainless steel in various acidic environments .................................................. 30

14. Corrosion fatigue S-N curves of smooth bar specimens exposed to various environments ......................................................... 32

15. Corrosion fatigue S-N curves of notched bar specimens exposed to various environments ......................................................... 32

16. Air and corrosion fatigue curves for a 13Cr-Fe alloy (austenitized at 950°C, tempered 680°C) in a 10% ammonia nitrate ........................................ 33

17. Schematic of types of corrosion fatigue behavior ............................................................................. 35

18. Summary of fatigue crack growth data for AISI 403 ........................................................................ 38

19. Summary of fatigue crack growth data for AISI 403 in various marine environments ............ 39

20. Effect of test frequency and stress intensity on the growth rate of corrosion fatigue cracks in a 12% chromium steel exposed to water ...................... 41

21. Growth rates of fatigue cracks in a 12% chromium steel as a function of cyclic frequency, environment, and heat treatment .... 41

22. Effect of loading wave form on the fatigue crack growth rate of 12Ni5Cr3Mo steel below KISC in 3% sodium chloride solution .... 44

23. Diagram of compact-tension sample geometry .... 56

24. Typical closed loop system ................................................. 58

25. Diagram of load train .................................................. 60

26. Diagram of corrosion cell with load train and sample ................................................................. 61

27. Working diagram of Shaevitz LVDT ............... 68

xii
28. Schematic of sample showing the load line and gage line conversion .......................... 70

29. Sample calculation converting ΔV to crack length ................................................. 72

30. Example of fracture surface after fatigue testing showing the area of the machine notch, precrack zone, and the fatigue surface and final failure where the sample was pulled apart .......... 73

31. Schematic diagram for a vs N data reduction by means of incremental polynomial method ........ 76

32. Crack length vs cycles in air showing agreement between LVDT measurements and microscope .................................................. 81

33. Fatigue crack propagation rate, da/dN, vs stress intensity range, ΔK at 25°C showing agreement between optical and compliance techniques .................................................. 82

34. Fatigue crack growth rate vs ΔK in air at 10Hz and 40Hz, 25 and 100°C ............................. 83

35. Fatigue crack growth rate vs ΔK in water, pH7, 100°C tested at various frequencies .......... 93

36. Fatigue crack growth rate vs ΔK in water, pH7, 100°C, tested at various frequencies showing ΔK_{th} region ................................................................. 94

37. Fatigue crack growth rate vs ΔK in water, 25 and 100°C, pH 7 and 10 cycled at 10Hz ........ 95

38. Fatigue crack growth rates vs ΔK in 0.01M sodium chloride, pH10, 100°C tested at various frequencies ................................................................. 112

39. Fatigue crack growth rates vs ΔK in 0.01M sodium chloride, pH10, 100°C tested at various frequencies showing ΔK_{th} region ........... 113

40. Fatigue crack growth rates vs ΔK in 1M sodium chloride, cycled at 10Hz at various pH's .................. 114

41. Fatigue crack growth rates vs ΔK in sodium chloride and water, 25C cycled at 10Hz .... 116

xiii
42. Fatigue crack growth rates vs ΔK in 0.01M and 1M sodium sulfate, 100C tested at 10 and 40 Hz. ......................................................... 131

43. Fatigue crack growth rates vs ΔK in 1M sodium phosphate and 1M sodium silicate .......... 136

44. Open circuit potentials vs solution pH measured during fatigue crack propagation tests ................................................................. 142

45. Summary of the effect of the different environments studied on ΔKth ........................................... 146

46. Polarization curves of 403 stainless steel in 1M sodium chloride solutions at 100C and scan rate of 1000mV/min ........................................ 150

47. Polarization curves of 403 stainless steel in 0.01M sodium chloride at 100C and scan rate of 25 mV/min ................................. 151

48. Polarization curves of 403 stainless steel in 1M sodium sulfate solutions at 100C and scan rate of 1000mV/min ..................... 152

49. Polarization curves of 403 stainless steel in 0.01M sodium sulfate at 100C and scan rate of 25 mV/min ......................................... 153

50. Polarization curves of 403 stainless steel in 1M sodium phosphate and 1M sodium silicate at 100C and scan rate of 25 mV/min ......... 156

51. Plot of environmental crack growth rate in m/cycle as a function of test frequency for three ΔK values in water, 100C, pH7 .................. 160

52. Typical change in current density (i) and strain (ε) with time in a straining electrode experiment ............................................... 163

53. Plot of environmental crack growth rate in m/sec vs test frequency in water, 100C, for three ΔK values ........................................... 164

54. Plot of environmental crack growth rate vs stress intensity range, ΔK for the four frequencies studied ........................................ 165

xiv
55. Schematic showing process of film rupture and crack extension due to dissolution as in (A), two different test frequencies are shown in (B) where the frequency at the top is faster than the one below.......................... 167

56. Dissolution at the crack tip with more than one film rupture event and non-idealized crack extension................................. 174
# LIST OF PLATES

I. Microstructure of as received 403 stainless steel................................. 53

II. Microstructure of quenched and tempered 403 stainless steel.................. 54

III. Compact-tension sample used in corrosion fatigue crack propagation studies with LVDT extension tubes in place with teflon blocks........................................ 57

IV. Corrosion cell in place in MTS load frame with LVDT, thermometer, and reference electrode in place.................................................. 63

V. Compact-tension sample in MTS load frame with LVDT attached and traveling microscope in place.................................................. 67

VI. Fracture surface of sample fatigued in air at 25C, 10Hz shown at three stress intensity ranges and three magnifications: 500X, 1000X and 10,000X.......................... 85

VII. Fracture surface of sample fatigued in air at 10Hz, 25C at 3 stress intensity ranges and three magnifications: 500X, 1000X, and 10,000X.......................... 87

VIII. Fracture surface of sample fatigued in air at 40Hz, 25C at two stress intensity ranges and three magnifications: 500X, 1000X and 10,000X........................................ 90

IX. Fracture surface of sample fatigued in air at 25C, 40Hz at stress intensity ranges where $\Delta K_{th}$ was determined and shown at three magnifications: 500X, 1000X, and 10,000X........ 91
X. Fracture surface of sample fatigued in water, pH7 at 100C, 40Hz, at two stress intensity ranges at three magnifications 500X, 1000X, and 5000X.......................... 98

XI. Fracture surface of sample fatigued in water, pH7, 100C, 40Hz at two stress intensity ranges where $\Delta K$ was determined at three magnifications: 500X, 100X, and 10,000X.......................... 99

XII. Fracture surface of sample fatigued in water, pH6.5, 10Hz at three stress intensity ranges and three magnifications: 100X, 500X, and 1000X.......................... 100

XIII. Fracture surface of sample fatigued in water, pH7, 100C 1Hz at three stress intensity ranges and three magnifications: 100X, 500X, and 1000X.......................... 102

XIV. Fracture surface of sample fatigued in water, pH7, 100C, 0.1Hz at three stress intensity ranges and at three magnifications: 500X, 1000X, and 10000X............. 104

XV. Fracture surface of sample fatigued in water, pH6.5, 10Hz with striation spacing of $\approx 0.3\mu$ at magnifications of 500X, 1800X, and 10,000X.................... 107

XVI. Fracture surface of sample fatigued in water, pH6.5, 100C at 10Hz at $\Delta K20$ showing a grain with no evidence of striation markings................................. 108

XVII. Fracture surface of sample fatigued in water, pH7, 24C, 10Hz at three stress intensity ranges and three magnification: 100X, 500X, and 1000X......................... 109

XVIII. Fracture surface of sample fatigued in 0.01M sodium chloride, pH10, 100C, 10Hz at three stress intensity ranges and three magnifications: 100X, 500X, and 1000X........ 118

XIX. Fracture surface of sample fatigued in 1M sodium chloride, pH2, 100C, 10Hz at three stress intensity ranges and three magnifications: 100X, 500X, and 1000X....... 120

xvii
XX. Fracture surface of sample fatigued in 1M sodium chloride, pH10, 100°C at 10Hz at three stress intensity range and three magnifications: 100X, 500X and 1000X... 122

XXI. Fracture surface of sample fatigued in 0.01M sodium chloride, pH10, 24°C, 10Hz at three stress intensity ranges and three magnifications: 100X, 500X and 1000X... 124

XXII. Fracture surface of sample fatigued in 1M sodium chloride, pH10, 25°C, 10Hz at three stress intensity ranges and three magnifications: 100X, 500X, and 1000X... 126

XXIII. Fracture surface of sample used to determine ΔK at low stress intensity ranges photographed at three magnifications: 100X, 500X, and 1000X... 128

XXIV. Fracture surface of sample fatigued in 0.01M sodium chloride, 100°C 40Hz at low stress intensity ranges used to determine ΔK at plotted photographed at three magnifications: 100X, 500X, and 1000X... 129

XXV. Fracture surface of sample fatigued in 1M sodium sulfate, pH7, 100°C, 10Hz at three stress intensity ranges and at three magnifications: 100X, 500X and 1000X... 133

XXVI. Fracture surface of sample fatigued in 1M sodium phosphate, pH10, 100°C, 10Hz at three stress intensity ranges and three magnifications: 500X, 1000X, and 10000X... 138

XXVII. Fracture surface of sample fatigued in 1M sodium silicate, pH10.5, 100°C, 10Hz. Deposit is evident on the fatigue fracture... 141

xviii
1.0 INTRODUCTION

This research work has concerned itself with the corrosion fatigue crack growth properties of 403 stainless steel. The material is a 12% chromium steel in the quenched and tempered condition, whose primary application in industry is as steam turbine buckets. The environments of interest have been those which are found in steam turbine applications. The electric power generating industry is concerned with the corrosion fatigue properties of this material because of the rotating speeds and cyclic stressing that the buckets undergo.

The buckets are attached to the turbine by a serrated fir tree type design which introduces a notch in the base of the turbine blade; this area then becomes a potential source for crack growth. Consequently, a fracture mechanics approach to corrosion fatigue in chloride, sulfate, phosphate, and silicate solutions using compact-tension specimens was undertaken. The experiments were performed in non-pressurized solutions at room temperature and 100C.

This dissertation documents the experimental work undertaken, the results, and the crack growth model used to explain the fatigue crack growth observed. The
principle variables in this study have been the anions, the solution pH, and the test frequency. Since the operating turbine temperature is about 100C, the majority of the tests were conducted at that temperature although some room temperature work was conducted.
2.0 LITERATURE SURVEY

2.1 Introduction

Fatigue is defined as the tendency of a metal to fracture under repeated cyclic stressing. Corrosion fatigue is the reduction of fatigue resistance due to the presence of a corrosive medium; it is defined in terms of the mechanical properties of a material structure. There are three general variables which are encompassed in this research work. These are the metallurgical, mechanical, and environmental aspects of corrosion fatigue.

This literature survey encompasses these three topics. In the first part, the metallurgical development and use of 12% chromium steels is reviewed. In the second part the fracture mechanics variables encorporated in fatigue studies are reviewed; this section is focussed on the experimental variables used in this research project. The final part deals with the environmental effects on fatigue; it reviews the corrosion properties of martensitic stainless steels, the corrosion fatigue testing variables considered in the process, and the corrosion fatigue studies which have been performed on 12% chromium steels.
2.2 Metallurgical Aspects of 12% Chromium Steels

The main reason for the existence of stainless steels is resistance to corrosion. Chromium is the main alloying element, and the steel should contain at least 11%. (1) The 12% chromium steels fall into a group of stainless steels which are hardenable because sufficient austenite is formed at elevated temperatures to produce martensite upon cooling.

The original alloy in this group of steels was Type 420 developed in England for cutlery (2) with a carbon content around 0.3%; its usefulness was limited to applications where it could be used fully hardened. Lowering the carbon content produced a grade which could be tempered to produce a wide and useful range of hardnesses. Type 403 grew out of a need for a special quality alloy capable of meeting the numerous specifications required in the turbine industry. (3)

The trends in chromium alloying with reference to the iron-chromium-carbon phase diagram (4) are that chromium:

(1) in solid solution tends to eliminate the α-, γ transformation; (2) in solid solution, increases the time necessary for completion of any transformation; and (3) forms carbides readily which are soluble in high temperature austenite but almost insoluble in low temperature austenite or ferrite.

Essentially carbon free alloys with 12% chromium are soft and ductile, but when enough carbon is present to
produce austenite at elevated temperatures, the alloys may be heat treated to useful hardness ranges.

A look at the 0.1% section of the ternary phase diagram (Figure 1) shows that the amount of austenite formed depends on temperature and composition. Only steels fully austenitic at solution temperature will harden fully on cooling. Any delta ferrite at solution temperature remains in the structure and reduces the attainable strength. The upper temperature for transforming all ferrite except delta ferrite to austenite is 955°C (1750°F), and increasing this temperature may lead to the formation of delta ferrite even in steels wholly austenitic at lower solution temperatures (5); the presence of this soft ductile phase lowers the attainable strength of the alloy.

Secondary phases may form in these alloys; most of these phases are undesirable. These are carbides, Laves phase, chi, sigma, alpha prime, molybdates, columbides, borides and silicides. Most of these have deleterious effects on the mechanical properties.

Figures 2, 3, and 4 summarize the effect of heat treatment on the mechanical properties of martensitic stainless steels.
Figure 1. The 0.1% portion of the iron-chromium-carbon phase diagram. (4)
Figure 2. The effect of tempering temperature on the mechanical properties of 403 stainless steel. (2)
Figure 3. The effect of tempering temperature on strength and ductility. (28)

Figure 4. The effect of tempering temperature on fracture toughness. (28)
2.3 Fracture Mechanics Aspects of Fatigue

One of the more important applications of 403 stainless steels is as steam turbine blades (where operating temperatures do not exceed 480°C (900°F)); this industrial application is due to their excellent damping capacity along with the room temperature yield and fatigue strengths which are needed due to the length of these blades (36-60 in) and the high operating speeds (1500 ft/sec). (5) Since these blades are usually attached with fir-tree type serrated fastenings, the blade material must be evaluated for failure possibilities if a notch is present.

If one accepts the fact that real structures contain discontinuities, then the progressive crack extension due to the application of a load must be understood. It is in this area that fracture mechanics has become the primary approach to controlling fatigue failures.

It is not the intention of this survey to do a complete analysis of linear elastic fracture mechanics since there are several texts that do that very well (6, 7, 8), but rather to introduce the parameters which are important in the application of fracture mechanics to the field of fatigue control. The review of fracture mechanics is conducted by presenting work that has been done primarily on alloy systems which are pertinent to this research work. This includes areas such as subcritical crack growth and fatigue crack propagation along with mechanisms which are used to
describe crack propagation.

