STATISTICAL MODELING FOR THE CORROSION FATIGUE OF

ALUMINUM ALLOYS 7075-T6 AND 2024-T3

by

Carlos A. Arriscorreta

A dissertation submitted to the faculty of
The University of Utah
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Department of Mechanical Engineering

The University of Utah

May 2012

The University of Utah Graduate School

STATEMENT OF DISSERTATION APPROVAL

The dissertation of **Carlos A. Arriscorreta**

has been approved by the following supervisory committee members:

		Date Approved
David W. Hoeppner	, Chair	**3/5/2012**
Timothy Ameel	, Member	**3/5/2012**
Donald S. Bloswick	, Member	**3/5/2012**
Charles B. Elliott III	, Member	**3/5/12**
Kimberli Jones	, Member	**3/5/2012**

and by **Timothy Ameel** , Chair of

the Department of **Mechanical Engineering**

and by Charles A. Wight, Dean of The Graduate School.

ABSTRACT

It is well known that corrosion and simultaneous cyclic loading have a detrimental impact in the integrity of devices or structures. Understating these mechanisms is critical to ensure safety of aircraft. This work presents an extensive literature review on issues of corrosion mechanisms including pitting, exfoliation and intergranular attack. Moreover, models for phases of life and pitting corrosion are presented. Relevant definitions related to these failure modes are presented.

The nucleation of fatigue cracks from corrosion pits was investigated by evaluating the effects of two variables on the fatigue life of dog-bone specimens of aluminum alloys 7075-T6 and 2024-T3. The specimens were exposed to different levels of corrosion in an acidified saline solution of 3.5% NaCl. In addition, the specimens were exposed to concomitant fatigue and corrosion until failure by fracture occurred. SEM analysis indicated that fatigue cracks formed/nucleated from each pit, and subsurface mechanisms of degradation were identified associated with the pitting nucleation sites including subsurface pitting, cracking, tunneling and intergranular attack.

Failure data were analyzed by ANOVA methods and three transformations were evaluated to minimize the variance, including natural log, inverse square root and power with a lambda of 1/3. Contour and surface plots were developed to show how these variables impact the response of cycles to failure for the conditions evaluated.

The effects of stress are more detrimental than corrosion time on the fatigue life of the specimens for the values previously defined by the DOE matrix.

The research reported herein presents a methodology for accelerated corrosion fatigue of high strength aluminum alloys in an acidified saline environment. Subsequently a statistical based methodology to assess the impact of multiple variables into the fatigue life of specimens is presented. Statistical models are developed to assess the effect of two variables, stress and corrosion time into the fatigue life of the specimens. Stress levels were chosen to simulate conditions of current aircraft, such as fuselage bulkheads in the F-16. Development of statistical models to predict the behavior of materials will increase our ability to predict and prevent catastrophic structural failures thereby increasing the safety of our aircraft structures.

This work is dedicated to:

my Mom for unconditional love,

my brother and sisters for their support.

If we knew what it was we were doing,
it would not be called research, would it?
- Albert Einstein

Amat Victoria Curam

TABLE OF CONTENTS

ABSTRACT..iii

ACKNOWLEDGMENTS ix

CHAPTER

1. INTRODUCTION 1

Hypotheses 3
Experimental Program 4
Dissertation – Structure and Overview 10
References...13

2. EXFOLIATION CORROSION (EC) AND PITTING CORROSION (PC) AND THEIR ROLE IN FATIGUE PREDICTIVE MODELING: STATE OF THE ART REVIEW...17

Abstract……………………………… 17
Introduction...18
Phases of Life and Modeling……………………… 19
Corrosion in Aircraft Structural Aluminum Alloys 31
Intergranular and Exfoliation Corrosion 37
Corrosion Fatigue...40
Corrosion Pillowing and its Effect on Structural Integrity of Aircraft
Lap Joints 42
Pitting Nucleation Theories 43
Pitting Corrosion……………………………......................................44
Formation of Passive Films and their Growth 46
Structure of the Passive Film in Aluminum...47
Pitting Potential and Induction Time 52
Pit Growth Rate and Pit Morphology 53
Mechanisms of Pit Nucleation 55
Ion Migration and Penetration Models 60
Mechanical Film Breakdown Theories Chemico-Mechanical
Breakdown Theories 63
Pitting Corrosion Fatigue...66
Environmental Effects on "Short" Crack Behavior of Materials............72
Conclusions and Recommendations………………… 73

Appendix..77
References..84

3. CORROSION FATIGUE MODELING OF ALUMINUM ALLOY 7075-T6......104

Abstract…………………………………………………………………...104
Introduction……..……………………………………………………….105
Experimental Procedures…………………………………………….....108
Results……………………………………………………………………111
Discussion………………………………………………………………...123
Conclusions………………………………………………………………124
References………………………………………………………………...126

4. EFFECTS OF PRIOR CORROSION AND STRESS IN CORROSION FATIGUE OF ALUMINUM ALLOY 7075-T6……………………………………………..129

Abstract……………………………..……………………………………129
Introduction………………………………………………………………130
Methodology………………………….....……………………………….137
Results…………………………….………………………………………..139
Fractography……………………………………………………………...143
ANOVA –Box-Cox Transformations………………………………………. 148
Discussion………..………………………………………………………153
Conclusions………………………………………………………………155
References………………………………………………………………...157

5. EFFECTS OF PRIOR CORROSION AND STRESS IN CORROSION FATIGUE OF ALUMINUM ALLOY 2024-T3……………………………………………162

Abstract…………………………………...……………………………162
Introduction……………………………………...……………………………..163
Experimental Procedures………………………………………………168
Results and Discussion………………………………………………...171
Weibull Analysis…………………………………………………………185
Conclusions………………………………………………….…………190
References………………………………………………………………...191

6. CONCLUSIONS AND RECOMMENDATIONS 195

Research Contribution 197
Recommendations..199

ACKNOWLEDGMENTS

I would like to thank my committee members, Dr. Hoeppner, Dr. Ameel, Dr. Bloswick, Dr. Elliott, and Dr. Jones, for their guidance. Particularly, Dr. Hoeppner has been an inspiration for me, not only to become a better student, a better engineer, but also a better person. I will always be grateful for his advice.

I would like to thank QIDEC members Ms. Amy Taylor and Mr. Larry Smiltneek. Their frienship and assistance made my time in the lab more enjoyable.

Finally, I would like to express my gratitude and love for my mom and dad. Especially to my mom, for her advice, love, patience and support. Thanks to my brother and sisters, Edgar, Carolina and Alejandra, for their love and support.

CHAPTER 1

INTRODUCTION

It is well known that aircraft are exposed to the effects of environment and fatigue, and in many occasions the fatigue life is exceeded in aging aircraft. Understanding the mechanisms of corrosion and fatigue is critical to make decisions of life extension and incorporating this knowledge into design of new aircraft. Due to the inherent variability of these processes, statistical models are needed to make accurate assessments.

Corrosion fatigue has been studied since the late 1800s. Jones and Hoeppner summarized some of the authors that have been involved understanding these mechanisms [1]. Since 1837, failures from metal fatigue were noticed, with the first documented mention of corrosion fatigue was by Haigh in 1917 and McAdam in 1929 [2]. Research in the areas of pitting corrosion fatigue has been performed by Harmsworth [3], Chen, Liao, Wan, Gao and Wei [4], Lindley, McIntyre and Trant [5], Kondo [6], Kawai and Kasai [7], Hoeppner [8], and Goswami and Hoeppner [9]. These investigators concluded that pitting corrosion adversely affects the fatigue life of the structures. Clark and Hoeppner found that corrosion pits often would nucleate cracks, and the critical pits associated with these cracks were usually not from the deepest pit [10].

Corrosion fatigue involves a significant amount of variables, which makes modeling of this mechanism a challenging endeavor. Several scientists and engineers have proposed models, including the following: Harlow and Wei [11], Shi and Mahadevan [12], Xiuling and Rong [13], Atkinson et al.[14], Hoeppner, Chandrasekaran and Taylor [15], Hoeppner and Goswami [9], Hoeppner [16], Khan and Younas [17], Murtaza and Akid [18], Swift [19], Wanhill [20], Clark, G. [21], P. Bressolette, A. Chateauneuf [22], Liao, Bellinger and Komorowski [23], Ramsamooj and Shugar [24], and Rong [25].

In addition, research to understand the effects of corrosion and corrosion fatigue in high strength aluminum alloys has been documented. Such authors include Jones K et al. [26], Liao, Renaud and Bellinger [27], Wei et al. [28], Clark P. and Hoeppner [29], Jones K and Hoeppner [30, 31], Birbilis and Buchheit [32-33], Cavanaugh, Buchheit and Birbilis [34], Jones K and Hoeppner [35-36], Gangloff, Kiam and Burns [37], Sankaran, Perez and Jata [38], and Hoeppner [39-40].

Aluminum alloys 7075-T6 and 2024-T3 frequently are used in the manufacture of airframe components that are critical to assurance of airworthiness. Understanding the effects of corrosion fatigue on these alloys is essential for the integrity and reliability of these components. Research focusing on statistical modeling, such as reported herein, will increase the understanding of a structure through the phases of life and diminishing the effects of corrosion fatigue on structural integrity. Thus, it is envisioned that this work is one of the steps needed to continue to make aircraft structures safer, relative to the potential degradation from corrosion fatigue.

Hypotheses

The research reported herein focuses on developing models to predict with confidence the life of a structure exposed to simultaneous corrosion and fatigue. The following hypotheses were used as guidance for this research:

Hypothesis I. *Aluminum alloys 7075-T6 and 2024-T3 will dissolve by pitting when pre-exposed to an acidified saline environment. Furthermore, cracks will nucleate from pits and propagate until failure by fracture is reached*.

3.5% NaCl was used as the corrosive environment acidified to a pH~3. This is a common environment found in the literature. This hypothesis was clearly identified by use of metallurgical and scanning electron microscopes (SEM). The second technique allowed for subsurface evaluation, which revealed very interesting results, which are shown in subsequent chapters.

Hypothesis II. *Stress magnitude will have a greater deleterious impact as compared with corrosion exposure time on the fatigue life of the specimens.*

The effect of two variables into the life of the specimens was studied. Those variables included maximum stress and corrosion time. Statistical analyses of the results show what variables have greater impact in the life of the specimens. Knowing which variable has greater detrimental impact in the structural integrity of a structure is critical to make decisions, such as extending the life of structure, etc.

Hypothesis III. *Statistical models will predict with confidence the life of specimens exposed to stress and an acidified saline environment with limits defined by a DOE matrix.*

The ultimate goal of this research was to develop statistical significant models to predict the effects of stress and corrosion time in the life of the specimens. This was accomplished by developing protocols based on design of experiments (DOE) and analyzing the results with statistical methods include analysis of variance (ANOVA), with Box-Cox transformations to stabilize the variance. Statistical significant models were developed to predict the life of specimens as a function of maximum stress and corrosion time.

Experimental Program

This section discusses the experimental program and procedure used in the research reported herein. It shows the polishing regime, specimen preparation, pre-corrosion conditions and corrosion fatigue parameters.

Specimen Configuration and Polishing

A schematic of the fatigue test specimen selected for this study is shown in Fig. 1.1. All specimens were polished according to the following guidelines. Each specimen was polished through six steps. Each step produced a more refined surface finish. The steps included the following:

1) 240 grit silicon carbide polishing paper.
2) 320 grit silicon carbide polishing paper.
3) 400 grit silicon carbide polishing paper.
4) 600 grit silicon carbide polishing paper.
5) 1.0 μm alpha silica compound on a 12 inch diameter polishing cloth.
6) 0.3 μm alpha silica compound on a 12 inch diameter polishing cloth.

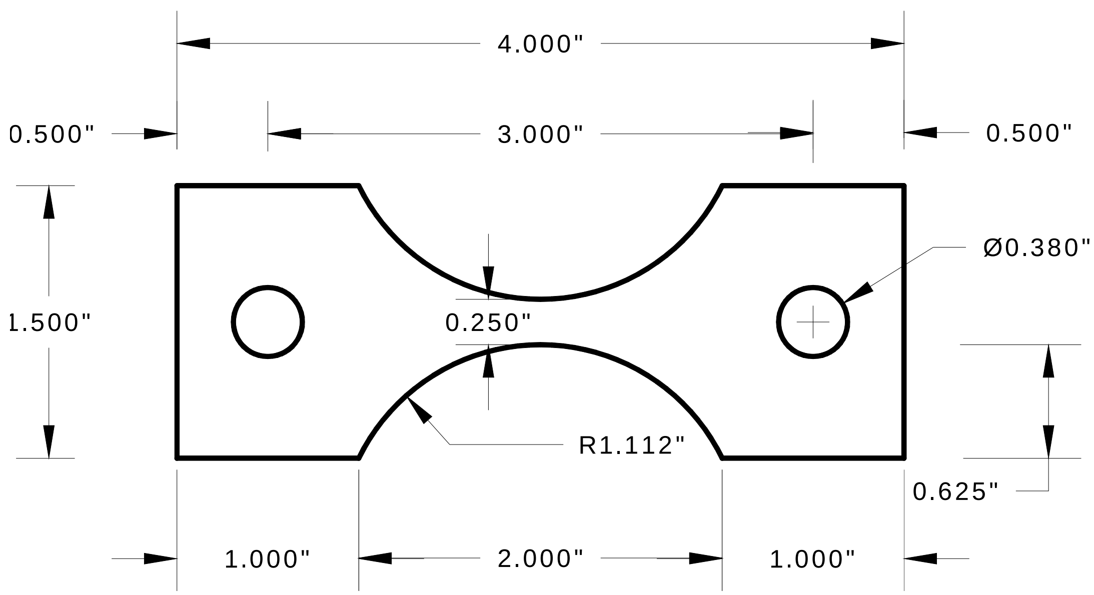


Fig. 1.1: Dog-bone Specimen for Corrosion Fatigue.

The side of the specimen not corroded was polished with steps 1 thru 4. The edges of the specimens were polished with 800 grit polishing paper, to minimize fatigue cracks nucleating from the edges or corners. Specimens were then cleaned with acetone in an ultrasonic bath and stored in a dessicator.

Prior Corrosion of Specimen

All specimens were prior corroded according to the following steps:

1) Solution preparation:
    a. Using distilled water, a 3.5 % NaCl solution was prepared. This is accepted in the literature to simulate the salinity of sea water. A calibrated scale was used to measure the NaCl.
    b. The solution was acidified with a 1 molar solution of HCl, until a pH of 3 was obtained. It is well known that aluminum alloys are prone to corrode at relatively low and high pH values. It was expected that at a pH of 3, conditions for pitting would be favorable. Calibrated pH meters were used to measure pH.
2) Prior corrosion: two sets of experiments were performed with different exposure times to the corrosive solution. The first set included preliminary studies performed on aluminum alloy 7075-T6 and the second set corresponded to experiments on AA 2024-T3.

    Prior to exposure to the solution specimens were coated with a finger nail polish. Experimentation was started after the nail polish had dried, usually about 30 minutes. A specific area on the surface of each specimen was left exposed for corrosion reaction. The area of exposure was approximately 40 mm^2.

a. Preliminary studies on AA7075-T6.

   i. Approximately half liter of solution was poured into a beaker.

   ii. Specimens were pre-exposed to an acidic saline environment for 24 and 48 hours. Two blocks were used, the first one with agitation of solution using a magnetic Fisher stirring plate, at a speed of three; and the second block with a stagnant solution. Specimens were exposed to the solution according to a DOE matrix (see chapter 3).

   iii. After corrosion the specimens were cleaned up with acetone in an ultrasonic bath, and stored in a dessicator.

b. Prior corrosion on AA 2024-T3

   i. Specimens were coated and immersed as indicated previously. However, time of exposure was modified to 24 or 72 hours according to a DOE matrix (see chapter 5). Multiple pilot tests were performed to assess the effect of prior corrosion at different levels from 24 to 120 hours. It was found that after 72 hours no significant impact of the corrosive solution was observed.

Pitting Characterization

Upon completion of prior corrosion, each specimen was examined to characterize pitting damage. This was accomplished utilizing a confocal microscope. Pitting damage was examined primarily for pit depth and topography.

Corrosion Fatigue

Specimens were simultaneously exposed to the acidified saline environment and cyclic loading as follows:

1) Corrosion: solution was prepared following the same procedure as explained previously. The flow rate through the environmental chamber was controlled to approximately 1 mL/min. The solution was not recycled. Fig. 1.2 is the environmental chamber used in this study.
2) Fatigue: testing was performed utilizing a 3.3 kip servo-hydraulic, controlled MTS load frame, provided by FASIDE International, Inc. The loading was controlled by an MTS TestStar system with TestWare to supply a waveform. Phenolic shims were used to minimize fretting between the specimen and machine grips.The parameters used include the following:
    a. Loading:
        i. Preliminary studies for AA7075-T6 included 17.5 ksi and 35 ksi. The first value is commonly used by previous investigators at the University of Utah. The upper value was approximately half of the yield strength of the material.
        ii. Additional testing for AA2024-T3, included loading values of 17 ksi and 22 ksi. It is known that aircraft such as the F-16 operate with stresses between 17 and 22 ksi, including critical areas such as the fuselage bulkheads. This was done to assure that the stress levels used had some degree of validity related to an operating fleet of aircraft.

Fig. 1.2: Environmental chamber setup

b. Stress ratio: R=0.1

c. Loading frequency: 10 Hz, loading frequency was reduced to 0.5 Hz during inspection intervals. This was done such that the crack could be accurately measured. Inspection intervals lasted 10-20 cycles.

d. Waveform was sinusoildal.

e. Loaded in L-T direction.

f. Specimens were exposed to simultaneous corrosion fatigue until failure by fracture was obtained.