2.3.1 Fracture Mechanics Methods

The recent development of fracture mechanics has shown that there are three primary factors that control the susceptibility of a structure to fracture (7); (1) material toughness \( K_{IC} \), (2) crack size \( a \), and (3) stress level \( \sigma \). Linear elastic fracture mechanics is based on an analytical procedure that relates the above three factors, i.e. it relates the stress-field magnitude and distribution in the vicinity of a crack tip to the normal stress applied to the structure, to the size, shape and orientation of the crack or discontinuity to the material properties.

To establish methods of stress analysis for cracks in elastic solids, it is convenient to define three types of relative movements of two crack surfaces shown in Figure 5. Mode I is the opening mode, Mode II is the sliding or shear mode, and Mode III is the tearing mode. Each of these deformation modes corresponds to a basic type of stress field in the vicinity of crack tips. In any problem, the deformation at the crack tip can be treated as one or a combination of these local displacements.

This research work is confined to Mode I type deformation, so further remarks are confined to that mode.
Figure 5. Three basic modes of crack surface displacements and the equations that describe the elastic-plastic field in the vicinity of a crack tip in a body subjected to Mode I deformation. (9)
The stress analysis method at the crack tip was developed by Westergaard (10) and used by Irwin (11) to describe the stress displacement fields at the crack tip as shown in Figure 5. These equations represent the case of plane strain and are exact in the limit as \( r \) approaches zero and are an approximation in the region where \( r \) is small compared with the x-y planar dimensions; they also show that the distributions are invariant in components subjected to Mode I deformation. Further, the magnitude of the elastic stress field can be described by the single parameter, \( K_I \), the stress intensity factor. Thus, the applied stress, crack shape, size, orientation and structural configuration of a component subjected to this deformation affect the value of \( K_I \), but do not alter the stress field distribution.

Unstable fracture can then be defined in terms of the stress intensity factor; it occurs when the stress intensity at the crack tip reaches a critical value \( K_C \). For Mode I deformation and plane strain conditions (small plastic zone) the critical stress intensity for fracture instability is \( K_{IC} \), which represents the inherent ability of a material to withstand a given stress field intensity at a crack tip and to resist progressive tensile crack extension. Dimensional analysis shows that \( K_{IC} \) must be linearly related to the applied nominal stress, \( \sigma \), and the square root of the crack length, \( a \), or the general form:
\[ K = \sigma \sqrt{a} Y \]  

where \( Y \) is a parameter that depends on the specimen and crack geometry. (The engineering units are \( \text{MPa} \sqrt{\text{m}} \) or \( \text{KSI} \sqrt{\text{in.}} \).)

Thus, the \( K_{IC} \) of a material represents the terminal conditions in the life of a component; the total useful life is determined by the time necessary to initiate a crack and to propagate the crack from subcritical size to the critical size. Crack initiation and propagation may be caused by cyclic stresses in the absence of an aggressive environment, by an aggressive environments under sustained load, or by any combination of these conditions.

2.3.2 Fatigue Crack Growth

Conventional fatigue testing generates design fatigue curves based on the prediction of cyclic life from data on nominal stress vs elapsed cycles (S-N) curves to failure. When using unnotched specimens, this type of data represents both the number of cycles required to initiate a crack in a specimen and the number of cycles required to propagate the crack to failure. The number of cycles corresponding to the endurance limit primarily represents initiation life. Consequently, S-N curves do not necessarily provide information on safe-life predictions in structures having surface irregularities or crack-like discontinuities since their existence may eliminate the crack initiation portion of the fati-
gue life of a component.

Crack propagation information, on the other hand, may be obtained from a number of sample geometries. Starting with a sharpened crack, cyclic loads are applied and the resulting change in crack length, \( a \), monitored as a function of the number of cycles, \( N \). The fatigue crack growth rate is determined from the \( a \) vs \( N \) curve. Paris and Erdogan (12) postulated that the stress intensity factor, \( K \), which is a function of stress and crack length, was the overall controlling factor in the fatigue propagation process, thus, fatigue propagation rates are generally plotted against the stress intensity range, \( \Delta K (\Delta K = K_{\text{max}} - K_{\text{min}}) \). Figure 6 show that this plot for steels can be divided into three regions: Region I exhibits a fatigue threshold cyclic stress intensity, \( \Delta K_{\text{th}} \), below which cracks do not propagate; Region II represents the fatigue crack propagation behavior represented by

\[
\frac{da}{dN} = A(\Delta K)^n
\]  

(2)

where \( da/dN \) is the fatigue crack growth rate, \( \Delta K \) is the stress intensity range defined above, and \( A, n \) are constants; Region III is where the rate of fatigue crack growth increases as \( K_{\text{max}} \) increases to either \( K_{IC} \) or \( K_C \). In some cases \( K_{IC} \) is replaced by \( K_C \) because \( K_{IC} \) may be affected by cyclic softening or hardening during the fatigue process.
Figure 6. A schematic representation of the fatigue crack growth in steel.
Fatigue Crack Growth in Region II

In the early 60's, a number of investigators tried to derive the power law expression which would explain crack growth. A number of these expressions have been derived for a number of materials. Crooker and Lange (13) have summarized much of this data. However, engineering estimates of crack growth in steels can be divided into three groups which reflect the microstructural difference. (7) Table 1 lists the fatigue crack growth rates in martensitic, ferrite-pearlite and austenitic steels; these groups reflect variations in mechanical properties which are also listed in the table.

Fatigue crack growth data for various strength martensitic steels, Figure 7, show that the primary factor affecting the growth rate in Region II is the $\Delta K$; mechanical and metallurgical properties have negligible effect on the crack growth. Clark (14) and Logsdon (15) have found slight variations in the growth law expression for 403 stainless steel fatigue tested in air. Clark determined

$$\frac{da}{dN} = 0.16 \times 10^{-8} \Delta K^{2.4},$$  \hspace{1cm} (3)

and Logsdon found

$$\frac{da}{dN} = 0.29 \times 10^{-8} \Delta K^{2.4}.$$  \hspace{1cm} (4)

A change in the stress ratio, $R (= \sigma_{\text{min}}/\sigma_{\text{max}})$ does not influence significantly the crack growth rate in this region. (16) In addition, Barsom (17) found that variation of the
<table>
<thead>
<tr>
<th>Steel</th>
<th>Rate Law</th>
<th>Yield Strength $\sigma_{YS}$ (KSI)</th>
<th>Tensile Strength $\sigma_{T}$ (KSI)</th>
<th>Strain Hardening Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic</td>
<td>$3.0 \times 10^{-10} \Delta K^{3.25}$</td>
<td>$30 &lt; \sigma &lt; 50$</td>
<td>$75 \leq \sigma &lt; 95$</td>
<td>$n &gt; 0.3$</td>
</tr>
<tr>
<td>Ferrite-Pearlite</td>
<td>$3.6 \times 10^{-10} \Delta K^{3.0}$</td>
<td>$30 &lt; \sigma &lt; 80$</td>
<td>$50 \leq \sigma &lt; 110$</td>
<td>$0.15 \leq n &lt; 0.3$</td>
</tr>
<tr>
<td>Martensitic</td>
<td>$0.66 \times 10^{-8} \Delta K^{2.25}$</td>
<td>$\sigma &gt; 70$</td>
<td>$\sigma &gt; 90$</td>
<td>$n &gt; 0.15$</td>
</tr>
</tbody>
</table>
Figure 7. Summary of fatigue crack propagation rates for martensitic steels. (7)
cyclic test frequency in a room temperature air environment, caused very little, if no change in the fatigue crack growth rates of the steels he investigated. He also studied the effect of cyclic wave form (sinusoidal, triangular, square, positive sawtooth (\(\uparrow\)), and negative sawtooth (\(\downarrow\))) on a 12Ni-8Cr-3Mo maraging steel; no effect was found by the form of the cyclic-stress fluctuation on the rates of fatigue crack growth.

Bathias and Pelloux (18, 19) have found that in martensitic steels tested under constant cyclic load, fatigue striations are observed on the fracture surface and each striation corresponds to one load cycle; it is a measure of the crack advance or local rate of advance of the crack front. They also confirmed the existence of a cyclic plastic zone within the monotonic plastic zone pictured in Figure 8; the reversed plastic zone is one-fourth the size of the monotonic zone.

**Mechanisms for Fatigue Crack Growth in Region II**

Most crack growth mechanisms in fatigue acknowledge that it takes place in two stages. The first stage is actually crack initiation and is characterized by propagation of the crack on a plane oriented at 45° to the stress axis and by crystallographic fracture facets. In stage II the plane of crack propagation is at 90° to the stress axis and the fracture surface is covered by striations running parallel to the crack front. Crack propagation rates in Stage II
Figure 8. Schematic of monotonic and cyclic plastic zones.
(20)
growth can reach microns/cycle, while in Stage I, the order is angstroms/cycle.

The mechanism of Stage II growth is known as the plastic blunting process. (21) Figure 9 proposed by Laird shows that as the tensile load of a cycle is applied as in 9a and 9b, a small double notch is formed; when the specimen is deformed to a maximum tensile stress, 9c, the stress concentration is lessened and the crack tip broadens to a semi-circular configuration. Upon compression, Figure 9d, the crack faces are crushed together, and the new crack surface created in tension is forced into the plane of the crack and partly folded by buckling the very front of the crack tip into another notch as in Figure 9e.

Modifications have been made to this process (22), but Beardmore and Feltner (23) have observed striations on low carbon martensitic steels, indicating that Stage II cracks grow by the blunting and sharpening process.

**Fatigue Crack Propagation in Region I (low ΔK)**

In Figure 6 it is obvious that the simple power relationship previously proposed is violated for low ΔK conditions (Region I); the crack growth rate diminishes rapidly to a low level. In this region it has been found that the stress ratio, \( R = \frac{\sigma_{\text{min}}}{\sigma_{\text{max}}} \), strongly affects the crack growth rate. (6) When a limiting stress intensity factor range (the threshold level, ΔKth) is defined, it represents a service operating limit below which fatigue damage is
Figure 9. Schematic of plastic blunting and sharpening process of fatigue crack propagation. (21)
highly unlikely. Table 2 lists the $\Delta K_{th}$ for some engineering alloys; it is evident that the $R$ ratio has a strong effect on $\Delta K_{th}$. Vosikovsky (24) has compiled data on the effect of stress ratio on ferritic and martensitic steels to show the effect of stress ratio on $\Delta K_{th}$. Paris et al (25) and McEvily and Gaallagher (26) also found that the $R$ ratio was significant in affecting the $\Delta K_{th}$ for material tested in air and vacuum.

Laird (21) has pointed out that the difficulty in understanding the mechanisms in the slow growth regime is the general lack of features on the fractures surfaces; there is a very small amount of plastic blunting at the tip so that the sharpening process on compression is minimized, such that resolvable striations will not be left on the fracture surface.

Benson and Edmonds (27) examined fracture surfaces of quenched and tempered martensitic steels tested in the $\Delta K_{th}$ region and found that the crack path was transgranular with respect to prior austenite grains and bore no relationship to the lath boundaries; they determined a $\Delta K_{th}$ value of 5.5 MPa$\sqrt{m}$ for $R=0.4$. In addition, when comparing $\Delta K_{th}$ to the fatigue limit, they found that tempered martensite had a low $\Delta K_{th}$ and a high fatigue limit indicating the conflicting requirements for resistance to crack initiation and crack growth in steels. The quenched and tempered structures also showed evidence of intergranular cracking at the low $\Delta K$'s.
<table>
<thead>
<tr>
<th>Material</th>
<th>$R$</th>
<th>$\Delta K_{th}$ (MPa $\sqrt{m}$)</th>
<th>$\Delta K_{th}$ (ksi $\sqrt{in.}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9310 Steel</td>
<td>0.25</td>
<td>-6.1</td>
<td>-5.5</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>-3.3</td>
<td>-3</td>
</tr>
<tr>
<td>A533B Steel</td>
<td>0.1</td>
<td>8</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>5.7</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>4.8</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>3</td>
<td>2.75</td>
</tr>
<tr>
<td>A508</td>
<td>0.1</td>
<td>6.7</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>5.6</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>T-1</td>
<td>0.2</td>
<td>-5.5</td>
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<tr>
<td></td>
<td>0.4</td>
<td>-4.4</td>
<td>-4</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>-3.3</td>
<td>-3</td>
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<tr>
<td>Ti-6 Al-4 V</td>
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<td>-6.6</td>
<td>-6</td>
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<td></td>
<td>0.33</td>
<td>-4.4</td>
<td>-4</td>
</tr>
<tr>
<td>18/8 Austenitic</td>
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<td>6.1</td>
<td>5.5</td>
</tr>
<tr>
<td>steel</td>
<td>0.33</td>
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<td>5.4</td>
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<tr>
<td></td>
<td>0.62</td>
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<td>0.74</td>
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<td>Copper</td>
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<td>2.3</td>
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<td>1.8</td>
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<tr>
<td></td>
<td>0.56</td>
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<tr>
<td></td>
<td>0.80</td>
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</tr>
<tr>
<td>60/40 brass</td>
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</tr>
<tr>
<td></td>
<td>0.33</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
<td>2.6</td>
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<td>0.72</td>
<td>2.6</td>
<td>2.4</td>
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<tr>
<td>Nickel</td>
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<td>7.2</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>6.5</td>
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<tr>
<td></td>
<td>0.71</td>
<td>3.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>

(Ref. 6)
This section has presented the major points concerned in applying fracture mechanics to the study of metal fatigue. The principle parameters involved in fatigue testing and evaluation which were used in this research project were reviewed. The next section covers the addition of an aqueous environment to the effects of fatigue.

2.4 Environmental Aspects of Fatigue

2.4.1 Introduction

Corrosion fatigue is the nucleation and growth of subcritical cracks due to the simultaneous action of aggressive environments and cyclic stresses; the complexity of the process is due to the fact that it includes elements of fatigue, stress corrosion cracking (SCC), hydrogen embrittlement (HE), pitting, intergranular and general corrosion. (28) The fatigue behavior of an environment-material system can be studied by establishing the deviation of the corrosion fatigue behavior for the system from the fatigue behavior of the material in a benign environment.

This portion of the survey presents the literature pertaining to martensitic stainless steels in terms of SCC, HE, pitting and corrosion fatigue; in the treatment of corrosion fatigue, the variables of corrosion fatigue testing and the mechanisms proposed for crack growth are presented.
2.4.2 Stress Corrosion Cracking-Hydrogen Embrittlement

Stress corrosion crack growth in a statically loaded structure is caused by interactions of chemical and mechanical processes at the crack tip. The highest plane-strain stress-intensity factor value at which subcritical crack growth does not occur in a material statically loaded in an aggressive environment is designated \( K_{ISCC} \). Because \( K_{ISCC} \) for an environment-material system defines the plane-strain \( K_{I} \) value above which SCC growth can occur under static loads, the corrosion fatigue behavior for the system could be altered when the maximum value of \( \Delta K (= K_{max} - K_{min}) \) in a given load cycle exceeds \( K_{ISCC} \).

McGuire, Troiano and Heheman (29) studied the susceptibility of 410 stainless steel to SCC in a 3% sodium chloride solution doped with sodium sulfide as function of the material strength level. They found that SCC occurred only when the alloy was heat treated to a yield strength level of 120KSI (827 MPa) at 25C and 175 KSI (1207 MPa) at 100C. Hydrogen permeation experiments as a function of applied potential found three regions: (1) increasing permeation with increasing cathodic polarization; (2) a cathodic protection potential range where no permeation occurred; and (3) an anodic region with localized corrosion and hydrogen permeation. These experiments indicated that strength level has no appreciable influence on hydrogen permeation.
Hoke (30) reported that induction melting of 410 stainless steel greatly improved the resistance to SCC in a similar electrolyte as used by McGuire et al. In this case arsenic was used as a poison, but he did not report either the heat treatment or strength levels of the steels he used.

Additional SCC work has been performed by McCord et al (31) on 403 stainless steel with a yield strength of 85 KSI (586 MPa) and a number of 12 % chromium steels with yield strengths below 116 KSI (800 MPa). Using dead weight loading in 3.5% sodium chloride solutions at 150°F (65°C), they found no failure occurred in the material after 4400 hrs of loading.

A study of the effect of tempering temperature on the SCC susceptibility of a 13% chromium martensitic steel in 3% sodium chloride at 25°C by Hewitt and Hockenbull (32) indicated that in constant load testing, the material tempered at 650°C showed no evidence of cracking but only pitting and general corrosion. Figure 10 and 11 are summaries of the effect of tempering temperature on SCC; tempering at 550°C and above results in little SCC effects.

By using the slow strain rate technique to determine the susceptibility of martensitic stainless steels to SCC in 3% sodium chloride solutions (cathodically polarized), Surey (33) found that a tempering of 600°C ($R_c 23$) resulted in the highest % reduction in area while specimens with a lower tempering treatment had a lower reduction in area; the tempering at
Figure 10. Effect of tempering temperature and stress intensity on the velocity of SCC cracks. (28)

Figure 11. Effect of tempering temperature on toughness ($K_{IC}$) and crack velocity in water of a 12% chromium steel.
600°C however, did not completely eliminate the susceptibility to SCC during cathodic polarization. On the other hand, polarizing the samples anodically while slowly straining, led to a minimum in the % reduction in area on samples tempered at 600°C.

In summary, the SCC behavior of martensitic stainless steels is strongly influenced by microstructural variations resulting from the heat treatment. (34)

2.4.3 General Corrosion and Pitting Behavior

Corrosion rate work (35) investigating the effect of chromium on the corrosion resistance of steels in water has shown that martensitic stainless steels have higher corrosion rates than ferritic and austenitic stainless steels; in general the trend is that the higher the chromium content the greater the corrosion resistance.

Examining the pitting potentials for a martensitic stainless steel, Johnson (36) found that the material is susceptible to pitting in solutions with chloride concentrations of 10-10,000 ppm; very little change of these potentials was noted in the pH range 3-8 at room temperature.

Figures 12 and 13 show the effect of heat treatment on pitting and the general corrosion rates for 410 stainless steels; in each case, corrosion rates can be greatly influenced by the tempering temperature. (2, 37)
Figure 12. Effect of heat treatment on corrosion rate of 410 stainless steel in a salt fog environment. (2)

Figure 13. Effect of heat treatment on corrosion rate of 410 stainless steel in various environments. (2)
In summary, the general corrosion resistance of the martensitic stainless steels is superior to carbon steel. (38) It is dependent on the heat treatment and the steels are susceptible to pitting attack.

2.4.4 Corrosion Fatigue

Having reviewed the corrosion behavior of martensitic stainless steels, it is possible to examine the corrosion fatigue aspects; first the S-N type information available is presented then it is followed by crack growth type discussions.

The effects of corrosion fatigue on stainless steels were initially studied through the testing of smooth or notched specimens under cyclic loads; the results were plots of the applied cyclic stress amplitude, S, as a function of the number of cycles to failure. Figures 14 and 15 show the tremendous effect water and chlorides have on the fatigue behavior of a 13% chromium steel.

Additional work on the effect of an aqueous environment on the fatigue limit is shown in Figure 16; Cowley et al. (39) demonstrated the electrochemical nature of the corrosion fatigue process by increasing the corrosion fatigue life of a 13% chromium steel in a 10% ammonium nitrate solution by anodic protection.
Figure 14. Corrosion fatigue S-N curves of smooth bar specimens exposed to various environments. (28)

Figure 15. Corrosion fatigue S-N curves of notched bar specimens exposed to various environments. (28)
Figure 16. S-N curves for a 13Cr-Fe alloy (austenitized at 950°C, tempered at 680°C) tested in air and in 10% ammonia nitrate in various conditions. (42)
A review of the S-N type of fatigue data (39, 40, 41) on 403 stainless steel has confirmed that whether the material is in a steam or chloride environment, there is a loss in the total fatigue life of the material from that in air. In addition, testing in chloride solutions produced pitting and intergranular fracture (40); the loss in fatigue life of the alloy was found to occur regardless or heat treatment.

In fatigue crack growth behavior, it is worthwhile to establish base-line data in a benign environment, then determine the environmental effect. Figure 6 showed the type of crack growth behavior that might be expected in a steel; the crack growth rate was plotted as a function of the stress intensity range, \( \Delta K \). It is also possible to plot crack growth rate, \( da/dN \), as a function of the maximum stress intensity, \( K_{\text{max}} \), and obtain a curve similar to Figure 6.

Figure 17 shows such a plot. The effect of the environment in corrosion fatigue is to enhance \( da/dN \) below the \( K_C \) and to possibly lower the threshold stress intensity value. Three types of corrosion fatigue are shown in Figure 17. Type A behavior represents a corrosion fatigue effect due to the synergistic action of the environment and the mechanical fatigue process. Type B behavior is representative of corrosion fatigue dominated by the static loading effects of SCC. When \( K_{\text{max}} < K_{\text{ISCC}} \), no corrosion fatigue takes place, but when \( K_{\text{max}} > K_{\text{ISCC}} \), a substantial increase in \( da/dN \) occurs due to corrosion fatigue. This type of behavior is often
Figure 17. Schematic of types of corrosion fatigue behavior. (43)
found with high strength steels in hydrogen environments. Most environment-material systems exhibit behavior similar to Type C, which is a combination of Types A and B.(43)

In corrosion fatigue, as in fatigue in a benign environment, the crack growth rate is a function of the stress intensity range. This relation, however, is also affected by the test frequency of the applied load, the shape of the wave form, the maximum stress intensity, as well as ΔK. Although in a benign environment, the measure of microscopic material damage (da/dN) produced by fatigue loading is a cycle dependent parameter, i.e. frequency independent, this behavior is valid only if the material is not strain rate sensitive or if the crack growth rate is not influenced by environmental attack.(44)

The following paragraphs discuss experimental studies which document the effect of fatigue testing variables on the crack growth rates observed in aqueous environments. The discussion centers on the fatigue behavior of steels with little or no SCC component.

**Effect of moisture on cyclic crack growth**

Studies of fatigue crack growth (45, 46) have found that materials which are resistant to sustained load cracking suffer an increased fatigue crack growth rate when exposed to water vapor. Logsdon (15) found that distilled water at 520°F (270°C), 1200 psi, had a moderate effect on the crack growth rate of 403 stainless steel.; his results are shown
in Figure 18 along with the heat treatments of the material studied.

Clark (14) generated fatigue crack growth data for 403 stainless steel with a heat treatment similar to #933 in Figure 18 in various marine turbine environments; he found that room temperature distilled water, seawater, and sulfurous acid had little effect on the crack growth over that in air. But in the same environment at 200°F (93°C), there was an enhancement of the crack growth rate. Figure 19 shows a summary of the effect of the various environments he studied; Table 3 summarizes the power law relationship for the curves in Figure 19.

Effect of cyclic frequency

The effect of test frequency on the crack growth rate is best demonstrated by Figures 20 and 21. Figure 20 is the effect on the crack growth rate of an untempered 12% chromium steel; the highest growth rates are at the slowest test frequency. This cyclic frequency dependence is typical of materials susceptible to SCC. Figure 21 shows the growth rate vs frequency at one value of ΔK; the large frequency effect is minimized when the material is tempered at 710°C, where no SCC behavior is noted.

Ferritic steels also have cyclic frequency dependent crack growth in water environments (47), while austenitic stainless steels are not affected by a water environment. (48)
(637) Austenitized at 1750°F (955°C) for 20 hrs, oil quench, tempered at 1140°F (620°C) for 32 hrs.

(933) Austenitized at 1750°F for 16 hrs, oil quench, tempered at 1150°F (627°C) for 27 hrs.

(484) Austenitized at 1750°F for 16 hrs, oil quench, tempered at 1100°F (590°C) for 27 hrs.

Figure 18. Summary of fatigue crack growth data for AISI 403. (15)
Figure 19. Summary of fatigue crack growth data for AISI 403 in various marine turbine environments. (14)
### TABLE 3

**FATIGUE CRACK GROWTH RELATIONSHIPS**

**FOR AISI 403 IN VARIOUS ENVIRONMENTS**

<table>
<thead>
<tr>
<th>Environment</th>
<th>Power Relationship for da/dN (in/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air, 75F</td>
<td>1.6 x 10^{-9} ΔK^{2.4}</td>
</tr>
<tr>
<td>Distilled Water, 75F</td>
<td></td>
</tr>
<tr>
<td>Sea Water, 75F</td>
<td></td>
</tr>
<tr>
<td>Sulfurous Acid, pH2, 75F</td>
<td>3.4 x 10^{-9} ΔK^{2.4}</td>
</tr>
<tr>
<td>Distilled Water, 200F</td>
<td>4.1 x 10^{-9} ΔK^{2.4}</td>
</tr>
<tr>
<td>Sea water, 200F</td>
<td></td>
</tr>
<tr>
<td>Steam, 212F</td>
<td>4.5 x 10^{-9} ΔK^{2.9}</td>
</tr>
<tr>
<td>Sulfurous Acid, pH2, 200F</td>
<td>1.0 x 10^{-10} ΔK^{4.2}</td>
</tr>
</tbody>
</table>

Ref. 14
Figure 20. Effect of frequency and stress intensity of the growth rate of corrosion fatigue cracks in a 12% chromium steel exposed to water. (28)

Figure 21. Growth rates of fatigue cracks in 12% chromium steel as a function of cyclic frequency, environment, and heat treatment. (28)
Gallagher and Wei (44) studied the effect of frequency on 12Ni maraging steel in salt water at stress intensities below $K_{\text{ISCC}}$. This study resulted in fatigue crack growth rates which were higher at the slower frequencies and slower at the higher frequencies. This behavior is similar to that of material which is susceptible to SCC, so that a mild frequency dependence is possible even if there is no SCC crack growth component.

The magnitude of the effect of frequency on the fatigue crack growth rate depends strongly on the environment-material system. Thus, each environment-material system must be characterized separately. Part of the frequency effect may be due to the amount of solution chemistry modification that occurs in the crack tip region. Brown (49) proposed that various forms of localized corrosion have the common feature of local acidification by hydrolysis, but excluded corrosion fatigue from this type of behavior due to the amount of pumping of the electrolyte that can take place. The alternate opening and closing of the crack results in pumping the electrolyte into and out of the crack on each load cycle which promotes mixing. Barsom (50) has reported a corrosion fatigue crack pH of approximately 3 for a 12Ni5Cr3Mo steel cycled at 0.1Hz in a near neutral 3% sodium chloride solution. Additional factors which influence modification of the crack electrolyte are wave form, stress ratio, and test geometry.
Effect of stress wave form

The effect of different wave forms, mentioned previously, was said to have no effect on the crack growth rate in air. A different situation exists in corrosion fatigue; it is illustrated in Figure 22 where the data show that in a sodium chloride solution, the crack growth rates under sinusoidal and triangular stress fluctuations are almost identical but higher than air. However, the environmental effects are negligible when the steel is subjected to a square wave fluctuation. The material in this situation was tested below $K_{ISCC}$, so that the sustained loading effect in the square wave shows negligible effects; thus, the environmental damage below $K_{ISCC}$ occurs only during transient loading. (7)

Effect of stress ratio, $R = \frac{K_{\text{min}}}{K_{\text{max}}}$

Although there was no effect of variations of $R$ in Region II crack growth in air, in corrosion fatigue it is a major variable. Generally, it appears that high $R$ ratios enhance the corrosion component of crack growth, while low $R$ ratios reflect more of the intrinsic material response. This response may be due to the amount of crack opening and closing which occurs during each fatigue cycle. Bamford and Moon (47) and Miglin (48) found that variations in the $R$ ratio affected the fatigue crack growth rates in ferritic and austenitic steels.
Figure 22. Effect of loading wave form on the fatigue crack growth rate of 12Ni5Cr3Mo steel below $K_{ISCC}$ in 3% sodium chloride solution. (7)
Effect of test temperature

Wei (51) found that the fatigue crack growth rates of a high strength aluminum alloy in distilled water is affected by the test temperature; he postulated a thermally activated mechanism for crack growth. The test temperature of the solution may also influence the chemistry of the solution at the crack tip, the kinematic viscosity and/or diffusion (52), all of which are factors that have to be taken into account if the electrochemical process is diffusion controlled.

Corrosion fatigue crack growth at low $\Delta K$ values

Only limited corrosion fatigue crack growth data have been obtained at low $\Delta K$ values. The data suggest that the threshold stress intensity factor, $\Delta K_{th}$, for steel is not affected by an aqueous test environment. Unfortunately, to establish $\Delta K_{th}$ within a reasonable test time, data are obtained at high frequencies where the environment has limited effect on the fatigue crack growth rate.

Paris et al (25) found that the crack growth rates were more sensitive to the stress ratio at the lowest growth rates considered to establish $\Delta K_{th}$ than they are at higher growth rates as in Region II crack growth. They found that in A533 and A508 steels crack growth rates in distilled water were slower than in air in the vicinity of the $\Delta K_{th}$. Similar results have been documented for 5% nickel steels (53).
Clark (14) found that the environment had little effect on the very slow fatigue crack growth rate properties of AISI 403, whereas, the R ratio had a significant effect on the very slow crack growth properties, i.e. the higher the R ratio, the lower the $\Delta K_{th}$. He established that the $\Delta K_{th}$ for 403 in air or water (75F and 200F) is 3.1 KSI in (3.4 MPa m) at a stress ratio of 0.9.

### 2.4.5 Corrosion Fatigue Crack Growth Mechanisms

A discussion of corrosion fatigue crack propagation mechanisms can generally be divided into two types: one type of crack growth is "true" corrosion fatigue due to the presence of an environment when SCC is absent; the other type is stress corrosion crack growth under cyclic loads. However, since the material investigated in this project was not susceptible to SCC (54), the mechanisms for corrosion fatigue crack growth discussed here are confined to those with no SCC component.