3) Postfracture characterization: as soon as the specimens failed by fracture, the fracture surface was analyzed with a scanning electron microscope. This enables identification of critical discontinuity and also characterization of subsurface damage such as tunneling, pitting, cracks, etc.

Dissertation - Structure and Overview

This dissertation was structured as a compilation of manuscripts that have been published or have been submitted for publication, as follows:

- Chapter 2 - *Exfoliation Corrosion (EC) And Pitting Corrosion (PC) and their role in Fatigue Predictive Modeling: State-of-the-Art Review*. This manuscript is a comprehensive study of the literature to establish a solid background for this research. It covers important aspects such as phases of life and modeling, corrosion in aluminum alloys, pitting corrosion, environmental effects on short crack behavior, etc. A compilation of definitions related to corrosion fatigue are presented. This manuscript was recently **published by International Journal of Aerospace Engineering** (Hindawi Publishing Corporation, Volume 2012, Article ID 191879, 29 pages). It was the result of approximately 3 years of work, which included extensive literature research (243 references), compilation of definitions, etc. In addition, this paper was invited for a special manuscript submission by Hindawi; however, other authors for unknown reasons did not present manuscripts for review and the paper was published in a regular journal issue.
- Chapter 3 - *Corrosion Fatigue Modeling of Aluminum Alloy 7075-T6*. Once a solid background was established by performing a comprehensive literature review, it was time to develop hypotheses and test these in the lab. As indicated in the previous section, a methodology to develop models was desired. It was important to base such experiments with statistical methodologies so that the results could be analyzed accordingly. Since the effect of two variables into the response was desired, design of experiments (DOE) was utilized to setup a testing

protocol. Initially, a full factorial design was chosen, with two levels of corrosion time and stress magnitude. The results were analyzed with ANOVA and Box-Cox transformations. Specimens were analyzed by using metallurgical and scanning electron microscopes (SEM) to establish the origin of failure. A statistical significant model was developed and is presented on this chapter. This manuscript was recently submitted for publication in ***Corrosion Science***.

- Chapter 4 - *Effects of Prior Corrosion and Stress in Corrosion Fatigue of Aluminum Alloy 7075-T6*. Once the methodology for testing was established and found to be adequate, further modeling was performed. Two additional Box-Cox transformations were evaluated, inverse square root, and power with lambda of 1/3. ANOVA indicates that these models are statistical significant. SEM revealed subsurface mechanisms, including pitting, tunneling and IGA. This paper was submitted and recently **accepted for publication** by **Corrosion - The Journal of Science and Engineering, by NACE.**
- Chapter 5 - *Effects of Prior Corrosion and Stress in Corrosion Fatigue of Aluminum Alloy 2024-T3*. Once the methodology for testing and developing models was established and found to be statistical adequate, it was desired to expand to other materials, including AA 2024-T3. Communications with Dr. Jones and Dr. Bloswick were helpful to improve the testing protocol by using stress levels of current applications such as bulkheads in the F-16, and increasing the number of replicates to ensure adequate confidence in the results. With such feedback the protocol was modified accordingly. Following the same methodology, specimens were exposed to both corrosive environment and fatigue

until failure. Post fracture analysis was done with SEM. Finally, analysis of data was performed as indicated previously with ANOVA and Box-Cox transformations including natural log and power with lambda of 1/3. Models obtained from this study were found to be statistical significant, and data fits Weibull distributions with 95% confidence.

This paper was also recently submitted to **Corrosion - The Journal of Science and Engineering, by NACE.**

- Chapter 6 is a summary of conclusions and recommendation from this study.

References

[1] K. Jones, D.W. Hoeppner, Pit-to-crack transition in pre-corroded 7075-T6 aluminum alloy under cyclic loading, Corrosion Science 47 (2005) 2185-2198.

[2] W. Schütz, Engng. Fract. Mech. 54 (2) (1996) 263–300.

[3] C.L. Harmsworth, Effect of corrosion on the fatigue behavior of 2024-T4 aluminum alloy, ASD Technical Report 61-121, 1961, pp. 1–7.

[4] G.S. Chen, C.M. Liao, K.C. Wan, M. Gao, R.P. Wei, Pitting corrosion and fatigue crack nucleation, in: W.A. Van Der Sluys, R.S. Piascik, R. Zawierucha (Eds.), Effects of the Environment on the Initiation of Crack Growth, ASTM STP 1298, American Society for Testing and Materials, 1997, pp. 18–31.

[5] T.C. Lindley, P. McIntyre, P.J. Trant, Met. Technol. 9 (1982) 135–142.

[6] Y. Kondo, Corrosion 45 (1989) 7–11.

[7] S. Kawai, K. Kasai, Fatigue Fract. Engng. Mater. Struct. 8 (2) (1985) 115–127.

[8] D.W. Hoeppner, Model for Prediction of Fatigue Lives Based Upon a Pitting Corrosion Fatigue Process, ASTM STP 675, American Society for Testing and Materials, 1979, pp. 841–870.

[9] T. Goswami, D.W. Hoeppner, J. Mech. Behavior Mater. 10 (5–6) (1999) 261–278.

[10] P.N. Clark, D.W. Hoeppner, J. Mech. Behavior Mater. 13 (2) (2002) 91–105.

[11] D.G. Harlow, R.P. Wei, Probability modeling and material microstructure applied to corrosion and fatigue of aluminum and steel alloys, Engineering Fracture Mechanics 76 (2009) 695-708.

[12] P. Shi, S. Mahadevan, Damage tolerance approach for probabilistic pitting corrosion fatigue life prediction, Eng Fracture Mech 68 (2001) 1493-1507.

[13] Z. Xiulin, W. Rong, On the corrosion fatigue crack initiation model and expression of metallic notched elements, Eng Fracture Mech 57 No. 6 (1997) 617-624.

[14] J. D. Atkinson, J. Yu, Z. Y. Chen, Z. J. Zhao, Modeling of corrosion fatigue crack growth plateux for RPV steels in high temperature water, Nuclear engineering and design 184 (1998) 13-25.

[15] D. W. Hoeppner, V. Chandrasekaran, A.M.H Taylor, Review of pitting corrosion fatigue models, Proceedings of 20th ICAF Symposium, Structural Integrity for the Next Millenium, Dayton OH, 2000 pp 253-276.

[16] D. W. Hoeppner, Model for prediction of fatigue lives based upon a pitting corrosion fatigue process, American Society for Testing and Materials, 1979.

[17] Z. Khan, M. Younas, Corrosion-fatigue life prediction for notched components based on the local strain and linear elastic fracture mechanics concepts, Int. J Fatigue Vol. 18 No. 7, pp 491-498, 1996.

[18] G Murtaza, R Akid, Empirical corrosion fatigue life prediction models of a high strength steel, Eng Frac Mech, 67, (2000) 461-474.

[19] S. Swift, Sticks and stones: could the words of aeronautical fatigue hurt us? 26th ICAF Symposium – Montreal June 2011.

[20] R. Wanhill, T. Hattenberg, Fractography based estimation of fatigue crack “initiation” and growth lives in aircraft components, NLR Technical Publication NLR-TP 2006-184, National Aerospace Laboratory, Amsterdam, Netherlands.

[21] G. Clark, Fleet recovery and life extension – some lessons learned. ICAF 2011: Structural integrity, influence of efficiency and green imperatives

[22] P. Bressolette, A. Chateauneuf, Probabilistic lifetime assessment of RC structures under coupled corrosion-fatigue deterioration processes, Structural Safety 31 (2009) 84-96.

[23] M. Liao, N. C. Bellinger, J. P. Komorowski, Modeling the effects of prior exfoliation corrosion on fatigue life of aircraft wing skins, Int J Fatigue 25 (2003) 1059-1067.

[24] D. V. Ramsamooj, T. A. Shugar, Modeling of corrosion fatigue in metals in an aggressive environment, Inh J Fatigue 23 (2001) S301-S309.

[25] W. Rong, A fracture model of corrosion fatigue crack propagation of aluminum alloys based on the material elements fracture ahead of a crack tip, Int J Fatigue 30 (2008) 1376-1386.

[26] K. Jones, S. R. Shinde, P. N. Clark, D. W. Hoeppner, Effect of prior corrosion on short crack behavior in 2024-T3 aluminum alloy, Corrosion Science 50 (2008) 2588-2595.

[27] M. Liao, G. Renaud, N. C. Bellinger, Fatigue modeling for aircraft structures containing natural exfoliation corrosion, Int J Fatigue 29 (2007) 677-686.

[28] R. P. Wei, G. S. Chen, K-C Wan, T. H. Flurnoy, Transition from pitting to fatigue crack growth – modeling of corrosion fatigue crack nucleation in a 2024-T3 aluminum alloy, Materials Science and Eng A219 (1996) 126-132.

[29] P. N. Clark, D. W. Hoeppner, Corrosion pitting behavior of 2024-T3 aluminum considering the effects of loading and sheet thickness, (2001) ASC 01-2552.

[30] K. Jones, D.W. Hoeppner, Prior corrosion and fatigue of 2024-T3 aluminum alloy, Corrosion Science 48 (2006) 3109-3122.

[31] K. Jones, D. W. Hoeppner, Pitting corrosion, grain boundaries, and constituent particles: which will win the crack nucleation race? ICAF 2005, Hamburg, Germany.

[32] N. Birbilis, R. G. Buchheit, Electrochemical characteristics of intermetallic phases in aluminum alloys, Journal of Electrochemical Society 152 (4) B140-B151 (2005).

[33] N. Birbilis, R. G. Buchheit, Investigation and discussion of characteristics for intermetallic phases common to aluminum alloys as a function of solution pH, Journal of Electrochemical Society 155 (3) C117-C126 (2008).

[34] M. K. Cavanaugh, R. G. Buchheit, N. Birbilis, Modeling the environmental dependence of pit growth using neural network approaches, Corrosion Science 52 (2010) 3070-3077.

[35] K. Jones, D. W. Hoeppner, Pit-to-crack transition in pre-corroded 7075-T6 aluminum alloy under cyclic loading, Corrosion Science 47 (2005) 2185-2198.

[36] K. Jones, D. W. Hoeppner, The interaction between pitting corrosion, grain boundaries, and constituent particles during corrosion fatigue of 7075-T6 aluminum alloy, Int J Fatigue 31 (2009) 686-692.

[37] R. P. Gangloff, S. Kim, J. T. Burns, Fatigue crack formation and growth from localized corrosion in Al-Zn-Mg-Cu, Eng Fracture Mech 76 (2009) 651-667.

[38] K. K. Sankaran, R. Perez, K. V. Jata, Effects of pitting corrosion on the fatigue behavior of aluminum alloy 7075-T6: modeling and experimental studies, Materials Science and Eng A297 (2001) 223-229.

[39] D. W. Hoeppner, The formation/nucleation of fatigue cracks in aircrafts structural materials, 26th ICAF Symposium Montreal (2011).

[40] D. W. Hoeppner, D Mann, J Weekes, Fracture mechanics based modeling of the corrosion fatigue process, NATO AGARD CP316 Corrosion Fatigue CESME Turkey 1981

CHAPTER 2

EXFOLIATION CORROSION (EC) AND PITTING CORROSION (PC) AND THEIR ROLE IN FATIGUE PREDICTIVE MODELING: STATE OF THE ART REVIEW [6]

Abstract

Intergranular attack (IG) and exfoliation corrosion have a detrimental impact on the structural integrity of aircraft structures of all types. Understanding the mechanisms and methods for dealing with these processes and with corrosion in general has been and is critical to the safety of critical components of aircraft. Discussion of cases where IG attack and exfoliation caused issues in structural integrity in aircraft in operational fleets is presented herein along with a much more detailed presentation of the issues involved in dealing with corrosion of aircraft.

Issues of corrosion and fatigue related to the structural integrity of aging aircraft are introduced herein. Mechanisms of pitting nucleation are discussed that include adsorption-induced, ion migration-penetration and chemico-mechanical film breakdown theories. In addition, pitting corrosion fatigue models are presented as well as a critical

[6] Reprinted with Permission from © Hindawi: Publishing Corporation. "Exfoliation Corrosion and Pitting Corrosion and Their Role in Fatigue Predictive Modeling: State-of-the-Art Review," International Journal of Aerospace Engineering, vol. 2012, Article ID 191879, 29 pages, 2012. doi:10.1155/2012/191879

assessment of their application to aircraft structures and materials. Finally environmental effects on short crack behavior of materials are discussed, and a compilation of definitions related to corrosion and fatigue is presented.

Key Words: Aircraft Structural Integrity, Corrosion Effects, Exfoliation Corrosion; Pitting Corrosion; Fatigue; Intergranular Attack; Corrosion Fatigue, Structural Integrity.

Introduction

This review article deals with the effects of intergranular attack and exfoliation corrosion on structural integrity of aircraft structures and materials with emphasis on aluminum alloys used over many decades for airframe components of military, commercial and general aviation aircraft. Aluminum alloys have been the material of choice for many components of airframes in the past and remain so even though some aircraft are using more titanium alloys and resin based composites in many airframe components. The general background on phases of life and methods for dealing with corrosion in general and aspects of HOLSIP (Holistic Structural Integrity Processes) paradigm are presented to some extent. (See www.holsip.com.) This is followed by a discussion of corrosion effects on SI (Structural Integrity) with some detail provided on significant effects of corrosion on maintainability and reliability of structures with extensive background material. Subsequently a section that describes intergranular attack and exfoliation in general terms follows which then is followed by a discussion of cases where IG attack and exfoliation caused significant structural integrity issues in aircraft in operational fleets. Studies oriented toward evaluating the effects of IG and exfoliation on fatigue behavior with emphasis on the long crack aspects is presented. The final section then presents recommended studies in order to develop and validate models to allow prediction and management of IG attack and exfoliation as part of a Holistic Structural Integrity Processes paradigm [1-69][7].

Phases of life and modeling

The phases of life of a structure may be classified according to the division in the Table 2.1. Thus, the total life ($\mathbf{L_T}$) of a structure is $\mathbf{L_T= L_1+L_2+L_3+L_4}$. Fig. 2.1 presents a depiction of the degradation process from a holistic perspective. The regions shown in Fig. 2.1, e.g. 1, 2, 3, and 4, illustrate the portion of life, on the abscissa, and the corresponding growth in discontinuity size plotted schematically on the ordinate. This article concentrates on the phases of life $\mathbf{L_1}$ **and** $\mathbf{L_2}$. That is, the corrosion process or processes that results in the formation or nucleation of a specific form of corrosion generating a specific form of discontinuity that is not necessarily a crack like discontinuity (EDS or MDS- see list of definitions in the appendix), and the development of short cracks and their propagation from the initial discontinuity state or from the evolved or modified discontinuity state (IDS- see the list of definitions in the appendix) formed by the mechanism in question. The requirement of the community to come up with <u>design methods</u> to deal with corrosion or other time based degradation, i.e. fatigue, creep, and wear, is essential and some of the elements are depicted in Fig. 2.2. This figure illustrates that most of the quantitative methods that have been developed used the concepts of mechanics of materials with an incorporation of fracture mechanics.

The sections of this article that follow will discuss the following major areas:

- General effects of corrosion on structural integrity.

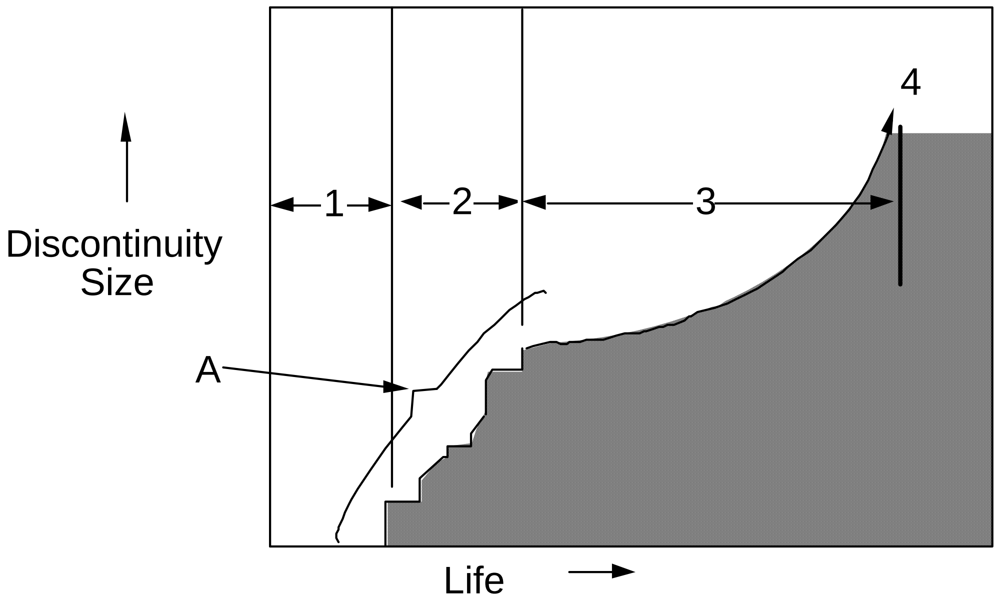
[7] Numbers in parentheses refer to the references in order of appearance.