Pyle et al (55) developed a working model for active dissolution during corrosion fatigue. Their model accounted for crack development as well as propagation. They recognized that when a metal is exposed to an environment while it is subjected to continuously applied cyclic stress, the extent to which fatigue crack initiation and propagation are influenced will depend on (1) the thermodynamic tendency of
the metal to react, (2) the reaction kinetics, and (3) the type of reaction and reaction products. In aqueous systems, the reaction can involve metal dissolution. They acknowledge the fact that the dissolution process in corrosion fatigue is located at the slip steps produced at the surface of the metal because of their enhanced reactivity. The dissolution can only occur at the step faces exposed to the electrolyte, and the amount of dissolution possible will depend on the rate of dissolution and cycling speed. They believed the process occurs as follows:

Dynamic plastic deformation during the tensile half cycle allows localized dissolution at step edges on the crack front. Reapplication of the tensile stress results in either further plastic deformation or mechanical propagation by brittle fracture. As the crack grows, the importance of dissolution compared to mechanical propagation changes and the environment becomes less important as the crack lengthens. The critical factor in the amount of dissolution that occurs is the slip step spacing.

Devereaux et al (56), while studying an aluminum alloy resistant to SCC in the solution in which they were studying corrosion fatigue, noted a similarity between SCC and corrosion fatigue. And although the crack tip environment in fatigue is of a transient nature, a process was envisioned where anodic dissolution is enhanced by plastic deformation,
which also inhibits the formation of an oxide film; an alternate mechanism would be the successive formation and rupture of an anodic film.

Pelloux (57) postulated that corrosion fatigue in aluminum in saline solutions may be explained by a mechanism of stress sorption cracking, i.e. weakening of metal bonds at the crack tip through the adsorption of the environment or its constituents.

Wei (51), on the other hand, while studying the enhancement of the fatigue propagation rate of aluminum in water, proposed a hydrogen embrittlement mechanism; the acceleration of the crack growth is caused by an increase in the crack tip stress intensity produced by a build-up of hydrogen pressure in internal "voids" ahead of the crack tip. The hydrogen results from the cathodic reduction reaction accompanying the dissolution of aluminum.

2.5 Summary

The literature survey has reviewed the metallurgical and mechanical properties of martensitic stainless steels. It has presented a fracture mechanics approach to fatigue and introduced the variables and mechanisms responsible for fatigue in benign environments. These principles were applied to the problem of corrosion fatigue. The effects of various parameters on the corrosion fatigue behavior of martensitic stainless steels were discussed, and finally some
models for corrosion fatigue crack growth were presented.

However, a definitive description of the corrosion fatigue process is not at hand due to the metallurgical, electrochemical and mechanical aspects of the process which must be taken into account. Although fatigue crack growth laws were presented and are useful from a structural design standpoint, they are of limited value because they do not account for, or incorporate, the environmental effects.

The section on corrosion fatigue outlined the factors which affect fatigue crack growth rates. Since these factors must be systematically controlled in order to sort out their effects, the experimental program of this research work held some of these parameters constant; for example only one waveform (sinusoidal), one stress ratio (R=0.5), and one material heat treatment were employed. The variables were cyclic test frequency, the aqueous environment, and the test temperature. The test matrix and experimental procedure are presented in the following section.
3.0 EXPERIMENTAL PROCEDURE

3.1 Introduction

Since the purpose of this research project was to determine the effect that various environments have on the fatigue crack growth of Type 403 stainless steel, there are a large number of experimental variables which had to be taken into account. These may be broadly classified as metallurgical, mechanical, and environmental. This part of the dissertation describes the experimental details that were employed to determine the effect that the environment had on fatigue using a linear elastic fracture mechanics approach to the problem. The first part of this section gives the details of the apparatus and instrumentation, as well as the material composition and material properties; the second section gives the procedural details.
3.2 Experimental Apparatus

3.2.1 Material

The alloy used in this project was supplied by Crucible, Inc. The mill chemistry is given in Table 4. Enough material was obtained so that all the test samples used in this experimental program came from the same heat to avoid minor heat to heat composition variations. The "as received" microstructure of the material is shown in Plate I.

The heat treatment for the material was similar to that used in the steam turbine industry and is detailed in Table 5; also listed in Table 6 are the mechanical properties for the material after heat treatment. Plate II shows the resultant microstructure consisting of tempered martensite with some delta ferrite.

3.2.2 Specimen Geometry

To establish the minimum fatigue life of a component, it is reasonable to assume that the component contains the largest discontinuity that cannot be detected by an inspection method. Consequently, the most successful approach to study fatigue crack propagation is based on fracture mechanics concepts. This approach utilizes a notched, fatigue cracked specimen with the same type of geometry used for $K_{IC}$ determinations.

The specimen used was a compact toughness specimen
TABLE 4
MILL CHEMISTRY OF 403 STAINLESS STEEL

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.48</td>
<td>0.019</td>
<td>0.01</td>
<td>0.30</td>
<td>11.71</td>
<td>0.10</td>
<td>bal.</td>
</tr>
</tbody>
</table>

TABLE 5
HEAT TREATMENT OF 403 STAINLESS STEEL

Austenitized at 950°C (1750°F) for 1 hr.
Air Cooled.
Tempered at 650°C (1200°F) for 1 hr.

TABLE 6
MECHANICAL PROPERTIES OF 403 STAINLESS STEEL

<table>
<thead>
<tr>
<th>Ultimate Tensile Strength</th>
<th>0.2% Offset Yield Strength</th>
<th>Elongation</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPa</td>
<td>KSI</td>
<td>MPa</td>
<td>KSI</td>
</tr>
<tr>
<td>784</td>
<td>113.8</td>
<td>682.4</td>
<td>100.3</td>
</tr>
</tbody>
</table>
Plate I. Microstructure of "as received" 403 stainless steel. (500X)
Plate II. Microstructure of quenched and tempered 403 stainless steel. (500X)
(CTS) with 0.5 in nominal thickness. It was designed with the dimensions outlined in ASTM specification E399-72. The sample diagram is shown in Figure 23. The specimens were L-T specimens, i.e. the rolling direction was normal to the crack plane and the width was in the direction of the crack propagation. Plate III shows a typical CTS specimen.

The stress intensity factor as a function of the change in applied load and crack length for fatigue is
\[
\Delta K = \frac{\Delta P}{BW^\frac{3}{2}} (Y)
\]

where:
- \( K \) = stress intensity factor, MPa\( \sqrt{m} \) (KSI in)
- \( \Delta K = K_{\text{max}} - K_{\text{min}} \)
- \( \Delta P \) = applied load, N (KIP)
- \( B \) = specimen thickness, m (in)
- \( W \) = specimen width, m (in)
- \( Y = f(a/W) \)
  \[
  = 29.6(a/W)^{1/2} - 185.5(a/W)^{3/2} + 655.7(a/W)^{5/2} - 1017(a/W)^{7/2} + 638.9(a/W)^{9/2}.
  \]

3.2.3 Closed Loop Servo-Hydraulic Fatigue Machine

All the experiments were performed on closed loop servo-hydraulic fatigue machines; one was a 100kip capacity Materials Testing Systems unit and the other one was a 20kip capacity unit manufactured by Instron, Inc. Figure 24 shows a typical closed loop system in a pictorial block diagram. The "closed loop" is a continuous path of
Figure 23. Details of compact-tension specimens (CTS) used in this project.
Plate III. Compact-tension sample used in corrosion fatigue crack propagation studies with LVDT extension tubes in place with teflon blocks.
Figure 24. Block diagram of typical closed-loop hydraulic testing system.
interacting elements. If this path is broken at any point while hydraulic pressure is applied to the servovalve, closed loop control is lost and the hydraulic actuator applies full force.

Testing was conducted in the lowest range necessary in each system to achieve the maximum loads required. All the testing was performed in tension to tension cycling with a sinusoidal wave form in the load control mode, i.e. the load range was held constant as the crack grew.

The $\Delta K_{th}$ determinations were conducted at a test frequency of 40 Hz, while the proagation tests were run at 40, 10, 1, and 0.1 Hz.

The sample was placed into the testing machine by means of a load train, which is diagramed in Figure 25; the details of the corrosion cell are shown in Figure 26 with the load train running through it. The sample grips or clevises and pins were machined from a Type 410 stainless steel (similar in composition to Type 403). The pull rods were machined from Inconel 600, but only a small portion of the lower pull rod, which was covered with teflon tape, was exposed to the solutions. Thus, galvanic coupling due to compositional differences were precluded.

The solution temperature was adjusted by means of heating tape wrapped around a pre-formed steel sheet that could be slipped on and off the teflon corrosion cell. The
Figure 25. Diagram of load train.
Figure 26. Diagram of corrosion cell with load train and sample in place.
temperature was controlled by means of a variac controller.

Naturally, when room temperature air tests were run, the teflon cell apparatus was not employed and the specimen was open to the air. The whole apparatus is picture in Plate IV.

3.2.4 Electrochemical Equipment

Monitoring the open circuit potential was accomplished with a standard calomel electrode (SCE). This electrode was in a saturated solution of potassium chloride located outside the corrosion test cell; it was connected to the test solution by means of a teflon tube with a nylon cord running through it. The chord was saturated with solution to provide conductivity between the two solutions. The specimen and reference electrode were connected to a Wenkin potentiostat to monitor the open circuit potential. A Leeds and Northrup Speedomax recorder were used to record the potential for the duration of a test.

3.2.5 Electrolytes

The electrolytes studied are listed in the test matrix in Table 7. The solutions were made of reagent grade salts and double distilled, demineralized water. The pH was adjusted with sodium hydroxide or the acid of the pertinent salt (such as hydrochloric, phosphoric or sulfuric acid.) The solutions were not deaerated; the only oxygen control exercised was by the boiling of a solution during a test.
Plate IV. Corrosion cell in place in MTS load frame with LVDT, thermometer, and reference electrode in place.
<table>
<thead>
<tr>
<th>Environment</th>
<th>Temperature (C)</th>
<th>Concentration (M)</th>
<th>pH</th>
<th>Freq. (Hz)</th>
<th>ΔK&lt;sub&gt;th&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>100</td>
<td>10</td>
<td>10</td>
<td>40</td>
<td>determin.</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>7, 10</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>25</td>
<td>10</td>
<td>7</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.1</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>25</td>
<td>0.01, 1.0</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.0</td>
<td>2,7,10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>100</td>
<td>0.01</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>40</td>
<td>determin.</td>
</tr>
<tr>
<td>Na&lt;sub&gt;3&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>100</td>
<td>1.0</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Na&lt;sub&gt;4&lt;/sub&gt;SiO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>100</td>
<td>1.0</td>
<td>10.5</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Constants: R = 0.5
Waveform: sinusoidal
3.3 Experimental Techniques

The crack growth measurements utilized a number of approaches, each of which is described in detail in this section. In addition, the computer programs used for data reduction are described along with a sample calculation for determining crack lengths from voltage readings.

3.3.1 Specimen Preparation

Surface finish was not a critical parameter for this test program. Each sample was sanded to a 240 grit finish to provide a uniform surface finish, however. All the sanding was done in a direction perpendicular to the direction of crack propagation. Specimens which were tested in air using optical crack length measurements were finished through 600 grit paper. Then the area through which the crack would grow was polished with 0.03 μ alumina using a small polishing wheel attached to a 3/8 in drill.

For precracking purposes all samples were polished in this manner.

3.3.2 Precracking Procedure

All the samples were precracked in air to an average 0.060 in beyond the machine notch. This type of precracking had a twofold purpose: the first was to generate a crack in the specimen with a stress intensity history which was known and which would not influence the mechanical crack growth during subsequent fatigue study; the second
purpose was to produce a sharp crack with a small plastic zone sufficiently distant from the machined notch so as to be free from residual stresses.

Precracking was accomplished in the load control, tension-tension sinusoidal mode with a stress ratio, $R=0.1$. This crack extension was accomplished in a series of steps starting at a high stress intensity, $27.5\text{MPa m} \ (25\text{KSI in})$ and decreasing to a $\Delta K$ value which would be the initial value for subsequent corrosion fatigue testing, $16.5\text{MPa m} \ (15\text{KSI in})$. All precracking was done at a frequency of 10 Hz.

3.3.3 Measurement Techniques

Crack lengths were measured in two ways. In air, when there was no corrosion cell, the crack was measured optically on the sample surface with a travelling microscope or via a compliance technique using a linear variable differential transformer (LVDT). A Gaertner 50X travelling microscope was used for the optical measurements; the crack length could be determined to $\pm 0.001 \text{in}$. Plate V shows a sample in the MTS load train with the LVDT attached and the travelling microscope in place.

The LVDT is an electromechanical transducer that produces an electrical output proportional to the displacement of a separate movable core. When the core is in the center position (Figure 27, core at 0), the output is zero; when the core is moved, a differential voltage is induced,
Plate V. Compact-tension sample in MTS load frame with LVDT attached and traveling microscope in place.
Figure 27. Working diagram for Shaevitz LVDT.
which varies linearly with changes in the core position. Figure 27 is a continuous plot of output voltages vs core position as a straight line passing through the origin.

The LVDT was mounted to the sample with teflon blocks and extension tubes as shown in Plate III. The LVDT body was mounted to one side of the machined notch, while the core was attached to the other side. Thus, as the crack grew, the specimen opened and the voltage difference, $\Delta V$, increased. The 440.22 A.C. conditioner on the MTS console was used as the signal conditioner. For long range testing, an Esterline-Angus recorder was used to record $\Delta V$. Two different LVDT's were used for this work; the $\Delta K_{\text{th}}$ determinations required a more sensitive LVDT than that used for the crack propagation studies.

Measurement of a crack length with an LVDT is based on the principle that as the crack grows, the specimen compliance increases thereby increasing the displacement at the gage line. Standard values of the compliance as a function of crack length are available in the literature for compact-tension specimens.\(^{(58)}\) These values correspond to the load line displacement. The compliance obtained from a fatigue test correspond to the gage line displacements. The standard load line values were converted to gage line values by means of similar triangles, as shown in Figure 28.

By using the compliance technique, it was possible to convert $\Delta V$ to crack length; a sample calculation is shown
Figure 28. Schematic of sample showing the load line and gage line conversion.

\[ \frac{Y}{b} = \frac{a + x}{a} \]

\[ \frac{BE \Delta \delta}{\Delta P}_{GL} = \left( \frac{a + x}{a} \right) \left( \frac{BE \Delta \delta}{\Delta P} \right)_{LL} \]
in Figure 29. Because of occasional variability in data collection, and as a correction for the shape of the crack front, it was necessary to insure that the $\Delta V$ measured at the start and end of a fatigue test was exactly equal to the initial and final crack lengths. Figure 30 shows a fractured surface after testing was completed. The Gaertener 50X traveling microscope was used to visually determine the average initial and final crack lengths.

3.3.4 Crack Growth Rate Test Procedure

All the tests were conducted in a similar manner whether in air or in solution. This section describes the test assembly procedure, LVDT placement, and load monitoring.

Initially, the teflon blocks were tightly bolted to the sample, and then the extender tubes were screwed into the blocks; the sample was then placed in the clevises and attached to the corrosion cell. Then the circular heater was placed around the cell, and the whole system with a teflon lid added, was screwed into the MTS load frame.

The LVDT was then positioned in its aluminum housing at the end of the extender tubes. The MTS oscilloscope was used to monitor the LVDT signal and insure that it was well within the linear range. Once the LVDT was mounted, a check on the load-displacement response was run; no test was run unless there was less than 0.15% hysteresis.
\[ \Delta \delta = \Delta V \cdot \text{slope of calibration curve for LVDT} \]

\[ \Delta V = 0.88 \text{ V (typical LVDT initial voltage reading)} \]

\[ \text{slope} = 0.00522 \text{ in/V} \]

\[ \Delta \delta = 0.00459 \text{ in.} \]

\[ \lambda = \frac{BEA \delta}{\Delta P} \quad \text{(compliance)} \]

\[ B = 0.5 \text{ in (specimen thickness)} \]

\[ E = 3 \times 10^7 \text{ lbs/in}^2 \quad \text{(elastic modulus)} \]

\[ \Delta P = 1300 \text{ lbs (test load range)} \]

\[ \lambda = 53.00 = f(a/W) \]

Then referring to the conversion of compliance values at the load line to compliance values at the gage line or by means of the polynomial fitted by the computer,

\[ a/W = 0.45 \quad \text{or} \quad a = 0.900 \text{ in.} \]

**Figure 29.** Typical calculation for conversion of \( \Delta V \) data to crack length.
Figure 30. Example of a fracture surface after fatigue testing showing area of machine notch, pre-crack zone on fatigue surface and final failure where the sample was pulled apart.
The heater on the cell was then plugged in and the specimen was allowed to reach 100°C, the test temperature. Meanwhile the test solution was brought to boiling on a lab burner. Then the solution was added to the test cell, and the whole system was allowed to reach the test temperature (usually a 10 min wait). Meanwhile, the reference electrode and a condenser were positioned.

Since the load control mode was used for testing, the MTS Amplitude Measurement Module (Model 440.51) and oscilloscope were employed. The load was monitored by setting the variable limits on the peak detector and setting error limits (±0.2%) on the load, then by watching the oscilloscope, the output signal was made to fall within these limits by adjusting the set point of span of the load signal.

For the 10Hz tests, the peak detector and oscilloscope were employed to measure ΔV. For the 1Hz and 0.1Hz test, an MTS 430 Digital Indicator with an Esterline-Angus recorder connected to it were used to measure ΔV.

The test sample was kept entirely immersed in solution for the duration of every test. For tests involving a loss of solution due to the long test duration, an additional solution reservoir was attached to the corrosion cell to ensure that the solution level did not drop.
3.3.5 Fatigue Crack Growth Data Reduction

Fatigue crack growth results are generally presented as log of the crack growth rate \( \frac{da}{dN} \) vs log of the stress intensity range, \( \Delta K \). From this plot a fatigue crack growth law of the form:

\[
\frac{da}{dN} = C(\Delta K)^n
\]

where \( C \) is a constant and \( n \) is the slope of the line in the log-log plot and can be calculated.

Data is obtained in terms of crack length, \( a \), measured optically or with a transducer, and the number of cycles, \( N \). This leads to a plot of crack length \( a \), vs the number of cycles, \( N \). From this, the derivative of \( a \) vs \( N \) at a number or points must be obtained along with the corresponding value of \( \Delta K \).

An incremental polynomial technique was used to convert a vs \( N \) data to \( \frac{da}{dN} \) vs \( \Delta K \). This method involves fitting a second order polynomial to sets of successive a vs \( N \) data points. Fitting functions are used which minimize the deviation between the fitted and observed crack lengths. The \( \frac{da}{dN} \) values are calculated from the derivative of the function of \( a \) vs \( N \).

Figure 31 shows schematically how the a vs \( N \) data is converted to \( \log \frac{da}{dN} \) vs \( \log \Delta K \). Since the a vs \( N \) curve is best described as parabolic, successive sets of seven data points were fit to a second order polynomial of the form (59)
Figure 31. Schematic diagram for $a$ vs $N$ data reduction by means of incremental polynomial method.
\[ a = b_0 + b_1 \frac{(N-C_1)}{C_2} + b_2 \frac{(N-C_1)^2}{C_2^2}, \]  
(7)

where \( b_0, b_1, \) and \( b_2 \) are regression parameters determined by a least squares criterion. \( C_1 \) and \( C_2 \) are scaling factors.

Then the crack growth rates are determined from the derivative of the above expression which is:

\[ \frac{da}{dN} = b_1/C_2 + 2b_2 \frac{(N-C_1)^2}{C_2^2}. \]  
(8)

The conversion of \( \Delta V \) data to crack length was accomplished by means of a computer program. The data for each sample evaluated consisted of the number of points considered, \( P_{\text{max}}, P_{\text{min}}, \) and the correction factor; then the \( N \) vs \( \Delta V \) data was read into the computer. The output consisted of crack length, \( a; \) number of cycles, \( N; \) crack growth rate, \( \frac{da}{dN}; \) the stress intensity range, \( \Delta K. \) This program also punched out a card deck of \( \log \frac{da}{dN} \) vs \( \log \Delta K, \) which was used with another program to generate the best fit straight line through the data points.

3.3.6 Fatigue Crack Threshold Determinations

The procedure for load monitoring, LVDT installation, \( \Delta V \) determinations, and test start-up were the same as in the previous section. However, in this portion of the program, the objective was to stop the crack growth by gradually decreasing the stress intensity range, viz the applied loads; all these tests were run at 40Hz.

The air determinations were made by following the crack with the travelling microscope and the LVDT; crack extension of 0.005 in or less could not be detected with the LVDT
because of the scatter in the $\Delta V$ readings created by cycling the sample at 40Hz. Also, as the load was decreased, the crack opening decreased, decreasing the $\Delta V$ and increasing the sampling error. The travelling microscope could detect crack growth to $\pm 0.001$ in.

The procedure here was to start the crack growing at the same value of $\Delta K$ at which the precracking had stopped, and allow the crack to extend beyond the previously formed plastic zone (approximately 0.020 in). Then the stress intensity range was decreased by 10% and the crack growth monitored. The crack growth rate and average $\Delta K$ were calculated and plotted as the data were generated. This step-wise procedure was continued until no crack extension was detected for $1 \times 10^5$ cycles. When this point was reached, the load was then increased to the level before the crack stopped growing to insure that it would indeed grow again. Thus, it was possible to bracket the value of $\Delta K_{th}$.

3.4 Fractography

After fatigue testing, the fracture surface of all the specimens was coated with Krylon acrylic spray to avoid further corrosion. Fractographic studies were conducted on the fracture surface using a JEOL scanning electron microscope. Since it was not possible to mount the entire sample into the microscope, the fracture surface was cut from the sample. The acrylic spray was removed from the sample prior
to its insertion into the microscope. Acetone immersion and ultrasonic cleaning were used for this purpose.

Fractographs were taken at low ΔK, medium ΔK, and high ΔK values where appropriate. At every ΔK location, pictures were taken at three magnifications.
4.0 EXPERIMENTAL RESULTS

4.1 Introduction

This section presents the results of this research work. It is divided into groups of data obtained in a particular electrolyte, i.e. the data are presented as results obtained in air, water, chlorides, etc. Fatigue crack growth data are followed by the fractographic results obtained in the scanning electron microscope. The open circuit potentials measured during the fatigue tests are summarized in a figure at the end of this section.

4.2.1 Fatigue Crack Growth Rates in Air

Figure 32 shows a plot of crack length vs the number of cycles for a sample fatigued in air at room temperature at 10 Hz; the figure shows the crack lengths obtained by the optical and compliance methods. Close agreement between the techniques is evident. Figure 33 is the plot of \( \frac{da}{dN} \) vs \( \Delta K \) for the data shown in Figure 32.

Figure 34 shows the results of tests in air at 10 and 40 Hz and at 25 and 100°C. There is little change in the crack growth rates due to the change in test frequency or temperature.
Air, 25°C
Crack Length vs. Cycles
R = 0.5, 10 Hz

Figure 32. Crack length vs cycles in air showing agreement between compliance measurement and microscope.
Figure 33. Fatigue crack propagation rate, da/dN, vs stress intensity range, ΔK, in air at 25°C showing agreement between optical and compliance techniques.
Figure 34. Fatigue crack growth rate vs $\Delta K$ in air at 10 and 40 Hz, 25 and 100 C.
The Paris power law for the linear portion of the crack growth is

\[
da/dN = 7.11 \times 10^{-11} (\Delta K)^{2.29} \text{ (m/cycle)} \quad (9)
\]

\[
eq 2.80 \times 10^{-9} (\Delta K)^{2.29} \text{ (in/cycle)}, \quad (10)
\]

which agrees with the crack growth rates reported by Barsom (7) and listed in Table 2 for martensitic steels. These results are also in agreement with those reported by Clark (14) and Logsdon (15).

Figure 34 also shows the slow crack growth region of \( da/dN \) where \( \Delta K_{th} \) was determined. That value is

\[
5.2 < \Delta K < 5.7 \text{ MPa}\sqrt{m}
\]

\[
4.7 < \Delta K < 5.2 \text{ KSI}\sqrt{in}
\]

for \( R=0.5 \).

4.2.2 Fractographic Results in Air

Plates VI and VII are collections of fractographs of the samples fatigued in air at 25 and 100°C, respectively, at 10 Hz. The rows of pictures represent three regions of the fracture surface investigated: 20\( \Delta K \), 25\( \Delta K \), and 30\( \Delta K \). The three columns are three magnifications of the areas investigated.

Both of these plates show striation steps which when viewed at 10,000X are seen as the striations for crack growth whose spacing corresponds with the crack growth rate for the particular \( \Delta K \)'s examined. These surfaces show no sign of intergranular crack growth.
Plate VI. Fracture surface of sample fatigued in air at 25C R=0.5, 10Hz at three stress intensity ranges ($\Delta K$) at three magnifications, 500X, 1000X, and 10,000X.
<table>
<thead>
<tr>
<th>10 ΔK</th>
<th>10μm</th>
<th>1μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 ΔK</td>
<td>10μm</td>
<td></td>
</tr>
<tr>
<td>20 ΔK</td>
<td>10μm</td>
<td></td>
</tr>
</tbody>
</table>
Plate VII. Fracture surface of sample fatigued in air at 100°C, R=0.5, 10Hz at three stress intensity ranges and at three magnifications, 500X, 1000X, and 10,000X.
Plate VII.
Plates VIII and IX show the fracture surfaces of samples cycled at 40 Hz; at $\Delta K > 15$, there are signs of fatigue striations corresponding to crack extension, but at $\Delta K = 5$, there are no clear striation markings. This result is probably due to the very low crack growth obtained in this region.
Plate VIII. Fracture surface of sample fatigued in air at 25°C, 40Hz at two stress intensity ranges and at three magnifications, 500X, 1000X, and 5000X.

Air - 25°C - 40 Hz
Plate IX. Fracture surface of sample fatigued in air at 25°C, 40Hz at stress intensity ranges where $\Delta K_{th}$ was determined and shown at three magnifications, 500X, 1000X, and 10,000X.
4.3.1 Fatigue Crack Growth Rates in Water

The results of fatigue crack growth in water are shown in Figures 35 and 36. Figure 35 shows the effect that cyclic frequency has on the crack growth rate in water at 100°C; the 40Hz data have growth rates lower than that at 10Hz, while at 1Hz and 0.1Hz, there is not much difference in the growth rates observed, although there is a frequency effect at the lower $\Delta K$ region. The air line is included to show that at all frequencies, there is an increase in the crack growth rates above those in air.

Figure 36 shows the slow crack growth area where the $\Delta K_{th}$ was determined. In water, 100°C, $R=0.5$, 40Hz,

\[ 4.4 < \Delta K_{th} < 5.2 \text{ MPa}\sqrt{m}, \]
\[ 4.0 < \Delta K_{th} < 4.7 \text{ KSI}\sqrt{in}. \]

Figure 37 shows the crack growth rates in water at 25 and 100°C with the pH of 7 and 10 fatigued at 10Hz. It is evident that the pH value has no effect on the crack growth, but the solution temperature does. The crack growth rate at 25°C is not as low as in air nor as high as in boiling water.

The power law expressions for fatigue crack growth in water under the various conditions studied are listed in Table 8.
Figure 35. Fatigue crack growth rate vs $\Delta K$ in water, pH7, 100°C tested at various frequencies.
Figure 36. Fatigue crack growth rates vs ΔK in water, pH7, 100°C tested at various frequencies showing the ΔKₜₗₐₜ region.
Figure 37. Fatigue crack growth rate vs ΔK in water, 25 and 100°C, pH 7 and 10 tested at 10Hz.
<table>
<thead>
<tr>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Frequency (Hz)</th>
<th>$C$ (m/cycle)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>100</td>
<td>40</td>
<td>$2.8 \times 10^{-9}$</td>
<td>1.46</td>
</tr>
<tr>
<td>7, 10</td>
<td>100</td>
<td>10</td>
<td>$2.3 \times 10^{-9}$</td>
<td>1.75</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>0.1</td>
<td>$9.0 \times 10^{-12}$</td>
<td>3.44</td>
</tr>
<tr>
<td>7, 10</td>
<td>25</td>
<td>10</td>
<td>$1.9 \times 10^{-9}$</td>
<td>1.45</td>
</tr>
</tbody>
</table>
4.3.2 Fractographic Results in Water

Plate X shows the fracture surface of a sample fatigued in water, pH7, 100°C at 40Hz. At ΔK20, there is evidence of both transgranular and intergranular fracture; at ΔK30, the intergranular features are no longer evident, and the fracture mode is primarily transgranular with secondary cracking or branching evident.

Plate XI is the fracture surface at the low ΔK (ΔK5) value where the ΔKth was determined. The surface retained its mixed mode character, but it seems that intergranular type fracture predominates.

Plate XII shows the fracture surface of a sample fatigued at 10Hz, 100°C, pH6.5. At ΔK20 and 25, the features appear intergranular with the grain boundary areas outlined; at ΔK30, the surface becomes more transgranular with secondary cracking appearing.