Table 2.1: Phases of Life. See Fig. 2.1. {from Hoeppner, 1971[69], 1982 [38], 1985 [39]}

• **FORMATION OR NUCLEATION OF DEGRADATION/DAMAGE BY A SPECIFIC PHYSICAL OR CORROSION PROCESS INTERACTING WITH THE FATIGUE PROCESS IF APPROPRIATE. CORROSION AND OTHER PROCESSES MAY ACT ALONE TO FORM/NUCLEATE THE DAMAGE. A TRANSITION FROM THE FORMATION/NUCLEATION STAGE TO THE NEXT PHASE MUST OCCUR. PHASE L_1 TO SOME OTHER PHASE.**
• **MICROSTRUCTURALLY DOMINATED CRACK LINKUP AND PROPAGATION ("SHORT" OR "SMALL" CRACK REGIME). PHASE L_2.**
• **CRACK PROPAGATION IN THE REGIME WHERE LEFM, EPFM, OR FPFM MAY BE APPLIED BOTH FOR ANALYSIS AND MATERIAL CHARACTERIZATION (THE "LONG" CRACK REGIME). PHASE L_3.**
• **FINAL INSTABILITY. PHASE L_4.**

NOTE: In some cases in practice not all the phases cited above occur.

The degradation process



A= "FIRST" detectable crack

1. Nucleation phase, "NO CRACK"

2. "SMALL CRACK" phase-steps related to local structure (Anisotropy)

3. Stress dominated crack growth, LEFM, EPFM

4. Crack at length to produce instability

Fig. 2.1: A depiction of the degradation process {after Hoeppner-1971 [69], 1982 [38] 1985 [39]}.

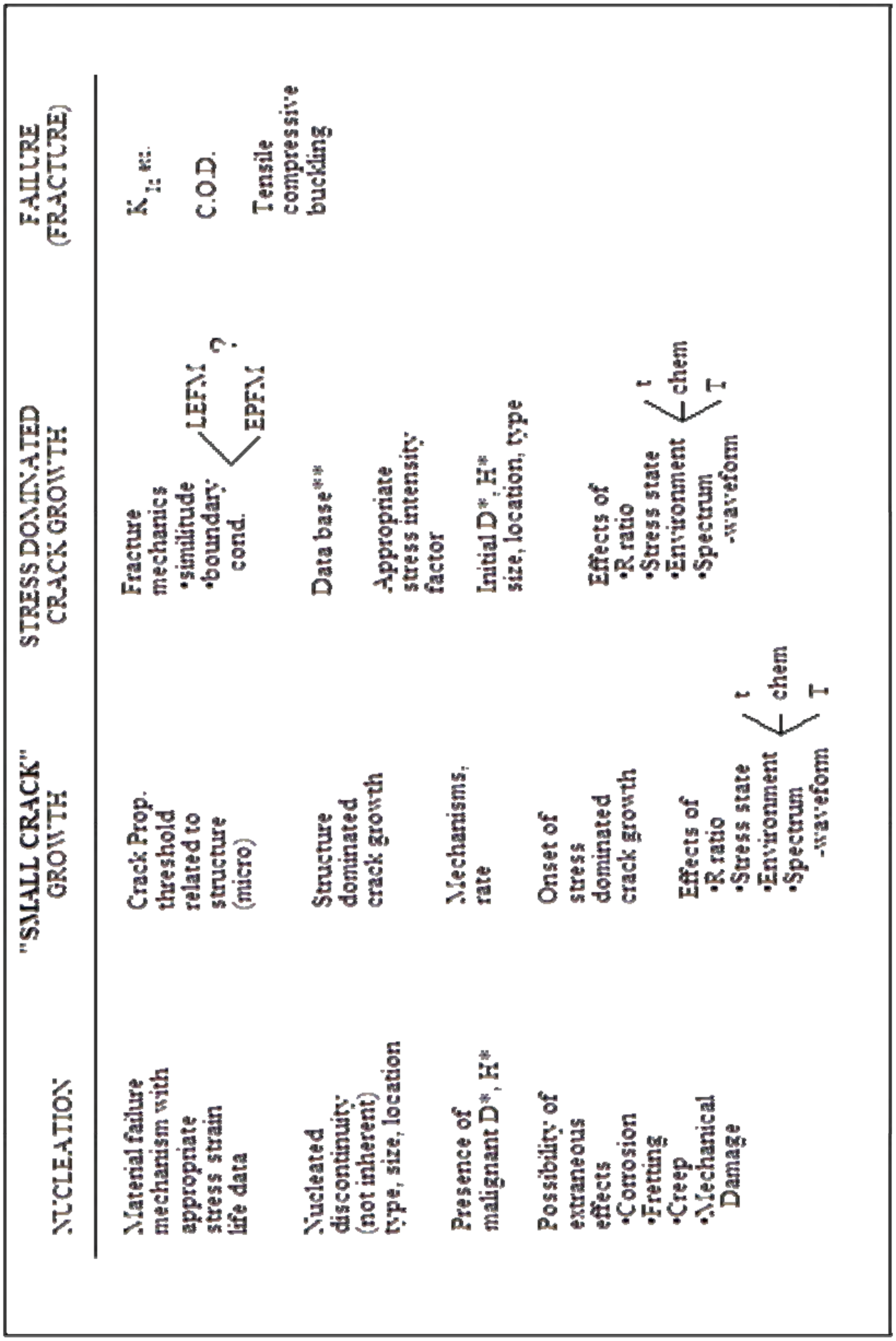


Fig. 2.2: Methods for each life phase {after Hoeppner-1971 [69], 1982 [38] 1985 [39]}.

- Intergranular attack and Exfoliation Corrosion (EC) in Aircraft Structural Aluminum Alloys. Efforts to date on Modeling Effects of Exfoliation Corrosion in Aircraft Structure with emphasis on fatigue and fatigue crack propagation behavior.

The issue of the effects of corrosion on structural integrity of aircraft has been a question of concern for some time [1-36]. The potential effects are many and they can be categorized as follows:

(An attempt has been made to provide as simple a statement of each potential problem as possible. In the discussion below the use of the terms global and local refers to the likely extent of the corrosion on the surface of a component. Global means the corrosion would be found on much of the component whereas local means the corrosion may be localized to only small, local areas.):

1) Reduction of section with a concomitant increase in stress (e.g., thickness change, etc.). Global or local.
2) Production of stress concentration. Local.
3) Nucleation of cracks. Local, possibly global. Source of Multiple-site cracking.
4) Production of corrosion debris. This may result in surface pillowing by various means, which may significantly change the stress state and structural behavior. Local and global.
5) Creation of a situation that causes the surfaces to malfunction. Local and global.
6) Cause environmentally assisted crack growth (EACG) under cyclic (corrosion fatigue or corrosion-fatigue) or sustained loading (SCC) conditions. Local.

7) Create a damage state that is missed in inspection when the inspection plan was not developed for corrosion or when corrosion is missed. Local and global.

8) Change the structurally significant item due to the creation of a damage state not envisioned in the structural damage analysis or fatigue and strength analysis. If the SSI is specified, for example, by location of maximum stress or strain, then the corrosion may cause another area(s) to become significant. Local or global.

9) Create an embrittlement condition in the material that subsequently affects behavior. Local or global.

10) Create a general aesthetic change from corrosion that creates maintenance to be done and does damage to the structure. Local or global.

11) Corrosion maintenance does not eliminate all the corrosion damage and cracking or the repair is specified improperly or executed improperly thus creating a damage state not accounted for in the design. Local or global.

12) Generation of a damage state that alters either the durability phase of life or the damage tolerant assessment of the structure or both.

13) Creation of a widespread corrosion damage (WCD) state or a state of corrosion that impacts the occurrence of widespread fatigue damage (WFD) and its concomitant effects. [1, 3, 4, 13, 15, 26, 27, 28, 32, 33, 34, 35, 36].

14) Produce a condition that may cause a loss of fail safety in conjunction with one or more issues noted above.

The question of whether corrosion, corrosion fatigue, corrosion/fatigue or and stress corrosion cracking (see appendix for definitions used herein) are safety concerns or just maintenance/economic concerns has been a point of discussion related to aircraft structural integrity for over 50 years. Nonetheless, a great deal of the aircraft structural integrity community believes that corrosion related degradation is just an economic or maintenance concern. The issue of type of corrosion and its effects on structural integrity has been addressed in other summaries. This brief introduction gives a summary of some of the compilations of information related to corrosion in general. The major section that follows presents more information on the studies to date that have focused or are focusing on intergranular attack and exfoliation corrosion.

It was with the issue of safety or economic concerns that led Campbell and Lehay [12] and Wallace, Hoeppner and Kandachar [13] to pursue the presentation of technical facts and knowledge to illustrate the potential for a safety issue as well as maintenance and/or economic issue. Finally, Hoeppner et al. [28] reviewed failure data obtained from USAF, USN, USA, FAA, and the NTSB related to aircraft incidents and accidents in the USA from 1975-1994 to evaluate further the potential for corrosion and fretting related degradation to be significant safety issues. A quote from the introduction to the paper [28] follows:

"*On July 25, 1990, a pilot and crew were killed when the right wing outboard of the engine nacelle separated from their Aero Commander (now Twin Commander) 680 while performing a geological survey. The aircraft entered an uncontrolled decent and crashed into a field near Hassela, Sweden. Investigations revealed that the wing failed due to corrosion pits, which nucleated fatigue cracks in the lower spar cap*"[28]. Although the accident occurred in Sweden, this accident sparked inspections of other Twin Commander aircraft worldwide. In November of 1991, Twin Commander released a service report detailing extensive cracking problems found in the lower spar cap of a

U.S. registry airplane. The Australian Civil Airworthiness Authority (CAA), on behalf of the Federal Aviation Administration (FAA), conducted fractographic analyses on ten cracks found in the component. The CAA determined that the cracks formed by intergranular attack, pits and resulted in stress corrosion cracks and that further extension occurred by fatigue. These failures will be referred to later in the section on IG and exfoliation and more detail will be provided. The mechanism overlap (two or more corrosion or degradation mechanisms being involved in change of damage state) frequently has been observed as documented by reference 13 as well.

The above example illustrates how corrosion pits and IG attack can severely jeopardize the structural integrity and safety of aircraft. In addition to corrosion, fretting and fretting fatigue have proven, on occasion, to be significant safety hazards. This article will not deal with fretting and fretting fatigue as the first author has written extensively about this elsewhere and these mechanisms of degradation were not to be included in this brief summary.

Although the aircraft industry directs a great deal of attention to safety concerns, for many years it has relegated corrosion and fretting to maintenance, economic, and inspection issues. While the industry has developed some corrosion/fretting prevention programs, it has not done what it possibly should to quantitatively evaluate the effects of corrosion/fretting on structural integrity. What attempts have been made in this area are sporadic and limited in number [28].

Walter Schütz addressed this issue further in the Plantema Lecture at ICAF [26]. Furthermore, anyone that doubts the potential catastrophic consequences of corrosion related degradation of aircraft structure would be assisted by reading Steve Swift's insightful presentation related to "The Aero Commander Chronicle" [27]. As a part of a technical paper delivered by Hoeppner et al. at ICAF-1999, they found the following with regard to pitting corrosion and pitting corrosion fatigue as listed in Table 2.2.

The examples shown in the table, taken with the general information cited in the references clearly show that corrosion related degradation is a significant safety issue in the assurance of structural integrity of aircraft. No such compilation has been done for exfoliation alone but needs to be done in the authors' opinion.

In recent years more emphasis has been placed on this issue of corrosion effects on structural integrity-especially after the fleet surveys subsequent to the Aloha Airlines accident (AA243) in 1988 [16]. Even though the NATO-AGARD community authorized the production of a manual on corrosion case studies and a great deal of information was presented in the manual published by AGARD [13] it is essential that the RMS deficiencies that may arise before accidents occur be recognized. This clearly has not been the case in all major fleets of aircraft whether they are military or commercial [12, 16, 19-22, 23, 26-28]. Another issue that is clear is that deficiencies in the analysis of failures and the databases exist [28, 29].

The potential regrettable occurrence of accidents from corrosion related crack formation/nucleation is a constant threat to aircraft safety. The following quote from the recent NATO RTO conference on fatigue in the presence of corrosion adds some understanding to the need for greater effort to understand the potential role of effects of corrosion on structural integrity.

> *"Some of the workshop papers discussed the significance of corrosion-fatigue as a safety issue or an economic issue. There is ample data to support the contention*

Table 2.2: Incidents from Pitting Corrosion and Corrosion Fatigue.

Aircraft	**Location of Failure**	**Cause**	**Incident Severity**	**Place**	**Year**	**From**
Bell Helicopter	Fuselage, longeron	Fatigue, corrosion and pitting present	Serious	AR	1997	NTSB
DC-6	Engine, master connecting rod	Corrosion pitting	Fatal	AK	1996	NTSB
Piper PA-23	Engine, cylinder	Corrosion pitting	Fatal	AL	1996	NTSB
Boeing 75	Rudder Control	Corrosion pitting	Substantial damage to plane	WI	1996	NTSB
Embraer 120	Propeller Blade	Corrosion pitting	Fatal and serious, loss of plane	GA	1995	NTSB
Gulfstream GA-681	Hydraulic Line	Corrosion pitting	Loss of plane, no injuries	AZ	1994	NTSB
L-1011	Engine, compressor assembly disk	Corrosion pitting	Loss of plane, no injuries	AK	1994	NTSB
Embraer 120	Propeller Blade	Corrosion pitting	Damage to plane, no injuries	Canada	1994	NTSB
Embraer 120	Propeller Blade	Corrosion pitting	Damage to plane, no injuries	Brazil	1994	NTSB
Mooney Mooney 20	Engine, interior	Corrosion pitting, improper approach	Minor injuries	TX	1993	NTSB
C-130	Bulkhead 'Porkchop' Fitting	Fatigue, corrosion pitting	Pressurization leaks	-	1995	LMAS
C-141	FS998 Main Frame	Corrosion pitting, stress corrosion cracking	Found crack during inspection	-	1991	LMAS

that it is definitely an economic issue. There is also ample data to support the contention that it has not been a significant safety problem. However, the problem is certainly a potential safety concern if maintenance does not perform *their task diligently. In addition, management must continuously update established maintenance and inspection practices to address additional real-time degradation threats for aircraft operated well beyond their initial design certification life. The economic issue alone is sufficient to motivate the support of research and development that can reduce the maintenance burden. This research will also reduce the threat of catastrophic failure from the corrosion damage." [Lincoln, J., Simpson, D., Introduction to Reference 36].*

Another quote from a different reference sheds further light on this issue [34-page 1-1].

"*At the present time, structural life assessments, inspection requirements, and inspection intervals, are determined by Durability and Damage Tolerance Assessments (DADTAs) using fracture mechanics crack growth techniques in accordance with the Aircraft Structural Integrity Program (ASIP). These techniques do not normally consider the effects of corrosion damage on crack initiation or crack growth rate behavior. Also, these techniques do not account for multiple fatigue cracks in the DADTAs of the structural components susceptible to WFD. For aircraft that are not expected to have significant fatigue damage for many years, such as the C/KC-135, this approach has severe limitations since it does not account for corrosion damage or WFD. The impact of corrosion damage and WFD on stress, fatigue life, and residual strength must be understood to ensure maintenance inspections and repair actions are developed and initiated before serious degradation of aircrew/aircraft safety occurs.*"

Thus, the community clearly now recognizes the potential impact of corrosion related degradation on structural integrity of aircraft. The need to understand the potential for the occurrence of corrosion on aircraft components is critical. Thus, to even begin the assessment of this potential the community needs to know the following:

- The chemical environment likely to be encountered on the structure of interest at the location of interest, The material from which the component is manufactured,
- The orientation of the critical forces (loads) applied externally and internally with respect to the critical directions in the material. The susceptibility of the material to occurrence of a given type of corrosion. The temperature of exposure of the component. The type of forces applied (i.e., sustained force or cyclic force-constant amplitude loading or variable amplitude loading). The type of exposure to the chemical environment (i.e., constant, intermittent), concomitant with the forces (corrosion fatigue or stress corrosion cracking) or sequentially with force (corrosion/fatigue or corrosion-fatigue),
- The rates of corrosion attack. The potential influence of the effects of corrosion on fatigue crack nucleation and propagation,
- The impact of any related corrosion degradation to residual strength,
- The potential for widespread corrosion damage to occur (WCD), and
- The potential impact of corrosion on the occurrence of widespread fatigue damage (WFD) and its impact on structural integrity.

Obviously this is a formidable list but the assessment of these items is possible to some degree to make the estimation of the effects of corrosion more accurate than they have been to date.

This article deals with the identification of the issues to be dealt with in establishing methods of estimating (predicting) the effects of corrosion. To do this various **models** are employed to be able to identify methods of establishing those components most susceptible to the ravages of corrosion.

Corrosion in Aircraft Structural Aluminum Alloys

General

Corrosion is an electrochemical reaction process between a metal or metal alloy and its environment [37]. For corrosion to occur, four conditions must exist viz. an anode, a cathode, an electrolyte, and an electrical path (flow of electrons). The anode and the cathode could be of two dissimilar metals or anodic and cathodic cells could be formed in the same metal alloy because of the potential difference in the constituent chemical elements or grain interior and grain or phase boundaries. Moreover, depending on the availability of oxygen (differential aeration cells) and electrolyte (differential concentration cells) on the surface of the metal alloy, special types of localized corrosion could occur. 2xxx (Al-Cu alloys) and 7xxx (Al-Zn alloys) series aluminum alloys are most commonly used in manufacturing aircraft structural components. This is currently true and has been true for some time. Depending upon strength and toughness requirements, different types of aluminum alloys such as 2024, 7075, 7178, and many others are used for commercial and military aircraft fuselage skins, wing skins, and other extrusions and forging such as stringers, and fuselage frames. In general, 2024-T3 is used for skins and 7075-T6 for stringers and frames although many applications of these and other alloys in the 2xxx and 7xxx families exist. Lap or butt splices are the common configuration for longitudinal joints whereas butt joints are for circumferential joints. A common joining method is riveting and in some cases it is in combination with adhesive bonding. In older aircraft, spot welding also can be found. As Wallace and Hoeppner mentioned in their AGARD report on "Aircraft Corrosion: Causes and Case Histories", in the initial stages, corrosion is in the form of filiform or pitting in the interior and exterior of fuselage skins [38]. Moreover, as noted in their report, crevice corrosion between the riveted sheets in fuselage joints is a significant issue and it is usually associated with the trapped small "stagnant solution." Furthermore, depending upon the chemical conditions this could lead to a combination of pitting, galvanic or exfoliation corrosion. As well, it is recognized that fretting corrosion/wear in faying surfaces and within fastener holes plays a role in the corrosion mechanisms within aircraft joints [38]. The process of corrosion may start early in the process of manufacturing and continues when the aircraft enters its service. Therefore, it has been realized that the corrosion prevention and control program (CPCP) should be planned concurrently from the initial design until the aircraft is out of service. Furthermore design allowables should be established as with other major integrity issues.