Plates XIII and XIV are the surfaces of samples fatigued at 1 and 0.1 Hz, respectively. At these slower frequencies, there are less intergranular features at ΔK20 and 25 than on the sample cycled at 10Hz; in fact, there are areas with striation spacings on the samples fatigued at the slower frequencies. These areas of transgranular fracture are where the crack growth rate is slower than it is in samples cycled at 10Hz. At ΔK30, secondary cracking is evident, which may account for the faster growth rate at ΔK30,
Plate X  Fracture surface of sample fatigued in water, pH7, 100°C, at 40 Hz showing two stress intensity range areas at three magnifications 500X, 1000X, and 5000X.
Plate XI. Fracture surface of sample fatigued in water, pH7, 100C at 40Hz showing two stress intensity range areas where $\Delta K_{th}$ was determined at three magnifications: 500X, 1000X, and 10,000X.
Plate XII. Fracture surface of sample fatigued in water, pH 6.5, 100°C at 10Hz at three stress intensity ranges and shown at three magnifications: 100X, 500X, and 1000X.
Plate XII.
Plate XIII. Fracture surface of sample fatigued in water, pH7, 100°C at 1Hz at three stress intensity ranges and three magnifications: 100X, 500X, 1000X.
Plate XIII.
Plate XIV. Fracture surface of sample fatigued in water, pH7, 100°C at 0.1 Hz at three stress intensity ranges and shown at three magnifications: 500X, 1000X, and 10,000X.
0.1 Hz than at $\Delta K_{30}, 10$Hz.

Plates XV and XVI show some high magnification photomicrographs of transgranular and intergranular fracture areas. Plate XV shows a mixed mode with a grain boundary delineated and a grain with striation spacings of $\sim 0.33\mu$, which correspond to the observed crack growth rate at $\Delta K_{20}$. Plate XVI is a grain which does not have any evidence of striations on its surface. These two plates show that it is possible to use the high magnification capability of SEM to differentiate intergranular type of crack paths from transgranular growth where striation spacings are left on the fracture surface.

Plate XVII is a fractograph of a sample fatigued in room temperature water; it too shows the mixed mode fracture at low $\Delta K$'s with more secondary cracking appearing at the higher $\Delta K$. 
Plate XV. Fracture surface of sample fatigued in water, pH 6.5 at 10 Hz with striation spacing of ~0.3 μ at magnifications: 500X, 1800X, and 10,000X.
Plate XVI. Fracture surface of sample fatigued in water, pH 6.5, 100°C at 10Hz shown at ΔK20 showing a grain face with no evidence of striation spacings.
Plate XVII. Fracture surface of sample fatigued in water, pH7, 24C at 10Hz at three stress intensity ranges and three magnifications: 100X, 500X, and 1000X.
Plate XVII.
4.4.1 Fatigue Crack Growth Rates in Sodium Chloride

In these solutions, tests were run at two concentrations of chloride, 1M and 0.01M at pH 2, 7 and 10.

Figure 38 shows the effect of test frequency on the fatigue crack growth rates in 0.01M sodium chloride, pH10, 100C. These results are similar to the growth rates obtained in water. The sample cycled at 40Hz had a crack growth rate faster than in air but slower than at 10Hz. The frequency effect was similar to the water results in that test frequencies slower than 10Hz did not produce an increase in the crack growth rate.

Figure 39 is slow crack growth region where $\Delta K_{th}$ was determined. In sodium chloride, 100C, pH10, R=0.5, 40Hz

$$4.4 < \Delta K_{th} < 5.2 \text{ MPa}$\sqrt{m}$,
$$4.0 < \Delta K_{th} < 4.7 \text{ Ksi}$\sqrt{in}.$$

An identical value for $\Delta K_{th}$ was obtained in 0.01M sodium chloride, pH2. Thus, solution pH had little influence on $\Delta K_{th}$.

Figure 40 shows the fatigue crack growth rates in 1M sodium chloride at 10Hz, pH 2, 7, and 10 at 100C. The crack growth rate was almost identical to the growth rate obtained in water, which also coincided with the growth rates obtained in 0.01M sodium chloride, pH10, 100C. Consequently, the effect of the chloride anion concentration and solution pH was no worse than that produced by boiling water.
Figure 38. Fatigue crack growth rates vs $\Delta K$ in 0.01M sodium chloride, pH10, 100°C tested at various frequencies.
Figure 39. Fatigue crack growth rates vs $\Delta K$ in 0.01M sodium chloride, pH10, 100°C tested at various frequencies and showing the $\Delta K_{th}$ region.
Figure 40. Fatigue crack growth rates vs $\Delta K$ in 1M sodium chloride, 100°C cycled at 10Hz at various pH's.
Figure 41 shows the data of chloride solutions and water at room temperature, 10Hz. The crack growth rate is faster than in air, but less than in the boiling solutions. And once again, the effect of chloride was no worse than that produced by water.

Table 9 lists the power law coefficients for the tests conducted in chloride solutions under various conditions.

4.4.2 Fractographic Results in Sodium Chloride

Plate XVIII is the fracture surface of a sample cycled at 10Hz, 100C in 0.01M sodium chloride, pH10; Plates XIX and XX are of samples cycled at 10Hz, 100C, in 1M sodium chloride pH2 and 10, respectively. All three samples have similar fracture features, which are like the surfaces produced in water, 100C, 10Hz.

Plates XXI and XXII show the samples fatigued at room temperature in 0.01M and 1M sodium chloride, pH10, respectively. There is less intergranular fracture in both these samples than on the samples fatigued at 100C; this appearance is also similar to the room temperature water results.

Plates XXIII and XXIV show the fracture surface of samples used to determine the $\Delta K_{th}$ values at pH 2 and 10 respectively. The features of mixed mode cracking are apparent in both plates, which are similar to the water results.
Figure 41. Fatigue crack growth rate vs $\Delta K$ in sodium chloride and water, 25°C cycled at 10Hz.
### TABLE 9

**POWER LAW COEFFICIENTS FOR FATIGUE CRACK GROWTH RATES IN SODIUM CHLORIDE SOLUTIONS**

\[
da/dN = C(\Delta K)^n
\]

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Frequency (Hz)</th>
<th>C (m/cycle)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>10</td>
<td>100</td>
<td>40</td>
<td>3.2 x 10^{-9}</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>1.9 x 10^{-9}</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>9.5 x 10^{-12}</td>
<td>3.45</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td></td>
<td></td>
<td>9.5 x 10^{-12}</td>
<td>3.46</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>10</td>
<td>7.4 x 10^{-10}</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>2.7,</td>
<td>100</td>
<td>10</td>
<td>1.9 x 10^{-9}</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>25</td>
<td>7.4 x 10^{-10}</td>
<td>1.71</td>
<td></td>
</tr>
</tbody>
</table>
Plate XVIII. Fracture surface of a sample cycled in 0.01M sodium chloride, pH10, 100C at 10Hz at three stress intensity ranges at three magnification: 100X, 500X, and 1000X.
Plate XVIII.
Plate XIX. Fracture surface of sample cycled in 1M sodium chloride, pH2, 100C at 10Hz at three stress intensity ranges shown at three magnifications: 100X, 500X, and 1000X.
Plate XX. Fracture surface of a sample fatigued in 1M sodium chloride, pH10, 100C at 10Hz at three stress intensity ranges and at three magnifications: 100X, 500X, and 1000X.
Plate XXI. Fracture surface of a sample fatigued in 0.01M sodium chloride, pH10, 24°C at 10Hz at three stress intensity ranges and shown at three magnifications: 100X, 500X, and 1000X.
0.01M NaCl - pH10 - 24°C
Plate XXII. Fracture surface of sample fatigued in 1M sodium chloride, pH10, 25°C at 10Hz at three stress intensity ranges and shown at three magnifications: 100X, 500X, and 1000X.
Plate XXII.
Plate XXIII. Fracture surface of a sample used to determine $\Delta K_{th}$ at low stress intensity ranges, photographed at three magnifications: 100X, 500X, and 1000X.
Plate XXIV. Fracture usrface of a sample fatigued in 0.01M sodium chloride, pH10, 100C at 40Hz at low stress intensity ranges used to determine $\Delta K_{th}$, photographed at three magnifications: 100X, 500X, and 1000X.
There was no evidence of pitting on these samples despite the fact that 403 stainless steel is susceptible to pitting. (2)

4.5.1 Fatigue Crack Growth Results in Sodium Sulfate

Figure 42 plots the fatigue crack growth rates in 0.01M and 1M sodium sulfate, 100°C at 10 and 40Hz. The results coincide with the chloride and water results at these frequencies; the growth rate is unaffected by a change in pH or anion concentration. This figure also shows the low crack growth rate area where $\Delta K_{th}$ was determined.

In sodium sulfate, 100°C, $R=0.5$, pH10, 40Hz,

$4.4 < \Delta K_{th} < 5.2 \text{ MPa}\sqrt{\text{m}},$

$4.0 < \Delta K_{th} < 4.7 \text{ KSI}\sqrt{\text{in}},$

which is the same value obtained in water.

Table 10 lists the power law coefficients for crack growth rates in sulfate solutions at 100°C.

4.5.2 Fractographic Results in Sodium Sulfate

Plate XXV shows the photomicrographs of a sample fatigued in 1M sodium sulfate, 100°C, pH10, at 10Hz. Only one fracture surface is shown here because of the similarities between these surfaces and those in chloride and water. This sample shows evidence of intergranular cracking at the lower $\Delta K$'s and secondary cracking at the higher $\Delta K$'s.
Figure 42. Fatigue crack growth rates vs ΔK in 0.01M and 1M sodium sulfate, 100°C tested at 10 and 40Hz.
### TABLE 10

**POWER LAW COEFFICIENTS FOR FATIGUE CRACK GROWTH RATES IN SODIUM SULFATE SOLUTIONS**

\[
da/dN = C (\Delta K)^n\]

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Frequency (Hz)</th>
<th>C          (m/cycle)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>10</td>
<td>100</td>
<td>10</td>
<td>2.3 x 10^{-9}</td>
<td>1.75</td>
</tr>
<tr>
<td>0.01</td>
<td>10</td>
<td>100</td>
<td>10</td>
<td>2.0 x 10^{-9}</td>
<td>1.75</td>
</tr>
</tbody>
</table>
Plate XXV. Fracture surface of sample fatigued in 1M sodium sulfite, pH7, 100°C at 10Hz at three stress intensity ranges and at three magnifications: 100X, 500X, and 1000X.
Plate XXV.
The results of fatigue crack growth tests in sulfate solutions at 100°C is that the anion concentration and solution pH produce behavior that is no worse than that produced by water at that temperature.

4.6.1 Fatigue Crack Growth Rates in Sodium Phosphate and Sodium Silicate

Figure 43 shows the fatigue crack growth results in 1M sodium phosphate and 1M sodium silicate, 100°C at 10Hz. In these solutions, the material had growth rates similar to those obtained in air. This figure also shows the low crack growth area used to obtain the $\Delta K_{th}$ in sodium phosphate, which was

$$5.2 < \Delta K_{th} < 5.7 \text{ MPa}\sqrt{m},$$
$$4.7 < \Delta K_{th} < 5.2 \text{ KSI}\sqrt{in}.$$

These values were identical to the $\Delta K_{th}$ values obtained in air.

Table 11 lists the power law coefficients obtained for these solutions.

4.6.2 Fractographic Results in Sodium Phosphate and Sodium Silicate

Plate XXVI shows the fracture surface of a sample fatigued in sodium phosphate, pH10, 100°C at 10Hz. The surface shows no evidence of intergranular cracking or dissolution. It is possible to measure striation spacings of ~0.1μ at $\Delta K_{25}$ which corresponds to the crack growth rate at that $\Delta K$. 
Figure 43. Fatigue crack growth rate vs $\Delta K$ in 1M sodium phosphate and 1M sodium silicate at 100°C.
TABLE 11

POWER LAW COEFFICIENTS FOR FATIGUE CRACK GROWTH RATES IN SODIUM PHOSPHATE SODIUM SILICATE SOLUTIONS

\[ \frac{da}{dN} = C(\Delta K)^n \]

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Frequency (Hz)</th>
<th>C (m/cycle)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}_3\text{PO}_4 )</td>
<td>10</td>
<td>100</td>
<td>10</td>
<td>( 1.3 \times 10^{-11} )</td>
<td>2.73</td>
</tr>
<tr>
<td>( \text{Na}_4\text{SiO}_4 )</td>
<td>10.5</td>
<td>100</td>
<td>10</td>
<td>( 2.5 \times 10^{-11} )</td>
<td>2.55</td>
</tr>
</tbody>
</table>
Plate XXVI. Fracture surface of sample fatigued in 1M sodium phophate, pH10, 100°C at 10Hz at three stress intensity ranges and at three magnifications: 500X, 1000X, and 5000X.
Plate XXVI.
value. This surface resembles that produced by fatigue in air (Plates VI and VII).

No fractographic studies were conducted on samples fatigued in sodium silicate solutions because of the precipitate which deposited on the sample. Plate XXVII shows a sample fatigued in the silicate solution with the deposit on it. It was not possible to remove the precipitate without affecting the substrate.

4.7 Open Circuit Potentials

Figure 44 shows the open circuit potentials vs pH of 403 stainless steel in the solutions studied. The potentials were measured during the length of a fatigue test, but little change was noted in the measured value during a test, consequently, the values plotted on this figure are average values.

There was no trend in the potential from one anion to another. But the potentials did become more active as the solution pH became more acidic as noted in the chloride solutions.

The hydrogen stability lines are also plotted on this figure. These lines correspond to the reaction

$$H_2 = 2H^+ + 2e \quad (11)$$

at 25 and 100°C.
Plate XXVII. Fracture surface of a sample fatigued in 1M silicate, pH10.5, 100C at 10Hz. Deposit is evident on the fatigue fracture surface.
Figure 44. Open circuit potentials vs solution pH measured during fatigue crack propagation tests.
5.0 DISCUSSION

5.1 Introduction

This section is organized by effects produced on the crack propagation by the variation in electrolytes, the solution pH, and test frequency. A model is presented for crack growth with the aim of explaining the crack growth behavior documented.

5.2 Effect of Environment

5.2.1 Air

In this research program, air was used as a reference environment despite the fact that Speidel (28) and Barsom (7) have noted corrosion fatigue effects in materials tested in air and compared to behavior in vacuum. The results from this work, however, have agreed favorably with those documented in the literature, indicating that air can indeed be a reference environment for 403 stainless steel. The fractographic studies of air environment samples indicate that the crack propagation is by the alternate blunting and sharpening process.

5.2.2 Water

The experimental results have shown that water is sufficient to produce an effect on the crack growth rate in all
the experimental conditions studied. This result is somewhat at variance with the published results of Logsdon (14) and Clark (15); they found that at room temperature, a distilled water environment had no effect on the fatigue crack growth rates. The conflict between these results is probably due to the difference in test parameters, such as the R ratio and test frequencies, as well as material heat treatment. There was agreement, however, in the boiling water effect, which increased the crack propagation rates in all cases.