Many types of corrosion mechanisms such as intergranular, exfoliation, pitting, crevice, fretting, microbiologically influenced corrosion, stress corrosion cracking, and hydrogen embrittlement have been found to occur in aircraft structural aluminum alloys [38]. Moreover, the synergistic effects of corrosion and the loading conditions have been found to initiate the corrosion fatigue failure process and the stress corrosion cracking failure process of aluminum alloy aircraft structural components. As identified, recently, in a report by the National Research Council's National Materials Advisory Board [39], corrosion in aircraft structural joints would result in the following: (i) significant changes in the applied stress because of material loss as well as corrosion product buildup that may cause “pillowing” or bulging of aluminum alloy sheet, (ii) hydrogen embrittlement that may result in reduced toughness, strength, and ductility of the material, and (iii) increase in fatigue crack growth rates that may severely hamper the planned inspection intervals. These issues have been discussed in workshops presented for the US-FAA and UCLA as well as FASIDE Int. Inc. workshops since 1971. In addition, the first author has frequently discussed the following other potential effects of corrosion on structural integrity.

- Production of localized stress concentrations that act as crack nucleation sites.
- Change of the structurally significant item (SSI).
- Modification of the fail safety by any of the above.

Moreover, recently, an attempt has been made to model loss of thickness due to crevice corrosion growth in a corroded lap joint.

Several metallurgical, mechanical and environmental factors influence the corrosion process in aluminum alloys [40]. Metallurgically induced factors include heat treatment, chemical composition of alloying element, material discontinuities such as the presence of voids, inclusions, precipitates, second phase particles, and grain boundaries as well as grain orientation. Environmental factors include temperature, moisture content, pH, type of electrolyte, and the time of exposure. Aircraft often are exposed to both external and internal environments. External surfaces of the aircraft are exposed to a variety of environments including rain, humidity, acid-rain, deicing fluid, industrial pollutants, hot and cold temperatures, dust, high content of deposits of exhaust gases from engines, and salts. In addition, the inside of the aircraft is affected by condensed moisture, spilled beverages, cargo leak, deicing fluid, lavatory seepage, and accumulated water in the fuel tank as well as others. Moreover, aircraft are exposed to wide ranges of environment depending upon their route and geographical location viz. tropical, marine, industrial and rural [38, 52].

In both military and commercial aircraft, internal and external wing structures as well as the fuselage bilge areas and flight control surfaces are found to be most affected by corrosion in a marine and tropical environment [41]. The major causes of corrosion in aging aircraft as observed in Indonesian aging aircraft were found to be due to spillage of toilet liquid, contamination due to spillage or evaporation from the cargo compartment, and contamination due to high humidity [42]. In addition, in these aircraft, corrosion was often found in the area surrounding the cargo compartment, wing structure, and landing gear. The types of corrosion found in these aircraft were of exfoliation, galvanic, filiform, and stress corrosion and among these exfoliation corrosion was found in most cases [42].

Several "structural issues" such as exfoliation, pitting, stress corrosion cracking, fatigue cracking, fastener corrosion, wear, fatigue and corrosion, delamination and disbonds have been observed in the U.S. Air Force aging aircraft as shown in Table 2.3 [39]. For example, in C/KC 135 fleet, crevice corrosion in the spot welded lap joint/doubler and corrosion around the steel fasteners on the upper wing skin have been recognized as significant corrosion issues [43]. In the later case, as was noted, there was a possibility of moisture from condensation or deicing solution trapped around fastener heads forming a galvanic couple. This was observed to result in intergranular attack of the grain boundaries leading to exfoliation [43].

Table 2.3: Corrosion and Fatigue Issues in the US Air Force Aging Aircraft.

	Type of aircraft	Issues
1	C/KC 135 (Tanker aircraft)	*Corrosion* between fuselage lap joints and spot welded double layers, around fasteners in the 7178-T6 aluminum upper wing skins, between wing skins and spars, between bottom wing skin and main landing gear trunnions, between fuselage skin and steel doublers around pilot windows, *Stress Corrosion Cracking* (SCC) of large 7075-T6 aluminum forging (fuselage station 620, 820, and 960), *corrosion and SCC* of fuselage station 880 and 890 floor beams, wing station 733 closure rib, and *corrosion* in the E model engine struts.
2	C-141B (Transport aircraft)	*Widespread Fatigue Damage* (WFD) in the fuel drain holes in the lower surfaces of the wings, *corrosion and SCC* in the upper surface of the center wing, *fatigue cracking and SCC* around the wind shield, *fatigue cracking* in the stiffeners in the aft pressure door, SCC in the fuselage main frames, and *corrosion* in the empennage.
3	C-5 (Airlifter)	*SCC* of the 7075-T6 aluminum mainframes, keel beam, and fittings in the fuselage, 7079-T6 fuselage lower lobe and aft upper crown.
4	B-52H (Bomber)	*Cracking* in the bulkhead at body station 694, *fatigue cracking* in flap tracks and in the thrust brace lug of the forward engine support bulkhead, *cracking* in the side skin of the pressure cabin, aft body skins, and upper surface of the wing.
5	F-15 (Fighter aircraft)	*Low-cycle fatigue cracking* in the upper wing surface runouts, upper wing spar cap seal grooves, front wing spar conduit hole, upper in-board longeron splice plate holes, *corrosion* in nonhoneycomb structure including fuselage fuel tank, the outboard leading-edge structure of the wings, and the flap hinge beam.
6	F-16 (Fighter aircraft)	*Cracking* of the vertical tail attachment bulkhead at fuselage station 479, fuel vent holes of the lower wing skin, the wing attach bulkhead at fuselage station 341, the upper wing skin, fastener problems on the horizontal tail support boxbeam, and the ventral fin.

Table 2.3 Continued

7	A-10 (Attack aircraft)	*Fatigue cracking in the wing* auxiliary spar cutout of the center section rib at wing station 90, outer panel front spar web at wing station 118 to 126, outer panel upper skin at leading edge. Fatigue cracking in the center fuselage forward fuel cell floor at the boost pump, forward fuselage gun bay compartment, forward fuselage lower longeron and skin at fuselage station 254, and center fuselage overwing lower floor panel stiffeners. Fatigue cracking in the aft nacelle hanger frame, thrust fitting and the engine inlet ring assembly skin/frame. Fatigue cracking in the main landing gear shock strut outer cylinder. *Exfoliation corrosion* in the 2024-T351 aluminum lower wing skin, 7075-T6 aluminum upper wing at the leading edge, 2024-T3511 aluminum lower front spar cap, 7075-T6 aluminum fuselage bottom skin 2024-T3/7075-T6 aluminum fuselage side skin and beaded pan, and 2024-T3511 aluminum horizontal stabilizer upper spar caps. *Pitting corrosion* in the 9Ni-4Co-0.3C steel wing attach fitting bushing and lug bore, main landing gear fitting attach bolts, 7075-T6 aluminum aft fuel cell aft bulkhead, and 2024-T351 center fuselage upper longeron. SCC in the wing attach bushing flange, and the main landing gear attach bolts.
8	E-3A (Airborne Warning and Control System)	*Fatigue and corrosion* in the 7178-T6 rudder skins, and spoiler actuator clevis. *Exfoliation corrosion* in the 7178-T6 upper wing skin, leading edge slats, main landing gear door, fillet flap, fuselage stringer 23, and magnesium parts. *Delamination* and disbonds in the windows, floor panels, and nose radome core. *Wear* in the antenna pedestal turntable bearings.
9	E-8 (Joint Surveillance and Attack Radar System)	*"Small" fatigue cracks* in fastener holes in the 7075-T6 aluminum stringers, in the 2024-T3 aluminum skins.
10	T-38 (Air training command aircraft	*Fatigue cracking* in the lower surface of the wing, lower wing skin fastener holes, wing skin access panel holes, milled pockets on the lower wing skin, and the fuselage upper cockpit longerons. *SCC* in the fuselage cockpit upper and lower longerons, fuselage forgings. honeycomb *corrosion* in the horizontal stabilizer (due to water intrusion), and the landing gear strut door

Examination of C/KC 135 fuselage lap splices (stiffened aluminum lap joint) revealed that outer skin corrosion was predominantly intergranular and exfoliation [44]. Moreover, extensive cracking was noted at these sites in the outer skin. In addition, extensive "pillowing" with more than 300% change in volume due to corrosion products along the faying surfaces was observed. In the rivet/shank region, severe localized corrosion and intergranular corrosion were observed. The fracture of rivet heads was attributed to high local stress due to environmentally assisted cracking at the junction. As well, in this study, solution samples were collected from selected areas of lap splice joints and the solution analysis showed the presence of several cations such as Al^{3+}, Ca^{2+}, Na^{+}, K^{+}, and Ni^{2+} and also anions Cl^{-}, SO_4^{2-}, and NO_3^{-}. Subsequent potentiodynamic tests using solution containing these ions led to the belief that dissolution rates could completely penetrate the fuselage outer skin during service life [44].

Thus, in addition to fatigue cracking, different corrosion mechanisms occur in aircraft structures depending upon their location, geometry, exposure to environment, and loading conditions. Research studies conducted within the Quality and Integrity Design Engineering Center (QIDEC) at the University of Utah as well as other related studies are briefly discussed below.

Intergranular and Exfoliation Corrosion

Exfoliation corrosion is believed to be a manifestation of intergranular corrosion. Intergranular corrosion results from either the segregation of reactive impurities or from the depletion of passivating elements at the grain boundaries. This makes the regions at or surrounding the grain boundaries less resistant to corrosion resulting in preferential corrosion. The high strength aluminum alloys such as 2xxx and 7xxx series are highly susceptible to intergranular corrosion [37]. Exfoliation corrosion is a form of intergranular attack that occurs at the boundaries of grains elongated in the rolling direction. The 7xxx series aluminum alloys are particularly less resistant to exfoliation corrosion because during heat treatment (to achieve maximum desirable strength) their constituent elements copper and zinc accumulate at grain boundaries leaving the adjacent region free of precipitates. As aluminum and aluminum intermetallic compounds are highly reactive in the EMF series as well as aluminum is anodic to copper in the galvanic series, the resulting galvanic couples cause the grain boundaries to preferentially corrode (intergranular attack). McIntyre and Dow have related the localized corrosion problems in the 7075-T7352 fuel tanks of underwater weapon systems to intergranular corrosion [45]. In their study, aluminum alloys 7075 and 6061 were exposed to artificial seawater containing nitrate ions. It was observed that accelerated intergranular corrosion occurred in 7075 alloys. From the test results, they hypothesized that refueling the improperly cleaned fuel tank may cause the propellant in contact with the small quantity of sea water remaining in the fuel tank. This resulted in the release of nitrate ions from an hydrolysis process leading to reduced pH that may cause the dissolution of the oxide film (localized corrosion). They further hypothesized that corrosion eventually propagates to the bulk regions of the alloy due to intergranular attack by the preferential corrosion of reactive $MgZn_2$ intermetallic compounds located at grain boundaries. This was found to be true for 7075 aluminum alloy but not for 6061 aluminum alloy because the latter does not contain either Cu or Zn as alloying element [45].

Reducing the impurities such as iron and silicon as well as heat treatment modifications in aluminum alloys have resulted in an increase in the resistance to exfoliation corrosion [46]. For example, overaged 7075-T7 alloys are more resistant to exfoliation corrosion when compared to 7075-T6 alloys. In addition, Rinnovatore showed that in the T6 temper, exfoliation corrosion resistance was found to be greater for forgings produced from rolled bar stock than forgings from extruded bar stock [47]. Moreover, it was shown that rapid quenching from the solution temperature in cold water increased exfoliation corrosion resistance of forgings tempered to T6.

Fatigue and exfoliation interactions have been studied. Mills reports that most of the studies have been performed during the last five years on this issue although Shaffer in 1968 reported significant reduction in the fatigue life of exfoliated extruded 7075-T6 spar caps [48]. Moreover, multiple crack nucleation sites were observed in 7075-T651 [49], and 2024-T3 [50] aluminum alloy specimens when the specimens were subjected to exfoliation corrosion and then fatigue tested under positive R values with constant amplitude loading. Mills found an 88% decrease in the fatigue life of the specimens with prior exfoliation corrosion damage when compared to specimens tested without prior corrosion damage. Chubb et al. showed in their study using panels containing fastener holes that the end grains exposed in the rivet holes would be the potential corrosion sites that could eventually result in multiple site damage.

In a recent study [48], experiments were performed to determine the effect of exfoliation on the fatigue crack growth behavior of 7075-T651 aluminum alloy. First the specimens were subjected to prior-corrosion damage using ASTM standard EXCO corrosive solution and then fatigue tested in corrosion fatigue environments of dry air, humid air, and artificial acid-rain. Test results indicated that prior-corrosion damage resulted in higher crack growth rates than when tested in dry air as well as in acid-rain environments when compared to uncorroded specimens. Fractographic analysis showed quasi-cleavage fracture close to the exfoliated edge of the specimens tested in all the three environments indicating embrittlement by prior-corrosion. Thus, embrittlement by prior-corrosion was stated to "result in accelerated crack nucleation, faster short crack growth, and earlier onset of fatigue phenomena such as multiple-site damage."

Corrosion fatigue

Corrosion fatigue is defined as "*the process in which a metal fractures prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels or fewer cycles than would be required in the absence of the corrosive environment*" [40]. Corrosion acting conjointly with fatigue can have major effects on materials in structures of aircraft. First, corrosion can create discontinuities (pits, cracks, etc.) that act as origins of fatigue cracks with significant reductions in life at all stress levels. In crack propagation, corrosion effects are well known to produce accelerated fatigue crack propagation. The combination of aggressive environment and cyclic loading conditions has been observed to accelerate crack growth rates in aluminum alloys. Several mechanisms were proposed to explain the corrosion fatigue process [37]. They are: (i) dissolution of material at the crack tip in corrosive environment, (ii) hydrogen embrittlement in which diffusion of hydrogen (a by product of corrosion process) into the lattice space that could weaken the atomic bonds thereby reducing the fracture energy, (iii) theory of adsorbed ions in which the transport of critical species to the crack tip results in lowering of the energy required for fracture, and (iv) film-induced cleavage in which it is hypothesized that crack speed would increase at the film-substrate interface when the crack grows through the low toughness oxide layer leading to the rupture of the film.

In general, corrosion fatigue effects on crack propagation are more pronounced at lower stress intensities whereas at higher stress intensities the crack propagates at such a high rate that the effects of chemical dissolution or localized embrittlement will be negligible. Several parameters affect corrosion fatigue crack propagation rates. For example, crack growth rates increase with increase in the stress intensity range. Also, at lower frequency corrosion fatigue effects will be more severe than at higher frequency because of the time dependent nature of the process. Increase in R value has been found to generally increase corrosion fatigue crack propagation rates. As well, increasing the concentration of corrosive species, lowering the pH, increasing the moisture content, and temperature usually result in more severe effects [40].

The most common corrosion fatigue environment that is simulated in laboratory testing is 3.5% NaCl as it is believed to result in severe general corrosion rates as well as it represents roughly the salinity of sea water. In addition, other environments such as humid air, salt sprays, and artificial acid rain (to simulate industrial pollutants) also are used to characterize corrosion fatigue crack growth behavior of aluminum alloys. As aircraft are exposed to several complex chemical environments both inside and outside, no single environment could simulate the actual condition. Therefore, a few studies used sump tank water that was considered close to a "realistic chemical environment" [51]. The quest for realistic corrosion fatigue environment led Swartz et al. [52] to collect and analyze solution samples from bilge areas, external galley and lavatories of five different airplanes. As a result, a new chemical environment was developed to perform corrosion fatigue crack growth experiments on 2024-T351, 2324-T39, 7075-T651, and 7150-T651 aluminum alloys. For all the alloys studied the fatigue crack propagation rates in synthetic bilge solution were found to be between the dry air and the 3.5% NaCl data. In another study [53], cyclic wet and dry environment was simulated in characterizing the corrosion fatigue crack growth rates in 2024-T351 aluminum alloy. It was hypothesized that during the dry cycle the partial evaporation of the aqueous solution may allow some chemical species to get deposited at the crack tip and then in the wet cycle when the rehydration occurs, corrosion could occur at a greater rate than before.

To simulate aircraft service corrosion, fatigue crack growth studies were conducted on service corroded 2024-T3 aluminum panels extracted from a C/KC-135 aircraft [54]. Test results showed that in some cases fatigue crack growth rates were two or three times greater in the corroded material, however, in other cases, there was little difference. It was observed that "the difference in the crack growth rates was due to high variability in the amount of corrosion damage between specimens".

Corrosion Pillowing and its Effect on Structural Integrity of Aircraft Lap Joints

Recently, some studies have shown that the increase in stress levels is not only because of the thickness loss due to corrosion but also due to the volume of the corrosion product build-up in a joint [55]. Also, evidences show that lap joints contain "faying cracks" under the rivet heads in the corroded areas. The complexity of this issue as explained by Komorowski et al. is that "the majority of the cracks had not penetrated the outer skin surface and appeared to grow more rapidly along the faying surface creating a high aspect ratio semi-elliptical crack and it is difficult to detect and affects the structural integrity of the joint" [55]. As reported by Krishnakumar et al. [56], the major corrosion product in the lap splices is found to be aluminum oxide trihydrate, an "oxide mix" which has a high molecular volume ratio to the alloy. As the oxide is insoluble, it is found to remain within the joint and in turn is responsible to deform the skins in the joint which usually gives a bulging appearance, commonly termed as "pillowing". Moreover, finite element analysis revealed that for a two layer joint the stresses due to 6% thinning due to corrosion resulted in stress more than the yield strength of 2024-T3 aluminum alloy [57]. In addition, "pillowing induced deformation" was observed on the corroded joints after removal of the rivets and the separation of the skin. Moreover, multiple cracks were found to nucleate from rivet holes. Fracture mechanics analysis has shown that as the pillowing increases, the stress intensity factor for the crack edge along the faying surface increases [58]. On the other hand, the stress intensity factor decreases for the crack edge along the outer surface. Therefore, it was hypothesized that pillowing produces compressive stresses in the rivet area on the outer surface because of the resultant bending stresses. At the same time, high tensile stress is produced on the faying surface resulting in more rapid growth of faying surface cracks in the direction of the row of rivets than through the skin towards the outer surface [58].

Pitting Nucleation Theories

Pitting corrosion is defined as “localized corrosion of a metal surface, confined to a point or small area that takes the form of cavities” [40]. Pitting is a deleterious form of localized corrosion and it occurs mainly on metal surfaces which owe their corrosion resistance to passivity. The major consequence of pitting is the breakdown of passivity, i.e. pitting, in general, occurs when there is breakdown of surface films when exposed to pitting environment. Pitting corrosion is so complicated in nature because “oxide films formed on different metals vary one from another in electronic conduction, porosity, thickness, and state of hydration” [59]. The empirical models that have been developed to understand the pitting process are closely related to the integrity of the metal oxide film. The salient features of the empirical theories related to pit nucleation mechanisms are mentioned in Table 2.4.

Therefore, nucleation of pits generally involves certain localized changes in the structure and properties of the oxide film. However, propagation of pits is related to the dissolution of the underlying bulk metal. Further discussion on this subject is presented later in this article.

Pitting Corrosion

Overview

Pitting is classified as a localized attack that results in rapid penetration and removal of metal at “small” discrete areas [84]. An electrolyte should be present for pitting to occur. The electrolyte could be a film of condensed moisture, or a bulk liquid. How and when pitting occurs on a metal depends on numerous factors, such as, type of alloy, its composition, integrity of its oxide film, presence of any material or manufacturing induced discontinuities as well as chemical and loading environment, to name a few. Many metals and their alloys are subject to pitting in different environments. These include alloys of carbon steels, stainless steels, titanium, nickel, copper, and aluminum [85].

Table 2.4: Pit Nucleation Theories

Proposed by	Theory
Evans et al. [60] (1929-30)	Proposed penetration theory. Ability of a chloride ion to penetrate the film was linked to the occurrence of pitting. Halide ions are assumed to be transported from the film-solution interface to the metal-oxide interface either by the application of electric field or exchange of anions.
Hoar et al. [61, 62] (1960s)	Assumed the adsorption of anions on the oxide surface as the key aspect in the pit nucleation process. Proposed "ion-migration" model that involves activating anions that enter the oxide film lattice without exchange thereby increasing the ionic conductivity of the film resulting in local high anodic dissolution rates and pitting. Proposed "mechanical" model in which it was assumed that adsorption of anions at the oxide-solution interface lowers the interfacial energy resulting in the formation of cracks in the protective oxide film under the influence of the "electrostatic repulsion" of the adsorbed anions. Suggested a concept of local acidification of pit as a critical factor in pit growth.
Uhlig [63] and Kolotyrkin [64] (1961-1967)	Proposed adsorption theory in which at a certain value of the potential (pitting potential) the adsorption of aggressive anions on the metal surface displaces the passivating species such as oxygen. Kolotyrkin suggested that adsorption of anions at preferred sites forming soluble complexes with metal ions from the oxide. Once such species leave the oxide, thinning of the film starts locally increasing the electric field strength which accelerates the dissolution of the oxide.
Sato [65, 66] (1971, 1982)	Proposed that at a critical potential an internal film pressure exceeds the critical compressive stress for film fracture. Considered thinning of film at local sites and suggested that pitting occurs only when a critical concentration of aggressive anions and a critical acidity is locally built up.
Macdonald et al. [67] (1981)	Proposed that metal vacancies may accumulate as a result of the diffusion of metal cations from the metal/film to the film/solution interface, forming voids at the metal/film interface. When the voids grow to a critical size the passive film will collapse leading to pit growth.

In passivated metals or alloys that are exposed to solutions containing aggressive anions, primarily chloride, pitting corrosion results in local dissolution leading to the formation of cavities or “holes”. The shape of the pits or cavities can vary from shallow to cylindrical holes and the cavity is approximately hemispherical [86]. The pit morphology depends on the metallurgy of the alloy and chemistry of the environment as well as the loading conditions. As observed first by McAdam in 1928, these pits may cause local increase in stress concentration and cracks may nucleate from them [87].

According to Foley [88], pitting corrosion of aluminum occurs in four steps: (1) adsorption of anions on the aluminum oxide film, (2) chemical reaction of the adsorbed anion with the aluminum ion in the aluminum oxide lattice, (3) penetration of the oxide film by the aggressive anion resulting in the thinning of the oxide film by dissolution, and (4) direct attack of the exposed metal by the anion.

The susceptibility of a metal to pitting corrosion as well as the rate at which pitting occurs on its surface depends on the integrity of its oxide film. Therefore, a brief overview of the mechanisms of the formation of passive film is discussed below.

Formation of Passive Films and their Growth

The following discussion on the oxide film formation and its growth is extracted from ref. [89].

Early investigators examined the effects of natural waters on metals by placing them outside. One investigator, Liversidge, in 1895, observed that an aluminum specimen,

> ... “*lost its brilliancy, and became somewhat rough and speckled with grey spots mixed with larger light grey patches; it also became rough to the feel, the grey*

parts could be seen to distinctly project above the surface, and under the microscope they presented a blistered appearance. This encrustation is held tenaciously, and does not wash off, neither is it removed on rubbing with a cloth" [90].

Liversidge proposed that a hydrated aluminum oxide had formed, but did not confirm this with further testing of the layer. He did, however, note that when weighed, the aluminum specimens gained weight with exposure, rather than losing weight [91]. It was later confirmed that the weight gain was due to formation of an oxide film [92]. Although Liversidge suggested the formation of an aluminum oxide film, subsequent investigators proposed other theories to explain the passive behavior of aluminum. Some of these were changes in the state of electric charge on the surface, changes in valence at the surface, and a condensed oxygen layer [93]. Dunstan and Hill proved the presence of the oxide film on the surface of the metals in 1911. Through experiments with iron, they determined that the passive film was reduced at 250 °F, the temperature at which magnetic iron oxide is reduced. Similar films were found on other metals [93]. Barnes and Shearer attempted to determine the constitution of passive films on aluminum and magnesium in 1908. They determined that aluminum formed hydrogen peroxide when reacting with water and that the passive film consisted of $Al_2(OH)_6$ [92]. This was later determined to be incorrect [94].

Structure of the Passive Film in Aluminum

It later was determined that this film on aluminum consists of an aluminum oxide created when the aluminum comes in contact with an environment. Generally, this film is amorphous; however, under certain circumstances it will develop one of seven crystalline structures:

1. Gibbsite (also called hydrargillite): (α-Al_2O_3•$3H_2O$)

2. Bayerite: (β-Al_2O_3•$3H_2O$)

3. Boehmite: (α-Al_2O_3•H_2O or AlO•OH)

4. Diaspore: (β-Al_2O_3•H_2O)

5. Gamma alumina: (γ-Al_2O_3)

6. Corundum: (α-Al_2O_3)

7. Combinations of aluminum oxides with inhibitors, for example ($2Al_2O_3$•P_2O_5•$3H_2O$)

Gibbsite and diaspore structures are not found during corrosion of aluminum, but are frequently found in bauxite ores. Boehmite, bayerite, gamma alumina, and corundum are sometimes found in the passive layers of aluminum under certain conditions. Additionally, bayerite is frequently found as a corrosion product during pitting of aluminum. Combinations of aluminum oxides with inhibitors are not understood very well in the literature, but it is known that they will combine with oxide layer to form improved corrosion resistance through changing the passive film structure. Several researchers have studied changes in the amorphous structure of the oxide film. In one investigation, the passive film formed on the pure aluminum sheet revealed changes in structure with an increase in temperature and oxygen content. Prior to heating, the structure was reported to be amorphous oxide. As the temperature was increased, the amorphous film thickened, formed boehmite, and bayerite. The rate of film formation increased with temperature, and with an increase in oxygen content, intergranular attack began. The researcher suggested the following sequence of events in the formation:

boehmite is nucleated at dislocation centers that are at the surface of the amorphous film; it then grows by a diffusion mechanism. During thickening of the boehmite, a process occurs that allows aluminum ions to escape into the solution, which results in bayerite growth [95].

Other investigations revealed that aluminum in the molten state would develop an oxide film of gamma alumina which will convert to corundum when exposed to dry air. Aluminum sheet in water at temperatures below 70 to 85 °C after long aging will develop a passive film consisting of bayerite. Boehmite is found on aluminum exposed to water at high temperatures (above 70 to 85 °C) [94]. More recently, researchers have found small regions of crystallized γ-alumina within the amorphous layers created during anodizing [96].

During exposure to air and water, alumina will form a passive film with a duplex structure. The film will consist of two layers, a permeable outer layer, and a protective, nonporous layer next to the metal's surface. In the case of an air environment, the protective layer is thicker and the permeable layer is comparatively thin. In the case of an immersion in water, the permeable layer is thicker and the protective layer is thinner. In both cases, the total thickness of the duplex film is the same [94].

The protective layer will quickly reach maximum thickness, with the permeable layer growing slower. The growth rate of each layer depends on a few parameters. In air, it is dependent on temperature; in water, it is dependent on temperature, oxygen content, pH, and the type of ions present in the electrolyte; and in anodization procedures, it depends on electrolyte and applied potential. The film is typically formed on pure aluminum when the pH of the solution is between 4.5 to 8.5 [94].

Other researchers have suggested that the permeable outer layer consists of hexagonal close-packed pores in pure aluminum. The size of these pores will depend on conditions of formation. Sealing processes in an attempt to improve the characteristics of the passive film sometimes controls these conditions of formation. In sealing processes, the pores are blocked or made smaller by boehmite or gamma alumina formation, nickel acetate is added to obstruct the pores, or dichromates or chromates can be added to create pores of a different structure [97].

The passive film formed on metals will differ according to the environment in which it forms. Studies done by Seligman and Williams in the 1920s illustrate this difference. In experiments with tap water, the presence or absence of certain impurities caused either the passive film to breakdown and the metal to corrode or, the film will become thick and less susceptible to corrosion. They determined that nitrates and chromates would combine with the passive film and serve to increase resistance of the passive film to localized corrosion [98]. Later studies emphasized this conclusion. One researcher found a film of 55,000 angstroms in distilled water and another found a film of only 4,800 angstroms for the same alloy (AA-1099) immersed in tap water [94]. Additionally, experiments performed by Bengough and Hudson on aluminum in sea water showed that the passive film varied with corroding liquid and with different alloying elements [91].

In a more recent paper, researchers determined that the reaction between aluminum and water takes place in three steps: formation of the amorphous oxide, dissolution of the oxide, and deposition of the dissolved products as hydrous oxide. In the first step, the amorphous oxide layer is formed and grows by the anodic and cathodic reactions present at the water/metal interface. The second step involves a hydrolysis reaction with the surface which depends on temperature, pH and aluminum concentration and the last step is accomplished when the resulting hydroxide is deposited on the surface. The rate at which the film will grow is controlled by the diffusion of water molecules through the existing layers. At temperatures between 50 and 100 °C, pseudoboehmite grows on the amorphous oxide. At 40 °C, however, bayerite crystallization occurs and with time will overcome the pseudoboehmite [99].

Upon exposure of an air-formed-film to water, the air-formed-film will break down and another film will form that is thicker and contains more water. The rate at which the film is reformed depends on the anions present and the temperature [94]. In more recent work, the water in the aluminum passive film has been stated to be a medium for the mobilization for aluminum cations and deposited anions [100].

In air, the thickness of the passive film is dependent on humidity. In higher humidity, the oxide layer is thicker. The growth rate of the film, however, does not depend on humidity. Rosenfeld et al. found that in high purity air, the growth rate was not changed. However, when small amounts of impurities were added, growth was accelerated in humid air [101]. In addition to impurities, the growth of the film is highly dependent on temperature. Below 200 °C, the film will grow only to a few hundred angstroms, above 300 to 400 °C, the rate gradually increases, between 400 and 600 °C, the film will grow to a thickness of 400 angstroms, at 450 °C, the film will crystallize to gamma alumina [94].

Pitting Potential and Induction Time

According to Smialowska [85], the susceptibility of a metal or alloy to pitting can be estimated by determination of one of the following criteria:

- Characteristic pitting potential,
- Critical temperature of pitting,
- Number of pits per unit area, or weight loss and
- The lowest concentration of chloride ions that may cause pitting.

One of the most important criteria to determine an alloy's susceptibility to pitting corrosion is to find the pitting potential, i.e., the potential at which the passive film starts to break down locally. The potential above which pits nucleate is denoted by E_p and the potential below, which pitting does not occur and above which the nucleated pits can grow, is often indicated by E_{pp}. Once the passive film begins to breakdown, the time it takes to form pits on a passive metal exposed to a solution containing aggressive anions, for example, Cl^-, is called the induction time or incubation time [85]. The induction time is meaningful in a statistical sense as it represents the average rate of reaction over the whole surface to produce a measurable increase in current. It should not be considered as the time to form the first pit. This is because "micro" pits have been observed to form during the induction time [88]. The induction time is usually denoted by τ. It is measured as the time required producing an appreciable anodic current at a given anodic potential. It is expressed as $1/\tau = k' (E-E_p)$, where E is the applied potential and K′ is a function of Cl^- ion concentration [102]. In general, pitting potential decreases with increasing Cl^- ion concentration.

The most commonly used relation for estimating t is based on an exponential relationship between time and activation energy i.e. $1/\tau = Ae^{-Ea/RT}$; the activation energy needed for pit nucleation can be obtained from an Arrhenius plot of log $(1/\tau)$ vs. 1/temperature [88]. As well, Hoar and Jacob [103] have proposed a relationship $1/\tau = K (Me)^m (X^-)^n$ to estimate the induction time. Where Me is the metal ion concentration, X^- is the halide ion concentration, and m and n are orders of reaction which are determined experimentally. Subsequent to the nucleation of pits it has been observed they grow. The following subsection presents a discussion of pit growth.

Pit Growth Rate and Pit Morphology

Godard [104] developed a simple but effective relation based on the experimental data to estimate the rate at which pits grow. The empirical relation he developed was $d = K (t^{1/3})$. Even though he found this relation when tested using aluminum, it was observed to be true for other materials in different types of water environments. In general, the rate of pit growth depends on several factors such as temperature, pH, properties of passive films, chloride ion concentration, presence of anions and cations in solution, and the orientation of the material [5]. The pit growth can be viewed as a direct interaction of the exposed metal with the environment.

Upon observing the geometry of the pits formed on 7075 aluminum alloy in halide solutions, Dallek [105] proposed a pit growth rate expression $i - i_p = a (t - t_i)^b$ in which current was expressed as a function of time. In this expression, i is the dissolution current, i_p is the passive current, t is the time, t_i is the induction time, a is the constant depending on the halide, and b is the constant depending on the geometry of the pit.

From this expression, a plot of log (i - i_p) vs. log (t - t_i) will give the slope b. Dallek predominantly observed pits of hemispherical shape. However, Nguyen et al. [106] have observed hemispherical pits at low potential on 1199 aluminum alloy in chloride solutions and at high potential they observed a porous layer film covered on the pit mouth with orifice at the center. This study indicated the effect of potential on the morphology of pits. Chloride ion concentration also was found to affect the pit morphology. Baumgartner and Kaesche [107] observed that in dilute to medium concentrated solutions, pit morphology was "rough" whereas at high concentration, pits were found to be "smooth and rounded." In addition, a recent study by Grimes [89] showed clearly the effect of loading conditions on the morphology of pits. This study was conducted on 7075 - T6 aluminum alloy in 3.5% salt water under three different loading conditions, viz. zero, sustained and cyclic. It was found that the pits propagated under cyclic loads were three times larger in cross sectional area when compared to those grown under sustained or zero load conditions. Also, it was found that most of the pits originated from the grain boundaries. This study concludes that the effect of both mechanical and chemical environment must be considered in pitting corrosion studies. However, when studying the effect of pitting on the fatigue life of aluminum alloy 7075-T6 in 3.5% NaCl solution, Li [108] found that although the test frequency (5 and 20 Hz) had a pronounced effect on the total corrosion fatigue life, the fatigue test frequency did not have any effect on the pit morphology. On the other hand, Chen et al. [109] have found that the size of the pit from which a crack nucleated was comparatively larger at the lower frequencies and stresses than at higher frequencies and stresses when fatigue tested using 2024-T3 aluminum alloy.