The appearance of the fracture surfaces of samples cycled in water indicate that there is more occurring in the water environment than just the mechanical damage of cyclic stressing. There is some evidence of striations in both the 25 and 100C water samples, but the appearance of intergranular features indicate that either dissolution or some other effect is aiding the crack growth. Since this material has been heat treated at a temperature where it is immune to stress corrosion cracking (Figure 10), the idea of imposing a stress corrosion component on the corrosion fatigue effect cannot be used to explain the enhanced crack growth rate over that in air.

The presence of a water environment became less of a factor at the low stress intensity range as the $\Delta K_{th}$ point was reached. Clark (15) observed a similar result when he
determined $\Delta K_{th}$ for 403 stainless steel in a water environment. Paris et al. (25) found that the environmental effect decreased at the low stress intensity ranges when they investigated the corrosion fatigue crack propagation behavior of A533 steel in water.

The problem in determining $\Delta K_{th}$ is that the frequencies used to determine the $\Delta K_{th}$ in a reasonable length of time are too rapid to allow the solution to have much of an effect. In addition, as the $\Delta K_{th}$ is approached, the amount of crack opening is decreased which decreases the accessibility of solution to the crack tip area. The combination of these processes lessens the importance of the solution on the $\Delta K_{th}$ value. In this research project, $\Delta K_{th}$ is only 14% less than it is air. An examination of the fractographs in the $\Delta K_{th}$ area in water, however, does show that the solution played a part in the crack growth process. Plate XI shows the intergranular character of the fracture surface at $\Delta K_{th}$. But the dissolution component was insufficient to accelerate the crack growth at these slow intensity levels. Figure 45 is a summary of the $\Delta K_{th}$ measured as a function of environment.

5.2.3 Sodium Chloride and Sodium Sulfate

The results have shown that the addition of either of these anions in either low (0.01M) or high (1M) concentration does not produce a fatigue crack growth rate either slower
Figure 45. Summary of the effect of the different environments studied and their effect on $\Delta K_{th}$. 

\[ \Delta K_{th} \text{ vs Environments} \]
or faster than water alone. These anions do produce a shift in the open circuit potential (Figure 44) which is pH dependent, but this shift is not significant in terms of fatigue crack growth rate.

Both of these salts have similar properties, which may account for their similar effect on 403 stainless steel. Both of these salts dissociate easily in aqueous solutions and both are pitting agents. Type 403 stainless steel is known to be susceptible to pitting attack. (2) The aqueous solutions of these salts are unbuffered so that although the pH of the bulk solution remained unchanged during a test, there are areas where localized acidification may occur. (49, 61) There is some doubt, however, if the acidification did occur, it it could remain localized due to the pumping action occurring as the sample is cycled.

Galvele (61) has found that the exposure of bare metal in the presence of a chloride solution (through straining electrode experiments) does not necessarily lead to localized corrosion unless the metal electrode potential is equal to or higher than the pitting potential. Shalaby (62) measured the pitting potentials of 403 stainless steel in sodium chloride and sodium sulfate solutions; these are listed in Table 12. Comparing these to the measured open circuit potentials plotted in Figure 44, indicates that the test sample was below the pitting potential in most cases; of course, the situation at the crack tip may be
<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration (M)</th>
<th>pH</th>
<th>Pitting Potential SHE(mV)</th>
<th>SCE(mV)</th>
</tr>
</thead>
<tbody>
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<td>-225</td>
</tr>
<tr>
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<td>-275</td>
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<td>725</td>
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<td>-</td>
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Ref. 62
slightly different since the potential measurement did not take place there, but certainly, the absence of pits in the fractographs of the samples from the chloride and sulfate solutions indicates that the potential at the crack tip was below the pitting potential. Therefore, there was no acceleration in dissolution due to the presence of the anion in that area.

A comparison of the fracture surface from the samples fatigued in chloride or sulfate with those fatigued in water indicate no differences among the three; the intergranular cracking in the salt solutions occurs at the same stress intensity values as it occurs in water.

5.2.4 Effect of pH

A look at the fatigue crack growth rates in water, chloride and sulfate solutions (Figures 37, 40 and 42, respectively) shows that pH has no effect on the crack growth rate. This result is quite unexpected in that a change in solution pH produces a marked change in the polarization behavior of 403.

Shalaby (62) measured the polarization curves for 403 stainless steel in 1M and 0.01M sodium chloride (Figures 46 and 47 respectively) and in 1M and 0.01M sodium sulfate (Figures 48 and 49, respectively) at 100°C. He found that in 0.01M sodium chloride (pH 7 and 10) and the sulfate solution of pH 7 and 10, 403 had a passive region; the open circuit potentials during a fatigue test in 0.01M sodium
Figure 46. Polarization curves of 403 stainless steel in 1M sodium chloride solutions at 100°C and scan rate of 1000 mV/min.
Figure 47. Polarization curves of 403 stainless steel in 0.01M sodium chloride at 100°C and scan rate of 25 mV/min.
Figure 48. Polarization curves of 403 stainless steel in 1M sodium sulfate solutions at 100°C and scan rate of 1000 mV/min.
Figure 49. Polarization curves in 0.01M sodium sulfate at 100°C and scan rate of 25 mV/min.
chloride, 1M and 0.01M sodium sulfate, pH 7 and 10
were at potentials which were in the passive region in their
respective polarization curves. In 1M sodium chloride, how­
ever, there was no passive region at any pH (Figure 46). An
increase in the crack growth rate would have been expec­
ted in this solution.

Duquette and Uhlig (63, 64) found that the corrosion
rate of iron in deaerated, neutral water and 3% sodium
chloride is approximately the same, i.e. 0.1 mg/dm²/day; they also found that changing the solution pH from 2 to 10
did not markedly affect the fatigue endurance limit measured
in reversed bending type testing. They theorized that the
corrosion rate had to reach a critical value before an ef­
fect on the fatigue endurance limit was detected. It may
be that there is not a significant difference in the cor­
rosion rates in the solutions considered here to produce an
affect on the corrosion fatigue crack propagation rate.

As a result, it is not possible to use the polarization
behavior to predict what will happen in terms of fatigue
crack growth effects. This inconsistancy in solution be­
behavior may be due to the fact that conditions at the crack
tip are very different from the bulk solution; concentra-
gradients or potential variations may arise at various
portions of the crack front which may then affect the total
crack growth rate observed. An added variable is the
reactivity difference between strained and unstrained metal, which may cause slight variations in the polarization response of the metal.

5.2.5 Sodium Phosphate and Sodium Silicate

The results of fatigue crack growth in the phosphate and silicate solutions (Figure 42) show that these anions do not increase the growth rate over that in air. These solutions are inhibitors which induce the formation of a passive film. The polarization behavior of 403, shown in Figure 50, indicates that the stainless steel passivates easily in these solutions.

The properties of these salts in solution are similar in that both produce a basic solution when dissolved in water by the anion extracting a proton from the water giving a weak acid and hydroxyl ion. Also, these salts are polyprotic; their anions undergo a series of stepwise reactions with water, depending on the values of the ionization constants and on the concentration of the salt. The solution can vary from the pH where the salt anion concentration is a maximum to the pH of pure water. The intermediate anions of these polyprotic salts can act as either acids or bases and will have buffer properties.

Consequently, both of these salts act as inhibitors by preventing the dissolution of iron in water. Corrosion in sodium phosphate is reduced by the formation of a film on
Figure 50. Polarization curves of 403 stainless steel in 1M sodium phosphate and 1M sodium silicate at 100°C and scan rate of 25 mV/min.
cathodic areas increasing the cathodic polarization and favoring the process of repassivation. (66) Sodium silicate acts much the same way; it forms a silicate layer on the metal surface which is self-healing when damaged. (67)

Figure 50 shows the polarization behavior of 403 stainless steel in 1M sodium phosphate and 1M sodium silicate. A comparison of these curves with the polarization curves of sodium chloride and sodium sulfate shows that the main difference among them lies in the height of the active peak and in the low passive current density obtained in the silicate solution. There is, however, no large difference between the passive current densities observed in the chloride and phosphate solutions. The difference observed in the corrosion fatigue behavior does, however, reflect the inhibitive properties of the silicate and phosphate solution. This effect is noted in the $\Delta K_{th}$ value also. Figure 45 shows the threshold value is restored to the value observed in air.

The fracture surface in Plate XXIV of a sample fatigued in phosphate resembles that of air (Plates VI and VII) complete with striation markings to sufficiently preclude any material dissolution. Therefore, polarization curves cannot be used as a criterion to predict corrosion fatigue crack growth; and the presence of either silicate or phosphate removed the detrimental environmental aspect of corrosion fatigue in an aqueous environment.
5.3 Effect of Test Frequency

In air, tests conducted at 10 and 40 Hz produced the same crack growth rates (Figure 34) indicating that the material is not strain rate sensitive. But in water and 0.01M sodium chloride, there was a frequency effect; this effect was nearly identical in both solutions. Figures 36 and 39 plot the crack growth rates as function of stress intensity for water and 0.01M sodium chloride, respectively, at frequencies of 0.1 to 40 Hz. The data suggest that even $\Delta K_{th}$ may be frequency dependent.

Because hostile environment effects decrease with increased cyclic-load frequency, the corrosion fatigue at $\Delta K_{th}$ at high cyclic-load frequencies would have a value close to air. Barsom (7) has noted that $\Delta K_{th}$ in a corrosion fatigue environment is frequency dependent in that $\Delta K_{th}$ increases as the test frequency decreases. Although the experiments presented here did not determine $\Delta K_{th}$ at frequencies of 1 or 0.1 Hz, there is an indication that $\Delta K_{th}$ would be frequency dependent in agreement with Barsom.

This result can be considered in terms of what occurs at the crack tip as the crack advances at low stress intensity values. There is still a blunting and sharpening process operating, but the process may be somewhat altered if it is assumed that an oxide film is present. The specifics of an oxide film formation is taken up in the model proposed
for crack advancement in an environment.

A further examination of Figure 36 indicates that the effect of frequency saturates at 10 Hz as far as increasing the crack growth rates as the frequency decreases. Figure 51 plots the crack growth rate per cycle in an environment with the crack growth rate per cycle in air subtracted out as a function of test frequency. This difference in growth is plotted at three stress intensity range values. At $\Delta K < 25$ MPa m, there is no frequency effect for frequencies less than 40 Hz. But $\Delta K < 25$ an increase in frequency results in higher crack growth rates; whereas at $\Delta K > 25$, an increase in frequency results in a decrease in the crack growth rate.

The fractography of the samples also appears to be $\Delta K$ dependent in that at low $\Delta K$'s there is evidence of intergranular fracture, while at $\Delta K > 25$ all the surfaces show evidence of secondary, transgranular cracking. The appearance of the intergranular facets is evidence of a corrosion or dissolution component for crack growth since the difference in composition between the grain boundary area and the grain itself, plus the mechanical interfacial differences would make the grain boundary a preferential dissolution site and crack path.

If corrosion rates are used to account for the amount of crack extension noted in Figure 51 on a per cycle basis, then the corrosion rate if iron in water or sodium chloride
Figure 51. Plot of environmental crack growth rate in m/cycle as a function of test frequency for three $\Delta K$ values in water, 100°C, pH7.
which is 0.1 ma/dm$^2$/day may be converted to a penetration rate of $1.45 \times 10^{-10}$ cm/sec. Converting this to penetration depth per cycle amounts to $1.45 \times 10^{-11}$ cm/cycle at 10 Hz, or $1.45 \times 10^{-10}$ and $1.45 \times 10^{-9}$ cm/cycle at 1 and 0.1 Hz, respectively. These penetration rates cannot account for the environmentally enhanced crack growth rates.

A different situation exists, if penetration rates are calculated from current measurements taken from a strained electrode. This data is rather limited, but it is available for iron in borate buffer pH9 at 25C. The reactivity of strained metal emerging as slip steps is quite different from that of an immersed unstrained metal. (55) Staehle et al (68) measured a current density of 1.0 A/cm$^2$ for strained iron which can be converted to penetration rate by using Faraday's Law:

$$\text{Penetration Rate (cm/sec)} = \frac{i A}{F n \rho}$$

with $i = 1.0$ A/cm$^2$

$A = 55.8$ gm/mole

$\rho = 8.0$ gm/cm$^3$

$F = 96,500$ coul/equiv

$n = 2$ equiv/mole

for iron dissolving as Fe$^{++}$. This results in $3.6 \times 10^{-5}$ cm/sec penetration. At 10Hz, the rate would be $3.6 \times 10^{-6}$ cm/cycle and at 1 and 0.1 Hz, it is $3.6 \times 10^{-5}$ cm/cycle and $3.6 \times 10^{-4}$ cm/cycle, respectively. Using this approach,
however, there is a higher penetration rate at the slower frequencies than at the higher frequencies, which is intuitively reasonable since the solution has a longer length of time to act on the crack tip at the slower frequencies. But the penetration rate alone does not take into account an oxide forming on the crack tip as the crack advances. In order to account for this action, a model for crack propagation is proposed.

5.4 Model for Dissolution Assisted Crack Growth

5.4.1 Anodic Dissolution Approach

A model for crack growth must take into account what occurs from the mechanical aspects of fatigue crack growth, then what effects the presence of an aqueous environment may add to the crack growth process. The process of film formation on an electrode may occur through the metal dissolution and oxidation. The reactions for stainless steel involve iron and chromium:

\[
\begin{align*}
Fe & = Fe^{++} + 2e, \\
3Fe^{++} + 4H_2O & = Fe_3O_4 + 8H^+ + 2e, \\
Cr & = Cr^{3+} + 3e, \\
2Cr^{3+} + 3H_2O & = Cr_2O_3 + 6H^+.
\end{align*}
\]

The mechanical model applied to crack growth by Laird (21) and operative in 403 as evidenced by the striations in air is that the crack opens and blunts upon the application of the tensile load and sharpens upon the compressive part of the fatigue cycle. In the presence of an aqueous
environment, the exposure of clean metal at the tensile part of the stroke results in metal dissolution due to film rupture. For 403 stainless steel passivation may occur easily due to the chromium, but the formation of the protective oxide is not an instantaneous reaction, especially on a strained material. (68) So there is momentary dissolution of the newly exposed metal, then upon the compressive portion of the stroke, there is the mechanical sharpening, probably along areas which had been preferentially dissolved during the tensile portion of the stroke. Since grain boundaries are usually areas of film discontinuities, they may be the areas of preferential dissolution.

To account for the frequency effect, one must appeal to the kinetics of passivation. Strained electrode studies have shown the high current spikes that occur upon straining. Figure 52 shows such a curve. A peak current density occurs and then falls off to \( \sim 0.1 \text{ A/cm}^2 \) after 0.011 sec.