Mechanisms of Pit Nucleation

In general, pit nucleation mechanisms are classified into three categories. (i) Adsorption-induced mechanisms, (ii) Ion migration and penetration models, and (iii) Mechanical film breakdown theories.

Adsorption-Induced Mechanisms

In this section mechanisms of pit nucleation based on the adsorption of aggressive anions at energetically favored sites are discussed. Many researchers including Uhlig et al. [110-112] Hoar et al. [103, 113] and Kolotyrkin [114] have suggested mechanisms related to the ion-adsorption concepts (see Table 2.5). Many of the mechanisms proposed in the literature consider this as a necessary step in the pit nucleation process. Uhlig [110-112] and Kolotyrkin [114] independently proposed that both oxygen and chlorine anions can be adsorbed onto the metal surfaces. When the metal is exposed in air, oxygen is adsorbed by the metal resulting in the formation of passive oxide film. Consequently, a chemical bond is established between the oxygen anion and the metal cation. This process is known in corrosion terminology as “chemisorptions.” Chemisorption results in the formation of a metal-compound that covers the surface of a metal. If aluminum is exposed in oxygen, the resulting compound is aluminum oxide, i.e., Al_2O_3. However, the type of compound that is formed on the metal surface depends on the environment in which the metal is exposed. For example, in the case of salt water, Cl^- ions in addition to oxygen are present. When oxygen is adsorbed, passivation of metal occurs whereas if chlorine anion is adsorbed, it does not result in passivation but breakdown of passivity occurs.

As proposed by Kolotyrkin [114], below the pitting potential, metals may prefer to adsorb oxygen and above this critical potential metals may adsorb halides, such as Cl^- This mechanism is termed "competitive adsorption" as the presence of different anions will compete with the oxygen to be chemisorbed by the metal. Therefore, at or above the pitting potential, chlorides and other aggressive anions if present, combine with the metal and then diffuse from the metal's surface into the solution. Subsequently, it combines with water in solution to form metallic oxides, hydrogen and chloride ions. These chloride ions are attracted to the surface of the metal and the process begins again. It was hypothesized by many researchers that the chloride ions might diffuse to regions of high energy such as inclusion, dislocations and other form of discontinuities.

Hoar et al. [103, 113] originally proposed a "complex ion formation theory" which stated that the formation of Cl^- containing complexes on the film-solution interface might lead to a locally thinned passive layer. This was proposed because Cl^- -containing complexes are more soluble when compared to complexes formed in the absence of halides. They assumed that a high-energy complex is formed when a small number of Cl^- ions jointly adsorb around a cation in the film surface, which can readily dissolve into solution. This creates a stronger anodic field at this site that will result in the rapid transfer of another cation to the surface where it will meet more Cl^- and enter into solution. Experimental support was provided for this concept by Strehblow et al [115] by conducting an investigation on the attack of passive iron by hydrogen fluoride. They found that the breakdown process occurred with complete removal of the passivated oxide layer. It was observed that hydrogen fluoride catalyzed the transfer of Fe^{3+} and Ni^{2+} ions from oxide into the electrolyte. As mentioned in a paper by Bohni [116], similar observation was made in another study by Heusler et al. regarding the influence of chloride containing borate and phthalate solutions on the passive film breakdown of iron. Different behavior of Cl^- and F^- ions in the pit nucleation process was proposed in a model by Heusler et al. Cl^- ions were suggested to form only two dimensional "clusters" leading to the localized thinning of the passive layer. However, it was proposed that F^- ions adsorb homogeneously on the oxide surface thereby promoting a general attack. It should be noted that the proposed models did not take into account material discontinuities such as point "defects", dislocations, inclusions, voids and others. Also, another model based on the concept of an increased probability of "electrocapillary film breakdown" was proposed by Sato [117] (see Table 2.5). Although Sato includes the effect of dislocations in this purely theoretical approach, no experimental evidence was found in the literature to support his model. However, Sato's theoretical model proposed that n-type passive oxide films are more stable than p-type films because of the difference in the band structure of electron levels.

From these studies it can be concluded that in addition to chloride anions, other anions such as chromate and sulphate also get adsorbed changing the nature of the compound. In addition, as observed by Richardson and Wood [118], enhanced adsorption takes place at the “imperfections or flaws” in the oxide film. These discontinuities in the film usually become the sites of anion adsorption. Nilsen and Bardal [119] have observed by measuring the pitting potential of four aluminum alloys (99% pure Al, Al-2.7Mg, Al-4.5Mg-Mn, and Al-1Si-Mg) and found that the pitting potential values for the four alloys were within only 25 mv. From this study, they concluded that alloy composition does not directly depend on the adsorption step of the process.

Table 2.5: Adsorption-Induced Mechanisms

	Proposed by	Summary	Description	Limitations
1	Uhlig et al. 1950-69 Kolotyrkin 1961 Hoar 1967	• Proposed concepts based on either competitive adsorption or surface complex ion formation.	• In competitive adsorption mechanism Cl^- anions and passivating agents are simultaneously adsorbed. Above a critical potential Cl^- adsorption is favored resulting in the breakdown of passivity. • Kolotyrkin suggested that there were critical Cl^-/inhibitor concentration ratios, depending on the potential above which pitting would occur.	• Occurrence of induction times varying with passive film thickness cannot be explained.

Table 2.5: Continued

2	Sato 1982	• Proposed a theoretical concept based on the potential dependent transpassive dissolution which depends on the electronic properties of the passive film. • The electrochemical stability of a passive film depends strongly on the "electron energy band structure" in the film.	• Stated that the critical potential above which potential-dependent dissolution of the film occurs will be less noble at the sites of chloride ion adsorption. • As a result of the increased dissolution rate above the critical potential, local thinning of the passive films occurs until a steady state is reached. • Proposed that the local thinning of the oxide film as a mechanism of pit "initiation" • Included the effect of dislocations similar to the influences of Cl^- ions.	• Knowledge of the electronic properties of passive films has not been fully understood. • Experimental evidence for this mechanism is lacking.

Ion Migration and Penetration Models

A few models (see Table 2.6) were proposed based on either penetration of anions from the oxide/electrolyte interface to the metal/oxide interface or migration of cations or their respective vacancies. This theory is based on the concept that Cl^- ions migrate through the passive film and results in breakdown of the film once they reach the metal/film interface. Hoar and Jacob [103] explain that when a critical potential is reached, smaller ions, like Cl^-, may penetrate the film under the influence of an electrostatic field which exists across the film. These aggressive anions prefer the high energy regions like grain boundaries and impurities as sites for migration because these regions produce thinner passive film locally. During the migration, the ions either pass through the film completely or they may combine with the metal cation in the midst of the film resulting in the formation of what is called a "contaminated" film, which is a better conductor than the "uncontaminated" film. This process results in an autocatalytic reaction, which encourages more ions to penetrate the film. This hypothesis is supported by some researchers as they have observed a higher concentration of Cl^- ions over thin films on the surface of iron as well as that the time to breakdown the film increases with the thickness of the film [120]. It was further hypothesized that Cl^- ions first fills anion vacancies on the surface of the passive film and then migrates to the metal/oxide interface. However, other works revealed that the time required for Cl^- to penetrate through the film is much longer than the induction time measured experimentally [116].

Later, Macdonald et al. [121] proposed a model in which the growth of the passive film was explained by the transport of both anions (e.g., oxygen ion) and cations (e.g., metal ion). Diffusion of anion from film-solution interface to metal-film interface

Table 2.6: Ion Migration and Penetration Models

	Proposed by	Summary	Description	Limitations
1	Hoar et al. 1965	• Presented that when the electrostatic field across the film/solution interface reaches a critical value corresponding to the critical breakdown potential, the anions adsorbed on the oxide film enter and penetrate the film.	• Favored sites for ion migration are suggested to be high-energy regions like grain boundaries and impurities where thinner passive films are produced. • If the aggressive ions meet a metal cation, contaminated film is produced that encourages further ions to penetrate the film. Then, this process continues as an autocatalytic reaction.	• Did not explain the observation that pits often form from mechanical breaks in the oxide film or from scratches.
2	Macdonald et al. 1981	• Presented a theoretical model to explain the chemical breakdown of passive film.	• Proposed that metal vacancies may accumulate as a result of the diffusion of metal cations from the metal/film to the film/solution interface, forming voids at the metal/film interface. When the voids grow to a critical size the passive film will collapse leading to pit growth.	• Surface discontinuities such as grain boundaries etc. were not considered in developing the model. • No direct observation of void formation was made. • As the measured induction times usually show a large scatter, definite quantitative agreement is difficult to obtain.

results in thickening of the film. Cation diffusion from the metal-film interface to the film-solution interface results in the creation of metal vacancies at the metal/film interface. These metal vacancies usually “submerge” into the metal itself. However, if the cation diffusion rate is higher than the rate of vacancy submergence into the bulk metal, the metal vacancies will increase leading to the formation of voids at the metal/film interface. This process is known as “pit incubation”. Subsequently, when the void reaches a critical size, the pit incubation period ends leading to the local rupture of the passive film. This eventually results in pit growth at that local site. Based on this theory, Macdonald et al expressed a criterion for pit “initiation” as stated below.

$(J_{ca} - J_m) * (t - \tau) = \xi$

where,

J_{ca} is the cation diffusion rate in the film,

J_m is the rate of submergence of the metal vacancies into the bulk metal,

t is the time required for metal vacancies to accumulate to a critical amount x

τ is a constant,

Also, in this model, the role of the halide ion in accelerating the film breakdown by increasing J_{ca} was suggested.

The ion penetration and migration theories do not include the effect of mechanical breakdown of the oxide film that may result because of the scratches from which pits can nucleate. Nor is the mechanical breakdown of the oxide film included that results from strain and local cracking of the oxide film.

In addition MacDonald et al [122] have proposed a "point defect" model for anodic films to calculate J_{ca} for "thin" films on the order of 10-40 A. Also, the "point defect" model could be used to calculate incubation times. Although, the "point defect" model was one of the most detailed models proposed, this model has some limitations as mentioned in Table 2.4.

Mechanical Film Breakdown Theories - Chemico-Mechanical Breakdown Theories

Pit nucleation models proposed so far based on the concepts of the “chemico-mechanical” breakdown of films have not included the effect of externally applied stresses (see Table 2.7). Sato [123] showed that a significant film pressure always acted on "thin" films that he attributed to "electrostriction". Sato expressed a relation between the film pressure, thickness and surface tension of the film as follows.

$p = p_o + [(\delta(\delta-1)\xi^2)/8\pi] - \gamma/L$ where p is the film pressure, p_o is the atmospheric pressure, δ is the film dielectric constant, ξ is the electric field, γ is the surface tension, and L is the film thickness. According to his hypothesis, both γ and L have significant influence on film pressure p. Based on this relation, Sato suggested that the adsorption of chloride ion significantly reduces the surface tension γ thereby increasing p. Also, he proposed that when p is above the critical value, the film might break down. In addition, Sato proposed that breakdown of the film occurs when it attains a thickness at which mechanical stresses caused by “electrostriction” become critical. Therefore, building up of critical stresses in the film could cause pitting. In addition to the aforementioned theory, some researchers have observed the influence of mechanically produced discontinuities (such as scratches in the passive film) on the formation of pits along those scratches [124].

Table 2.7: Chemico-Mechanical Breakdown Theories

	Proposed by	Summary	Description	Limitations
1	Sato 1971	• Proposed a breakdown mechanism for anodic films from thermodynamic considerations.	• Showed that thin films always contain film pressure due to "electrostriction". • Hypothesized that both the surface tension of the film and the film thickness has a significant effect on film pressure. • Proposed that adsorption of chloride ions, depending on their concentration, greatly reduces surface tension.	• Experimental proof is not found.
2	Sato 1982	• Derived an equation for the work required to form a cylindrical breakthrough pore in the passive film.	• Proposed that for a pit nucleus to grow to macroscopic size a critical radius corresponding to critical pore formation energy must be exceeded.	• Experimental proof is not found. • Microstructural parameters such as grain boundaries, inclusions that may influence pitting "initiation" were not considered.

If there is a scratch in the passive film that sets up a local anodic site, which will eventually, be the preferred site for pit to form. This smaller anode/cathode ratio results in higher local potential leading to the nucleation of pits. Other researchers proposed a similar theory that is related to the value of product of the length of the discontinuity and the current density. Assuming a unidirectionally growing pit, if this value exceeds a critical value, the discontinuity such as “fissures” in the oxide film may form a local area of low pH leading to the formation of pits from them. This happens due to the difference in the pH at the local site (fissure) when compared to the bulk solution. It was proposed that a fissure of size in the order of 10^{-6} cm could be a limiting condition for this to happen [125].

Hoar [113] also assumed that the presence of pores or “flaws” could mechanically stress and damage the passive films in contact with an aggressive solution. Moreover, Hoar assumed that aggressive anions would replace water and reduce surface tension at the solution-film interface by repulsive forces between particles, producing cracks.

In conclusion, there is no full agreement among the researchers regarding the mechanisms of pit nucleation. However, as the pitting process itself is a complex one, the commonly accepted view is that the first step in the pit nucleation process is the localized adsorption of aggressive anions on the surface of the passivated metal. Several experimental studies also have indicated that the preferred sites for the passage of anions through the oxide film are the discontinuities present in an alloy. Such discontinuities are non-metallic inclusions; second phase precipitates, pores or voids, grain or phase boundaries as well as other mechanical damages [85]. These discontinuities eventually may become pit nucleation sites. The aforementioned theories on pit nucleation are based purely on electrochemical concepts. However, the breakdown of surface film is dependent not only on the solution conditions (e.g., pH), and the electrochemical state at the metal/solution interface, but also on the nature of the material as well as the stress state. In addition, the aforementioned pit nucleation mechanisms did not take into account the material parameters such as the microstructural effects, inherent discontinuities such as voids, inclusions, second phase particles as well as the externally applied stress. Moreover, localized corrosion also may take place at slip bands during fatigue loading [126].

Once the pit is formed, the rate of pit growth is dependent mainly on the material, local solution conditions and the state of stress. Cracks have been observed to form from pits under cyclic loading conditions. Therefore, to estimate the total corrosion fatigue life of an alloy, it is of great importance to develop some realistic models to establish the relationship between pit propagation rate and the stress state. Furthermore, pitting corrosion in conjunction with externally applied mechanical stresses, for example, cyclic stresses has been shown to severely affect the integrity of the oxide film as well as the fatigue life of a metal or an alloy. Therefore, to understand these phenomena, some models based on pitting corrosion fatigue mechanisms have been proposed as discussed below.

Pitting Corrosion Fatigue

Linear Elastic Fracture Mechanics (LEFM) concepts are widely used to characterize the crack growth behavior of materials under cyclic stresses in different environmental conditions. It is important to note that both pitting theory and crack growth theory have been used in model development as follows. Pit growth rate theory proposed by Godard is combined with fatigue crack growth concepts. The time to form/nucleate a Mode I crack from the pit (under cyclic loading) could be modeled using LEFM concepts. Based on this idea, a few models [127-130] were proposed since 1971 (see Table 2.8). All of the models assume hemispherical geometry for the pit shape and the corresponding stress intensity relation is used to determine the critical pit depth using

Table 2.8: Pitting Corrosion Fatigue Models [137-235].

	Proposed by	Summary	Description	Advantages/ Limitations
1	Hoeppner (1971 - current)	• Proposed a model to determine critical pit depth to nucleate a Mode I crack under pitting corrosion fatigue conditions. • Combined with the pit growth rate theory as well as the fatigue crack growth curve fit in a corrosive environment, the cycles needed to develop a critical pit size that will form a Mode I fatigue crack can be estimated.	• Using a four parameter Weibull fit, fatigue crack growth threshold (ΔK_{th}) was found from corrosion fatigue experiments for the particular environment, material, frequency, and load spectrum. • The stress intensity relation for surface discontinuity (half penny shaped crack) was used to simulate hemispherical pit. i.e.) $K = 1.1\,\sigma\sqrt{\pi\left(\frac{a}{Q}\right)}$ where, σ is the applied stress, a is the pit length, and Q is the function of a/2c, S_{ty}. • Using the threshold determined empirically, critical pit depth was found from the stress intensity relation mentioned above. • Then, the time to attain the pit depth for the corresponding threshold value was found using $t = \left(\frac{d}{c}\right)^3$ where, t is the time, d is the pit depth, and c is a material/environment parameter.	• This model provides a reasonable estimate for hemispherical geometry of the pits. • This model is useful to estimate the total corrosion fatigue life with knowledge of the kinetics of pitting corrosion and fatigue crack growth. • This model did not attempt to propose mechanisms of crack nucleation from corrosion pits. • Quantitative studies of pitting corrosion fatigue behavior of materials can be made using this model. • This model is valid only for the conditions in which LEFM concepts are applicable. • Material dependent.

Table 2.8: Continued

2	Lindley et al. (1982)	• Similar to Hoeppner's model, a method for determining the threshold at which fatigue cracks would grow from the pits was proposed.	• Pits were considered as semi-elliptical shaped sharp cracks • Used Irwin's stress intensity solution for an elliptical crack in an infinite plate and came up with the relationship to estimate threshold stress intensity values related to fatigue crack nucleation at corrosion pits. i.e.) $\Delta K_{th} = \dfrac{\Delta\sigma\sqrt{(\pi a)\left[1.13-0.07\left(a/c\right)^{1/2}\right]}}{\left[1+1.47\left(a/c\right)^{1.64}\right]^{1/2}}$ where, $\Delta\sigma$ is the stress range, a is the minor axis, and c is the major axis of a semi-elliptical crack. • From the observed pit geometry i.e. for a/c ratio, threshold stress intensity can be calculated. • For the corresponding a/c ratio, critical pit depth can be estimated.	• The proposed stress intensity relation can be used in tension - tension loading situations where stress intensity for pits and cracks are similar. • Critical pit depths for cracked specimens can be estimated using the existing threshold stress intensity values. • This model is valid only for the conditions in which LEFM concepts are applicable. • Material dependent.

Table 2.8: Continued

3	Kawai and Kasai (1985)	• Proposed a model based on estimation of allowable stresses under corrosion fatigue conditions with emphasis on pitting. • As corrosion is not usually considered in developing S-N fatigue curves, a model for allowable stress intensity threshold involving corrosion fatigue conditions was proposed.	• Considered corrosion pit as an elliptical crack. • Based on experimental data generated on stainless steel, new allowable stresses based on allowable stress intensity threshold was proposed. i.e.) $\Delta\sigma_{all} = \frac{\Delta k_{all}}{F\sqrt{\pi h_{max}}}$ Where, ΔK_{all} can be determined from a da/dN vs. ΔK plot for a material, h_{max} is the maximum pit depth, and F is a geometric factor.	• Using this model, allowable stress in relation to corrosion fatigue threshold as a function of time can be estimated. • Material dependent. • This model is valid only for the conditions in which LEFM concepts are applicable.

Table 2.8: Continued

4	Kondo (1989)	• Corrosion fatigue life of a material could be determined by estimating the critical pit condition using stress intensity factor relation as well as the pit growth rate relation.	• Pit diameter was measured intermittently during corrosion fatigue tests. • From test results, corrosion pit growth law was expressed as $2c \propto C_p t^{1/3}$ where, 2c is the pit diameter, t is the time, and C_p is an environment/material parameter. Then, critical pit condition (ΔK_p) in terms of stress intensity factor was proposed by assuming pit as a crack. $\Delta K_p = 2.24\sigma_a\sqrt{\pi c\alpha / Q}$ where, σ_a is the stress amplitude, a is the aspect ratio, and Q is the shape factor. • Critical pit condition was determined by the relationship between the pit growth rate theory and fatigue crack growth rates. $c = c_p (N/f)^{1/3}$ Where, N is the number of stress cycles, f is the frequency, and 2c is the pit diameter. • The pit growth rate dc/dN was developed using ΔK relation as given below. $dc/dN = \left(\frac{1}{3}\right) C_p{}^3 f^{-1} \alpha^2 \pi^2 Q^{-2} (2.24\sigma_a$ dc/dN was determined using experimental parameter C_p. • Finally, the critical pit size $2C_{cr}$ was calculated from the stress intensity factor relation. i.e.) $2C_{cr} = (2Q/\pi\alpha)(\Delta K_p/2.24\sigma_a)^2$	• The aspect ratio was assumed as constant. • Material and environment dependent.

the crack growth threshold (ΔK_{th}) that is found empirically. For hemispherical pit geometry, these models provide a reasonable estimate for the total corrosion fatigue life. However, it is well known that corrosion pit morphology varies widely. Thus, this aspect must eventually be dealt with in LEFM models that attempt to deal with pit growth and the ultimate nucleation of crack(s) from pit(s).

As mentioned before, the combined effect of corrosion and the applied cyclic loading have been shown to produce cracks from corrosion pits. In addition, pits have frequently been the source of cracks on aircraft that are operating in fleets. Depending upon the fatigue loading and corrosion conditions, some studies have shown that the crack formation/nucleation site may change from slip bands to corrosion pits [132]. This observation was made when fatigue tested at reduced strain rates in Al-Li-Cu alloy. Another study also showed an anodic dissolution in slip bands in Al-Li-Zr alloy at high stress levels whereas at low stress levels fatigue cracks nucleated from corrosion pits [133]. Therefore, it was hypothesized that at higher stress levels, conditions are favorable to form cracks from slip bands before the corrosion pit reaches the critical condition to favor the nucleation of crack from it. In addition, a recent study also showed that larger pit was formed at lower stress and frequency. It also was observed in 2024-T3 (bare) aluminum alloy in NaCl solution that once pits formed from the constituent particles, because of the applied cyclic stresses, the pits coalesced, laterally and in depth to form larger pits from which crack was observed to nucleate [134]. Therefore, modeling the transition of a pit first to a “short” crack and then to a “long” crack is considered to be important in characterizing the total corrosion fatigue life of a material as discussed in the next section [127, 135,136].

Environmental Effects on "Short" Crack Behavior of Materials

A few “small” crack studies under corrosion fatigue conditions have been performed to characterize the transition of a pit to a “small” crack. In 2024 aluminum alloy, Piascik and Willard have shown a three times increase in crack growth rates of “small” cracks in salt water environment when compared to air. Moreover, their studies clearly have observed the transition of pits formed at the constituent particles to intergranular “microcracks” and then to transgranular fracture path once the crack reaches the depth of 100 mm. In addition, the increase in “small” crack growth rates was observed even at very low mode I ΔK (<1 MPa $\sqrt{m}$). As well, Kondo (1989) also observed in two low alloy steels that “short” cracks from pits propagated at ΔK that is well below the threshold value of a long crack for these materials.

In a recent in-situ fatigue study, prior pitted 2024-T351 and 7075-T651 aluminum alloy specimens exhibited faster crack growth rates in the “short” crack regime when compared to specimens without prior corrosion damage (A. Hoeppner [now A. Taylor] 1996). This study showed that prior corrosion damage did influence the “small” crack growth rates. It also was observed that the 7075 aluminum alloy specimen had faster crack growth rates compared to the 2024 aluminum alloy specimens. Also, in this study cracks were observed to form from pits on the prior corroded specimens whereas on the specimens without any prior corrosion damage, cracks formed from constituent particles.

In addition to a few previous studies (Hoeppner, 1971, 1979) in which pitting was modeled statistically with different materials and specimen types, recently, as discussed before in this article, there was a study demonstrating corrosion fatigue induced "short" crack formation from pits (Akid and Murtaza, 1992). Also, recent studies (Ma and D. Hoeppner, 1994, Grimes, 1996, and A. Hoeppner, 1996) have shown that pits form in different shapes depending upon environment and loading conditions in contradiction to general assumption that pits have hemispherical shape. Although this assumption simplifies the modeling part of research (Kondo, 1989), further studies to characterize the formation of cracks from pits in the "short" crack regime must be evaluated as indicated by A. Hoeppner (1996). Apart from these studies the literature search has not found any "short" crack studies to evaluate the formation of cracks from pits and their crack morphologies and paths. Moreover, fretting mechanism(s) in conjunction with fatigue and corrosion may further aggravate this.

Conclusions and Recommendations

The review of the literature clearly shows that much progress has been made on modeling the effects of corrosion on material behavior and structural integrity. It is clear that to date the models have centered on characterizing the corrosion and modeling the effects of the corrosion as one or more of the following:

- Section change that affects the area/volume that modifies the stress.
- Formation/Nucleation of localized debris that may modify the stress (part of pillowing) that modifies the stress or stress intensity.
- Nucleation of intergranular corrosion that is involved in pillowing that modifies the stress or stress intensity.
- Nucleation of localized corrosion (pitting, fretting, etc.) that modifies the local stress and may ultimately nucleate cracks.
- Production of products of corrosion that produce localized embrittlement effects that may alter the material behavior and produce accelerated crack propagation.

All of the above have been reviewed in the preceding sections and lead to the recognition that one of the most pressing issues to be resolved is the actual quantitative characterization of the corrosion in relation to the physical damage state that is underway. Some of this has been accomplished in the past with the efforts of the past at the U. of Utah as discussed in the earlier sections of this article. From the work of L. Grimes at Utah as well as additional efforts at the U. of Utah, the use of the confocal microscope will be of great assistance in characterizing the three-dimensional (3-D) surface "damage" that results from corrosion of various forms.

Within the last few years interest in Corrosion and the Effects of Corrosion has picked up in part due to numerous failures in many industries including nuclear power plants, gas and oil pipelines and aircraft to name a few. Roberge [238-240] has introduced excellent reference books on aspects of corrosion and also a web page (www.corrosion-doctors.org) that contain a wealth of information related to many of the topics covered in this paper. A recent issue of business week [241] states that the USA DOD spends "22.9 billion a year fighting rust." There is little doubt this number will become much larger and more of the structures in use in aircraft and many other applications age and it is unlikely more funds will be appropriated to replace many aging aircraft components. Thus, many of the issues covered herein will become more important in both the design, operational and maintenance strategies to combat the issue of corrosion. This also is clear from the fact that the USA DOD has established a Corrosion Policy and Oversight Office Congress in the pentagon as was mandated by the US Congress in 2003. It remains to be seen whether this will result in significant cost savings to combat corrosion and reduce the number of accidents from corrosion related issues.

Even though fracture mechanics based modeling has been extremely useful in modeling the effects of corrosion on structural integrity it has taken many simplifications and, depending on the manner in which the fracture mechanics is used in the model, has resulted in downgrading the real corrosion characterization issue and understanding the 3-D nature of the corrosion degradation process. New tools and models will have to be brought to bear on the formation/nucleation and growth of the corrosion with or without load of either sustained (SCC) or cyclic nature (EANC/F)-(Environmentally-assisted nucleation and cracking with fatigue loading). Furthermore the transitions of corrosion to actual cracks will have to be understood to improve the models that currently exist and any new ones that may be developed. Aspects of this were discussed by Hoeppner [242] and Swift [243] in recent ICAF meetings. No doubt more attention will be focused on this in the future.

The characterization of chemically dependent short crack propagation and modeling of it will have to be much better understood. One area not addressed in the article is the effect of either prior corrosion and/or concomitant corrosion on either fatigue crack propagation or stress-corrosion cracking. Both of these issues are extremely important to the overall area of model development and consideration should be given to expanding at many laboratories in the future. The importance of corrosion to DOD activities within the USA has recently been noted.

The following chapter builds upon the principles and concepts as explained previously. It is a preliminary assessment of statistical modeling of corrosion fatigue for AA7075-T6. This chapter shows how the methodology for testing was established and presents a statistical significant model. It was recently submitted for publication at Corrosion Science.

Acknowledgments

The authors wish to express appreciation to the former Dr. John DeLuccia who provided valuable comment and insights for the preparation of this paper. In addition, we express our deep appreciation to FASIDE International Inc. and the University of Utah for provision of facilities and a magnificent library system. Ms. Amy Taylor and Dr. Chandrasekaran provided much valuable input over a period of years. We appreciate all their efforts. The following three individuals provided extensive discussions on the topics covered herein: Mr. Nick Bellinger and Mr. Jerzy Komorowski (both of NRC-IAR-Canada), and Mr. Craig Brooks (AP/ES-USA). We are grateful for the many discussions and interactions with them over many years.

Appendix

List of definitions related to Corrosion Fatigue and Stress Corrosion Cracking. Corrosion Related Definitions of terms for use in CFSD Phase II, CMI and CP programs. Prepared by David W. Hoeppner, P.E., Ph.D. 1999-2011. Significant input into the preparation of this document has been made by the following: Nick Bellinger, Graeme Eastaugh, and Jerzy Komorowski- All of NRC, Ottawa, Ontario, Canada. Mr. Craig Brooks, APES Inc. Dr. Charles Elliott, Dr. Paul Clark, Ms. Amy Taylor-University of Utah and FASIDE International Inc. This document is still undergoing change. Please submit recommendations to the corresponding author.

ADP- Age degradation process. Any one of or combination of physical or chemical degradation such as fatigue, environmental effects (corrosion on metals and joints), creep, wear, and synergisms of these.

CLD- Crack like discontinuity. A discontinuity that meets the criteria for a crack. A stress singularity exists near or at the tip of the discontinuity, no "traction forces" exist on the surfaces of the discontinuity.

DADTA- Durability and damage tolerance analysis. The procedure of performing a durability and damage tolerance analysis.- Analysis of the ability of the airframe or component to resist damage (including fatigue cracking, environmentally assisted cracking, hydrogen induced cracking, corrosion, thermal degradation, delamination, wear, and the effects of foreign objects), and failure due to the presence of damage, for a specified period of unrepaired usage. From JSSG-2006.

Defect- (Various definitions exist.) The most common definition is any feature that is outside the boundary conditions of a given component/product design that will make the component/product incapable of meeting its requirements when it is needed. Defects are also defined related to product manufacturing and also related to representation of the product.

DEP- Discontinuity evolution process. The specific process by which a population of discontinuities evolves.

DNP- Discontinuity nucleation process. Any one or more or specific physical or chemical processes that may form discontinuities not inherent to a material. Example- in some materials fatigue deformation occurs by dislocation movement and the production of slip bands on external or internal surfaces. The slip band is thus a nucleated discontinuity. Example two. In some Aluminum alloys intrinsic particles are known to nucleate corrosion pits if the Pitting Potential for nucleation is achieved. The pit is formed by a DNP.

DS- Discontinuity state. See IDS, EDS, and MDS below.

DSEP- Discontinuity state evolution process. The specific physical or chemical processes by which the discontinuity state evolves. The major forms of time dependent or related phenomena by which the state is changed are corrosion (more generally environmental degradation), creep, fatigue, wear and sequential combinations and synergisms of them. SEE EDS below.

DSER- Discontinuity state evolution response. Any change in state of an IDS population.

EAC- Environmentally assisted cracking. May occur under sustained load from either applied load or "residual stresses" EAC_{sl}. May also occur under either constant amplitude cyclic forces or variable amplitude cyclic forces $EAC_{fatigue}$.

ECD- Equivalent corrosion damage. A modified discontinuity state (MDS) at some specific time that is made equivalent to a crack size often referred to as a "flaw" to start a residual life analysis by subcritical crack growth analysis.

EDS- Evolving discontinuity state. The description of the evolution of the discontinuity and the progression of changes to the discontinuity or population of discontinuities over time and cyclic load exposures. (Subsequent to either the nucleation of a discontinuity or the activation of an IDS by a specific physical or chemical process acting alone or conjointly the resultant discontinuity or population of them may evolve in state with time or cyclic load exposure. Various metrics are used to describe the EDS).

EIFS- Equivalent initial flaw size. A term used to describe a discontinuity size usually determined by extrapolation from a set of fatigue data. The EIFS has no direct relationship to any specific IDS.

FCP- Fatigue Crack Propagation. Extension of a crack under cyclic or repeated loads. The stages of crack propagation are divided into four phases, viz.; 1) small or short crack propagation, long crack propagation in the linear elastic regime, and long crack propagation in either the elastic-plastic or fully plastic regime.

IDS- Initial discontinuity state. The initial (intrinsic) population of discontinuities that are in a structure made of a given material as it was manufactured in a given geometric form. The IDS is a geometric and material characteristic that is a function of composition, microstructure, phases and phase morphology, and the manufacturing process used to process the material. The geometric and material discontinuities can be modeled separately.

Examples of material IDS types include constitutive particles, inclusions, grain boundaries, segregated phases, phase boundaries, voids (vacancies, microporosity, and porosity), intrinsic cracks, etc. Manufacturing processes such as machining and assembly can introduce additional discontinuities at fasteners, fillets, etc., that extend the tail (larger discontinuity sizes) of the IDS distribution.

IDS_{ms}- Initial material discontinuity. The initial population of intrinsic material discontinuities. See IDS.

IDS_{mfg}- Initial manufacturing discontinuity. The resultant effect on the population of discontinuities from a given manufacturing process or sequence of manufacturing processes including joining of the three major types (viz. mechanical joining, thermal joining, adhesive bonding).

$IDS_{geo.}$- Initial geometric discontinuity. The initial geometric discontinuities in a product. These often are generally referred to as a “notch”.

MDS- Modified discontinuity state. The physical state of a discontinuity or damage state at any given time in its evolution. Various metrics may be used to describe the state. Example-a crack has grown to a given size and it is an MDS at a specific time and thus size. Example 2-A corrosion pit has grown to state at some point in time. The IDS may progress (EDS) to various MDS values through the mechanisms of corrosion, creep, fatigue, wear or combinations of these over time.

PSE- Principal structural element.

Safe Life- A term usually taken to mean structural design based on ideal continuum mechanics assumptions and practices without consideration of cracks or crack like discontinuities based on the assumptions of homogeneity and continuity. In traditional safe life design toughness, sub critical crack growth, directed inspection and inspection intervals are not dealt with for fatigue, corrosion and related items.

SSL-Structurally significant location. The significant locations on a structure determined by the potential behavior and changes in state that may occur in the structure related to its use under conditions of interest.

List of definitions related to Corrosion Fatigue and Stress Corrosion Cracking

The following definitions are taken from ASTM Standards volume 03.02-Wear and Erosion; Metal Corrosion, ASTM, Philadelphia, PA, 1994
Standard G15-97a-Standard Terminology Relating to Corrosion and Corrosion Testing.

corrosion fatigue-the process in which a metal fractures prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower levels or fewer cycles than would be required in the absence of the corrosive environment. G15-99b, p69.

corrosion fatigue strength-the maximum repeated stress that can be endured by a metal without failure under definite conditions of corrosion and fatigue and for a specific number of stress cycles and a specified period of time. G15-99b, p69.

exfoliation corrosion-corrosion that proceeds laterally from the sites of initiation along planes parallel to the to the surface, generally at grain boundaries, forming corrosion products that force metal away from the body of the material, giving rise to a layered appearance. (G15-99B).

pitting-corrosion of a metal surface, confined to a point or small area, that takes the form of small cavities.

stress-corrosion cracking--a cracking process that requires the simultaneous action of a corrodent and sustained tensile stress. (This excludes corrosion-reduced sections which fail by fast fracture. It also excludes intercrystalline or transcrystalline corrosion which can disintegrate an alloy without either applied or residual stress.)