To know how much crack growth is occurring due to the action of the environment on a time basis rather than on a per cycle basis, the data plotted in Figure 51 is replotted in Figure 53 as crack growth per sec vs frequency. At all stress intensities, then, the crack growth rate is proportional to frequency. It further appears that the growth rate begins to saturate at 10Hz and would level off at frequencies exceeding 40 Hz. Figure 54 plots the crack growth
Figure 52. Typical change in current density ($i$) and strain ($\varepsilon$) with time in a straining electrode experiment. (68)
Figure 53. Plot of environmental crack growth rate in m/sec vs test frequency in water, 100°C for three ΔK values.
Figure 54. Plot of environmental crack growth rate vs $\Delta K$ for the four frequencies studied.
rate due to an environmental effect vs the stress intensity range. It is apparent from both Figures 53 and 54 that the environmental effects are greatest at the highest frequencies and that the effect is strongly $\Delta K$ dependent at the slower frequencies. It reaches an almost $\Delta K$ independent point at 40Hz. It appears that if the trend were continued, a frequency would be reached when the environmental effect of crack growth would be stress intensity independent.

The environmental crack growth plotted in Figure 53 can be expressed as

$$i \propto f$$

where $i$ is the current density which can be calculated from the crack growth using Faraday's Law and $f$ is the test frequency. From a conceptual standpoint, it is possible to visualize a process where there is a film covered crack tip, then as the film is broken, there is a high dissolution rate which drops off as in Figure 52, until the next film rupture event; if these events are close together, the crack tip spends more time at high current densities than it does at lower ones. If the time between events is increased then the crack tip area would still undergo the high current spikes, but it would have more time for repassivation, film repair, and thickening. The situation which is envisioned in this process is illustrated in Figure 55.
Figure 55. Schematic showing process of film rupture and crack extension due to dissolution as in (A); two different test frequencies are shown in (B) where the frequency at the top is faster than the one below.
Diegle and Vermilyea (69) have measured the strains needed to fracture iron oxide films formed in caustic solutions and found that at 85°C the fracture strain of relatively thin Fe$_3$O$_4$ ($<100\AA$) is $<3 \times 10^{-4}$. Consequently, very small strains are needed to rupture the films that may form at the crack tip. One problem in using this type of measurement, however, is that the strains needed to rupture a film that is forming as in Figure 52 are different from the strain needed to fracture films that have already formed and are subsequently ruptured, as in the Diegle and Vermilyea work. It can be noted in Figure 52 that the maximum current density occurs while the electrode is straining and does not start to decrease until the straining stops. But despite this added complication, the Diegle-Vermilyea measurement does provide some measure of the strain needed for oxide rupture.

An understanding of the relation between the dissolution rate and frequency can be gained by considering the situation drawn in Figure 55, where the current spikes that occur due to film rupture events are idealized. Then the average current density measured as crack growth rate is

$$i_{ave} = \frac{i_{max} \cdot n \cdot t_D (1/f)^{-1}}{}$$

where $i_{ave}$ is the current density from the crack growth rate, $n$ is the number of film rupture events, $t_D$ is the time spent at high current density and $f$ is the cycle frequency. Then if $\dot{\varepsilon}$ is average strain rate, the total strain can be
expressed as

\[ \varepsilon_{\text{tot}} = \dot{\varepsilon}/f = n(\dot{\varepsilon}_D + \dot{\varepsilon}_{\text{th}} + \dot{\varepsilon}_{\text{rup}}) \]  

(18)

where \( n, f, \) and \( t_D \) are as previously defined, \( t_{\text{th}} \) is the time spent in film thickening (Figure 55), and \( t_{\text{rup}} \) is the time it takes to rupture the film. Then if \( \varepsilon_{\text{rup}} = \dot{\varepsilon}_{\text{rup}} \),

\[ n = \frac{1}{f(t_D + t_{\text{th}} + (\varepsilon_{\text{rup}}/\dot{\varepsilon}))} \]  

(19)

and substituting into Equation 17 gives

\[ i_{\text{ave}} = \frac{i_{\text{max}} t_D f}{(t_D f + t_{\text{th}} f + (f\varepsilon_{\text{rup}}/\dot{\varepsilon}))} \]  

(20)

but if \( \varepsilon \propto f \), then \( \dot{\varepsilon} = \alpha f \),

\[ i_{\text{ave}} = \frac{i_{\text{max}} t_D f}{(t_D f + t_{\text{th}} f) + (\varepsilon_{\text{rup}}/\alpha)} \]  

(21)

where \( \varepsilon_{\text{rup}} \) is the strain needed to rupture the oxide.

But if \( (t_D f + t_{\text{th}} f) >> (\varepsilon_{\text{rup}}/\alpha) \), which might occur at high strain rates where the cycling is so fast that the crack tip area is always at high current densities, then

\[ i_{\text{ave}} = \frac{i_{\text{max}} t_D f}{(t_D f + t_{\text{th}} f)} \]  

(23)

\[ i_{\text{ave}} = \frac{i_{\text{max}} t_D}{(t_D + t_{\text{th}})} \]  

(24)

and the situation is frequency independent. The maximum
dissolution would be diffusion limited. If on the other hand, the situation was one where \((\varepsilon_{rup}/\alpha) > (t_D f + t_{th f})\),
\[
i_{ave} = \frac{i_{max} t_D f}{(\varepsilon_{rup}/\alpha)}, \tag{25}
\]
and the average current density is frequency dependent, which is the situation observed in the crack growth rate vs frequency dependence in Figure 53.

To test the validity of this model, it is necessary to solve for \(i_{ave}\) and compare it to the current density calculated from the data; this involves knowing \(i_{max}\), \(t_D\), \(t_{th}\), and \(\varepsilon_{rup}\). But there is not enough information to determine all these parameters; however, if \(t_D\) and \(i_{max}\) are estimated, then \(t_{th}\) and \(\varepsilon_{rup}\) can be calculated and substituted into Equation 22 such that \(i_{ave}\) may be calculated.

For this approximation it is possible to express Equation 25 as
\[
i_{ave} = kf
\]
where \(k\) may be found from Figure 53 and,
\[
k = \frac{i_{max} t_D}{\varepsilon_{rup}} = 1.38 \text{ A-sec/cm}^2
\]
for \(\Delta K 25\) and \(\alpha \approx 1\). As a first approximation, let \(t_D \approx 10^{-3} \text{ sec}\) (a lower limit value from straining electrode experiments) and \(i_{max} \approx 30 \text{ A/cm}^2\), then \(\varepsilon_{rup} = 0.022\).
From Equation 24, it is possible to solve for the ratio of thickening to dissolving times,

\[
\frac{t_{th}}{t_D} = \frac{i_{\text{max}}}{i} - 1,
\]

where \( i \) is the maximum current density at 40 Hz; Table 13 lists the environmental crack growth rates at \( \Delta K_{25} \) and their equivalent values in terms of current density, \( i \), which were calculated from Faraday's Law (Equation 12).

Solving for \( t_{th} \) and keeping \( i_{\text{max}} = 30 \ \text{A/cm}^2 \), and \( i = 24.1 \ \text{A/cm}^2 \) gives \( t_{th} = 0.245 \ t_D \). Now, it is possible to solve for \( i_{\text{ave}} \) in Equation 22 using the above values; these current densities are listed in Table 13. Additional calculations are tabulated for different values of \( i_{\text{max}} \) and \( t_D \); the parameters used to solve for \( i_{\text{ave}} \) in Equation 22 are listed in the lower portion of the table.

There is a fair degree of agreement between the calculated and the experimental values, although the values for \( \varepsilon_{\text{rup}} \) are too high at the lower current values. At \( i_{\text{max}} = 150 \ \text{A/cm}^2 \), and \( t_D = 10^{-3} \ \text{sec} \), then \( \varepsilon_{\text{rup}} = 0.11 \), which is a reasonable strain value. The results from this analysis indicate that straining electrode studies to date do not strain fast enough. The electrodes need to be strained in times of \( \approx 10^{-3} \ \text{sec} \) to measure the current transient. The difficulty in applying these calculations is the inability to independently calculate values for the parameters in
<table>
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<th>Frequency (Hz)</th>
<th>da/dt (m/sec)</th>
<th>$i$ (A/cm$^2$)</th>
<th>$i_{ave}$ (A/cm$^2$)</th>
<th>$i_{ave}$ (A/cm$^2$)</th>
<th>$i_{ave}$ (A/cm$^2$)</th>
<th>$i_{ave}$ (A/cm$^2$)</th>
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Equation 22. However, Equation 22 does qualitatively describe the environmentally enhanced crack growth.

The fractography is in keeping with this development. An intergranular component may be expected since a grain boundary area would be expected to be a preferential site for film rupture, but striations would also be expected because of the mechanical aspects of the growth process.

Evidence is support of this model has been published by Ford and Silverman (70); they found that the fatigue crack propagation rate of 304 stainless in water at 97°C has the same crack growth vs frequency dependence as predicted here.

This model, of course, has its limitations since it necessarily simplifies the events occurring at the crack tip. It was assumed that the film rupture events are confined to the crack tip region. This may not be the case. The process may be more complicated as shown in Figure 56.

An additional problem with this approach is that the crack growth process is relatively insensitive to a change in the bulk solution pH. A filmed electrode approach may be used in neutral to alkaline solutions where stability diagrams (72) indicate that iron and chromium oxides are stable, but at acid pH's both the stability diagrams and the polarization behavior indicate that there is no passive region or stable oxide. A more complicated situation
Figure 56. Dissolution at the crack tip with more than one film rupture event and non-idealized crack extension.
may exist at the crack tip due to localized potential differences. But the behavior documented in water and sodium chloride is consistent with a dissolution process.

An additional limitation is that it is assumed that the strain needed to rupture the film is reached as an abrupt step function of the thickness. In reality, the strain needed to fracture a film may change gradually as the film thickens. Such a situation makes the events occurring at the crack tip more complex and may lead to more than one film rupture event per cycle, especially if the film is not a uniform thickness.

5.4.2 Hydrogen Embrittlement Approach

One of the principles of the corrosion process is that an oxidation reaction, such as iron dissolution, is accompanied by a reduction reaction; both reactions must occur simultaneously and at the same rate on the metal surface. Hydrogen evolution is a common reduction reaction in acid or deaerated media:

\[ 2H^+ + 2e = H_2. \]

But in order for this reaction to occur, the hydrogen evolution reaction must be thermodynamically favored. The measurement of the open circuit potential in the bulk solution indicated that the samples were not at such a potential. But, the conditions at the crack tip may be different; the
conditions may favor hydrogen evolution. A possible mechanism of hydrogen embrittlement involves the reduction of hydrogen ions to adsorbed hydrogen atoms at the crack tip, adsorption of the atoms and diffusion of hydrogen atoms to a position immediately below the crack tip surface. Once a critical hydrogen content is reached, the crack may grow to the depth where the hydrogen is effective and the cycle may start again. This mechanism assumes, as in the previous dissolution process, that the reaction rate at the crack tip is localized there.

As a first approximation, it is possible to calculate the diffusion distance for hydrogen during one fatigue cycle at the frequencies considered. This calculation uses $D = 10^{-7} \text{ cm}^2/\text{sec}$ (73) for hydrogen in iron at 90°C. Table 14 lists the hydrogen penetration distances. It is evident that the penetration distance decreases as the frequency increases. It appears that the damaged area would be less at 40Hz than at 1 Hz, and the crack growth rate would be greater at the slower frequencies. This type of damage would then be reflected in the crack growth rate. But Figure 53 shows that the environmental crack growth component increases as the frequency increases; this behavior is not consistent with the trend in Table 14.

Thus, the frequency dependence is not consistent with a hydrogen diffusion mechanism. But it is possible that
since the film rupture model postulates a higher number of film rupture events, and therefore, higher dissolution at the faster frequencies, then hydrogen entry may be the rate controlling process.

There is evidence in the literature that dynamic hydrogen charging coupled with simultaneous deformation degrades the mechanical properties of steels (71) enhancing crack propagation. The degree of degradation, however, is dependent on the hydrogen fugacity and strain rate. With the results presented here it is not possible to determine how susceptible the material is to hydrogen embrittlement. Additional controlled potential experiments are needed to establish what kind of fatigue behavior occurs in the presence of hydrogen charging.
TABLE 14

HYDROGEN PENETRATION DISTANCES

\[ \bar{x} = \sqrt{D t} \quad (74) \]

\[ D = 10^{-7} \text{ cm}^2/\text{sec} \quad (73) \]

<table>
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<th>Frequency (cycles/sec)</th>
<th>Period (sec)</th>
<th>( \bar{x} ) (( \mu ))</th>
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<td>1.0</td>
</tr>
<tr>
<td>40</td>
<td>0.025</td>
<td>0.5</td>
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</table>
6.0 CONCLUSIONS

(1) The crack growth rate in air is unaffected by cyclic frequency and temperature (25 and 100°C); the crack extension is by alternate blunting and sharpening process. The $\Delta K_{th}$ is $5.2 < \Delta K_{th} < 5.7$ MPa m, at $R=0.5$.

(2) The crack growth rates in water are higher than in air at both room temperature and 100°C; they are insensitive to a pH change from 7 to 10. The $\Delta K_{th}$ at 100°C, 40Hz, $R=0.5$ is $4.4 < \Delta K_{th} < 5.2$ MPa m. The crack growth rate was affected by a change in test frequency.

(3) The crack growth rates in sodium chloride are approximately the same as in water regardless of chloride concentration (0.01M and 1M) and solution pH (2, 7, and 10); the $\Delta K_{th}$ in 0.01M sodium chloride, pH2 and 10, 40Hz, 100°C, $R=0.5$ is the same as water. The frequency dependence in 0.01M sodium chloride, pH10, is similar to water.

(4) The crack growth rates in sodium sulfate are approximately the same as in water regardless of sulfate concentration (0.01 and 1.0M) and pH (7 and 10); the $\Delta K_{th}$ in 0.01M sodium sulfate, pH10, 100°C, 40Hz is the same as water.

(5) The crack growth rates in sodium phosphate are approximately the same as in air; the $\Delta K_{th}$ in 1M sodium phosphate, pH10, 100°C, 40Hz is the same as air.
(6) The crack growth rates in sodium silicate are approximately the same as in air.

(7) The fractographic studies showed that in the sodium chloride, sodium sulfate, and water solutions, there was an intergranular cracking component along with a transgranular component and striation markings at low stress intensity ranges. No intergranular cracking was found in the samples fractured in the sodium phosphate solutions.

(8) It was not possible to correlated the polarization behavior of 403 stainless steel in the electrolytes studied with the corrosion fatigue crack growth rates observed; polarization behavior is insufficient to predict corrosion fatigue effects.

(9) The environmental component of crack growth on a time basis was found to be proportional to the test frequency; a dissolution model was developed in light of these results using a passivation kinetics approach.
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