The following definitions are taken from <u>ASTM Standards volume 03.01-Metals-Mechanical Testing; Elevated and Low Temperature Tests; Metallography</u>, ASTM, Philadelphia, PA, 1998.,

E1823-96-Standard Terminology Relating to Fatigue and Fracture Testing.

corrosion fatigue-the process by which fracture occurs prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels or fewer cycles than would be required in the absence of the corrosive environment. E1823-96, p1016.
(Note slight word differences between this definition of corrosion fatigue and the one above. It is possible that these differences have been eliminated in the newer version of G15. I am checking into this.)

environment assisted cracking, EAC-a cracking process in which the environment promotes crack growth or higher crack growth rates than would occur without the presence of the environment. E1823-96, p1028. Same definition in E 1681-95, p944 (see below).

fatigue- the process of progressive localized permanent structural change occurring in a material subjected to conditions that produce fluctuating stresses and strains at some point or points and that may culminate in cracks or complete fracture after a sufficient number of fluctuations. E1823-96, p1019.

The following definition is taken from <u>ASTM Standards volume 03.01-Metals-Mechanical Testing; Elevated and Low Temperature Tests; Metallography</u>, ASTM, Philadelphia, PA, 1998.

E7-97a- Standard Terminology Relating to Metallography.

stress-corrosion crack-a crack which may be intergranular or transgranular depending on the material, resulting from the combined action of corrosion and stress, either external (applied) or internal (residual). E7-97a, p52.

The following definitions are taken from <u>ASTM Standards volume 03.01-Metals-Mechanical Testing; Elevated and Low Temperature Tests; Metallography</u>, ASTM, Philadelphia, PA, 1998,

E 1681-95-Standard Test Method for Determining a Threshold Stress Intensity Factor for Environment-Assisted Cracking of Metallic Materials Under Constant Load.

stress-corrosion cracking, SCC-a cracking process that requires the simultaneous action of a corrodent and sustained tensile stress. E1681-95, p943.

environment-assisted cracking, EAC-Same as above in E1823-96. E1681-95, p944.

We have found no standard definitions for either corrosion-fatigue or corrosion/fatigue. Thus, unless someone can find a standard or suggest one for our work it is suggested we stick with only standard terminology. We have added some other definitions in the following appendix. These terms all are some I have heard used at conferences and our various team meetings. Thus, I have added them.

Additional definitions (The definitions in this section are not standard definitions.)

Corrosion+fatigue: Fatigue occurs in a material/structure that has undergone corrosion. The fatigue may occur as either pure fatigue or corrosion fatigue. See ASTM definitions previously supplied.

Corrosion-fatigue: Fatigue occurs in a material/structure that has undergone corrosion. The fatigue may occur as either pure fatigue or corrosion fatigue. See ASTM definitions previously supplied.

Corrosion/fatigue: Fatigue occurs in a material/structure that has undergone corrosion. The fatigue may occur as either pure fatigue or corrosion fatigue. See ASTM definitions previously supplied.

Fretting fatigue: Fatigue occurs in the presence of fretting. Thus, the action is concomitant. This situation occurs in many holes with fasteners moving in the holes or on faying surfaces in splice joints.

Fretting +fatigue: Fatigue occurs on a material/structure that has undergone fretting. The fatigue may occur as either pure fatigue or corrosion fatigue.

Fretting/fatigue: Fatigue occurs on a material/structure that has undergone fretting. The fatigue may occur as either pure fatigue or corrosion fatigue.

(Prior corrosion)+fatigue: Fatigue occurs in a material/structure that has undergone corrosion. The fatigue may occur as either pure fatigue or corrosion fatigue. See ASTM definitions previously supplied.

(Prior corrosion)/fatigue: Fatigue occurs in a material/structure that has undergone corrosion. The fatigue may occur as either pure fatigue or corrosion fatigue. See ASTM definitions previously supplied.

Mechanism overlap: The interaction of more than one degradation mechanism in generation of the degradation condition in a material/structure.

Missed corrosion+fatigue: Fatigue occurs in a material/structure that has undergone corrosion. The fatigue may occur as either pure fatigue or corrosion fatigue. See ASTM definitions previously supplied.

Missed corrosion/fatigue: Fatigue occurs in a material/structure that has undergone corrosion. The fatigue may occur as either pure fatigue or corrosion fatigue. See ASTM definitions previously supplied.

SSI/corrosion: A structurally significant item designated by its propensity to become a critical item based on the potential for corrosion degradation of any type.

SSI/corrosion fatigue: A structurally significant item designated by its propensity to become a critical item based on the potential for corrosion fatigue degradation.

SSI/fatigue: A structurally significant item designated by its propensity to become a critical item based on the potential for fatigue degradation. These sites are usually determined by durability and/or damage tolerance assessment.

SSI/fatigue/durability: A structurally significant item designated by its propensity to become a critical item based on the potential for fatigue degradation as determined by the durability assessment.

SSI/fatigue/damage tolerance: A structurally significant item designated by its propensity to become a critical item based on the potential for fatigue degradation as determined by the damage tolerance assessment.

SSI/fretting fatigue: A structurally significant item designated by its propensity to become a critical item based on the potential for fretting fatigue degradation.

SSI/SCC: A structurally significant item based on its propensity to undergo the degradation mechanism of stress corrosion cracking. See the ASTM standard previously supplied on stress corrosion cracking.

SSL/corrosion: A structurally significant location designated by its propensity to become a critical location based on the potential for corrosion degradation of any type.

SSL/corrosion fatigue: A structurally significant location designated by its propensity to become a critical location based on the potential for corrosion fatigue degradation.

SSL/fatigue/durability: A structurally significant location designated by its propensity to become a critical location based on the potential for fatigue degradation as determined by the durability assessment.

SSL/fatigue/damage tolerance: A structurally significant item designated by its propensity to become a critical location based on the potential for fatigue degradation as determined by the damage tolerance assessment.

SSL/fretting fatigue: A structurally significant item designated by its propensity to become a critical location based on the potential for fretting fatigue degradation.

SSL/SCC: A structurally significant location based on its propensity to undergo the degradation mechanism of stress corrosion cracking. See the ASTM standard previously supplied on stress corrosion cracking.

LOCAL CORROSION-Corrosion of a skin or web (wing, fuselage, empennage, or strut) not exceeding one frame, stinger, or stiffener bay) or Corrosion of a single frame, chord, stringer, or stiffener, or Corrosion of more than one frame, chord, stringer, or stiffener but, no corrosion on two adjacent members on each side of the corroded member.

WIDESPREAD CORROSION-Corrosion of two or more adjacent skin or web bays defined by frame, stringer or stiffener spacing. Or Corrosion of two or more adjacent frames, chords, stringers, or stiffeners.

LEVEL 1 CORRROSION-Corrosion damage occurring between successive inspections that is LOCAL and can be re-worked/blended out within allowable limits as defined by the manufacturer. Or Corrosion damage that is LOCAL but exceeds allowable limits and can be attributed to an event NOT TYPICAL of the operator's usage of other airplane's in the same fleet. Or Operator experience over several years has demonstrated only light corrosion between successive inspections but latest inspection and cumulative blend-out now exceed allowable limits.

LEVEL 2 CORROSION-Corrosion occurring between successive inspections that requires re-work/blend-out which exceeds allowable limits, requiring a repair or complete or partial replacement of a principal structural element as defined by the original equipment manufacturer's structural repair manual. Or Corrosion occurring between successive inspections that is WIDESPREAD and requires blend-out approaching the allowable re-work limits.

LEVEL 3 CORROSION-Corrosion found during the first or subsequent inspections, which is determined (normally by the operator) to be a potential urgent airworthiness concern requiring expeditious action.

The above are taken from Boeing Commercial Airplane Company and FAA documents.

References

[1] Stress Corrosion Cracking in Aircraft Structural Materials, AGARD Conference Proceedings Series 18, Report of a two day Symposium held by the Structures and Materials Panel of AGARD in Turin, Italy, 18,19 April, 1967, NATO-AGARD, 64 Rue De Varenne, Paris, France, 1967.

[2] Fundamental Aspects of Stress Corrosion Cracking, Editors: Staehle, R. W, Forty, A. J., van Rooyen, D., Proceedings of a conference held at the Ohio State University, 11-15Sept. 1967, NACE-1, National Association of Corrosion Engineers, Houston, TX, 1969.

[3] Effects of Environment and Complex Load History on Fatigue Life, ASTM STP 462, Proceedings of the Symposium on Effects of Environment and Complex Load History on Fatigue Life held in Atlanta, GA, 29Sept. -4Oct., 1968, Edited by M. Rosenfeld, D.W. Hoeppner, and R. I. Stephens, ASTM, Philadelphia, PA., 1970.

[4] Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, Editors:, Devereux, O., McEvily, A. J., Staehle, R. W., Proceedings of the Conference held at the University of Connecticut, 14-18June1971, NACE-2, National Association of Corrosion Engineers, Houston, TX, 1973.

[5] Brown, B. F., Stress-Corrosion Cracking in High Strength Steels and in Titanium and Aluminum Alloys, Naval Research Laboratory, Washington, D.C., 1972.

[6] Hall, L. R., Finger, R.W., Spurr, W.F., “Corrosion Fatigue Crack Growth in Aircraft Structural Materials”, AFML-TR-73-204, Boeing Company, September, 1973.

[7] Pettit, D., Ryder, J., Krupp, W., Hoeppner, D., “Investigation of the Effects of Stress and Chemical Environments on the Prediction of Fracture in Aircraft Structural Materials”, AFML-TR-74-183, Lockheed California Company, December, 1974.

[8] Corrosion-Fatigue Technology, ASTM STP 642, Proceedings of a Symposium held in Denver, CO, 14-19 Nov.1976, Edited by H. L. Craig, Jr., T.W. Crooker, and D. W. Hoeppner, ASTM, Philadelphia, PA, 1978.

[9] Aircraft Corrosion, AGARD Conference Proceedings No. 315, Papers presented at the 52nd Meeting of the AGARD Structures and Materials Panel Meeting held in Cesme, Turkey, 5-10 April 1981, NATO-AGARD, 64 Rue De Varenne, Paris, France, 1981.

[10] Corrosion Fatigue, AGARD Conference Proceedings No. 316, Papers presented at the 52nd Meeting of the AGARD Structures and Materials Panel Meeting held in Cesme, Turkey, 5-10 April 1981, NATO-AGARD, 64 Rue De Varenne, Paris, France, 1981.

[11] Corrosion Fatigue, ASTM STP 801, Proceedings of the Symposium on Corrosion Fatigue: Mechanics, Metallurgy, Electrochemistry, and Engineering held in St. Louis,

MO21-22 OCT. 1981, Edited by T. W. Crooker, B. N. Leis, ASTM, Philadelphia, PA., 1983.

[12] Hoeppner, D. W., Chandrasekaran, Venkatusen, "Corrosion and Corrosion Fatigue Predictive Modeling- State of the Art Review", Report of FASIDE International Inc., April 30, 1998.

[13] Wallace, W., Hoeppner, D., Kandachar, P. V., "Aircraft Corrosion: Causes and Case Histories", AGARD Corrosion Handbook, Vol. 1, , AGARD-AG-278-Vol. 1, 1985.

[14] ASM Handbook, Vol. 13, Corrosion, ASM International, Metals Park, Ohio, 1987.

[15] The Boeing Company, Corrosion Prevention and Control, Manual for Training Operators of Boeing Commercial. Aircraft, Seattle, WA, 1988.

[16] NTSB Metallurgist's Report, "Aloha Airlines Flight 243," Materials Laboratory Report 88-85, 1988.

[17] Environment Induced Cracking of Metals, Editors: Gangloff, R. P., Ives, M. B., Proceedings of the conference held in Kohler, WI, 2-7Oct. 1988, NACE-10, National Association of Corrosion Engineers, Houston, TX, 1990

[18] ASM Handbook, Volume 18, Friction, Lubrication, and Wear Technology, ASM International, Metals Park, Ohio, 1992

[19] Naval Aviation Safety Program, US Navy, OPNAVINST 3750.6Q CH-1, OP-05F, March 1991.

[20] Federal Aviation Administration, Aircraft Accident and Incident Synopses Related to Corrosion, Fretting, and Fatigue for the Period 1976-1993, obtained July 1994.

[21] National Transportation Safety Board, Aircraft Accident and Incident Synopses Related to Corrosion, Fretting, and Fatigue for the Period 1975-1993, obtained July 1994.

[22] Federal Aviation Administration, Aircraft Accident and Incident Synopses Related to Corrosion, Fretting, and Fatigue for the Period 1976-1993, obtained July 1994.

[23] Karpala, F., Hageniers, O.L., "Characterization of Corrosion and Development of a Broadboard Model of a D Sight Aircraft Inspection System", Phase 1, Diffracto Ltd., Report to DOT, August, 1994.

[24] United States Air Force, Navy, and Army, Aircraft Accident and Incident Synopses Related to Corrosion, Fretting, and Fatigue, obtained June-August 1994.

[25] Cooke, G. Vore, P. J., Gumienny, C., Cooke, G. Jr., "A Study to Determine the Annual Direct Cost of Corrosion Maintenance for Weapon Systems and Equipment in the

United States Air Force" , Final Report, Contract Number F09603-89-C-3016, SEPT., 1990.

[26] Schütz, W., "Corrosion Fatigue-The Forgotten Factor in Assessing Durability", ICAF 95, Estimation, Enhancement and Control of Aircraft Fatigue Performance, Vol. 1, Edited by J. M. Grandage, G. S. Jost, Proceedings of the 18th Symposium on the International Committee of Aeronautical Fatigue, 3-5 May, 1995, Melbourne, Australia, EMAS, Warley, West Midlands, U.K., 1995, pp 1-52.

[27] Swift, S. J., "The Aero Commander Chronicle", ICAF 95, Estimation, Enhancement and Control of Aircraft Fatigue Performance, Vol. 1, Edited by J.M. Grandage, G.S. Jost, Proceedings of the 18th Symposium on the International Committee of Aeronautical Fatigue, 3-5 May, 1995, Melbourne, Australia, EMAS, Warley, West Midlands, U.K., 1995, pp 507-530..

[28] Hoeppner, D. W., Grimes, L., Hoeppner, A., Ledesma, J., Mills, T., Shah, A., " Corrosion and Fretting as Critical Aviation Safety Issues", ICAF 95, Estimation, Enhancement and Control of Aircraft Fatigue Performance, Vol. 1, Edited by J.M. Grandage, G.S. Jost, Proceedings of the 18th Symposium on the International Committee of Aeronautical Fatigue, 3-5 May, 1995, Melbourne, Australia, EMAS, Warley, West Midlands, U.K., 1995, pp 87-106..

[29] Brooks, C. L., Liu, K., Eastin, R.G., "Understanding Fatigue Failure Analyses Under Random Loading Using a C-17 Test Report", ICAF 95, Estimation, Enhancement and Control of Aircraft Fatigue Performance, Vol. 1, Edited by J. M. Grandage, G.S. Jost, Proceedings of the 18th Symposium on the International Committee of Aeronautical Fatigue, 3-5 May, 1995, Melbourne, Australia, EMAS, Warley, West Midlands, U.K., 1995, pp 449-468.

[30] ASM Handbook, Vol. 19, Fatigue and Fracture, ASM International, Metals Park, Ohio, 1996.

[31] Schmidt, C. G., Crocker, J. E., Giovanola, J. H., Kanazawa, C. H., Schockey, "Characterization of Early Stages of Corrosion Fatigue in Aircraft Skin", Final Report, Contract No. 93-G-065, SRI International Final Report to DOT, Menlo Park, CA, Report No. DOT/FAA/AR-95/108, February, 1996.

[32] Cole, G. K., Clark, G., Sharp, P. K., Implications of Corrosion With Respect to Aircraft Structural Integrity, DSTO –RR-0102, AMRL, Melbourne, Australia, March, 1997.

[33] Aging of U.S. Air Force Aircraft, Report of the Committee on Aging of U.S. Air Force Aircraft, NMAB (National Materials Advisory Board), Commission on Engineering and Technical Systems, National Research Council, Publication NMAB-488-2, 1997.

[34] Boeing, Corrosion Damage Assessment Framework, Corrosion/Fatigue Effects on Structural Integrity, Report D500-13008-1, USAF Contract No. F9603-97-C-0349. 1998.

[35] Paul, C., Mills, T., "Corrosion/Fatigue", Presentation made at AeroMat, 1998.
"A Study to Determine the Cost of Corrosion Maintenance for Weapon Systems and Equipment in the United States Air Force", Final Report, Contract Number F09603-95-D-0053, February 1998.

[36] Fatigue in the Presence of Corrosion, RTO Proceedings 18, Papers Presented at the Workshop of the RTO Applied Technology (AVT) Panel, held in Corfu, Greece, 7-9 October, 1998, AC/323(AVT) TP/8, NATO, Research and Technology Organization, BP 25, 7 Rue Ancelle, F-92201, Neully-Sur-Seine, Cedix, France, 1999.

[37] Jones, D., Principles and prevention of corrosion, Macmillan Publishing Co., N.Y., 1992, pg. 4.

[38] Hoeppner, D. W., "Estimation of component life by application of fatigue crack growth threshold knowledge" in Fatigue, Creep and Pressure Vessels for Elevated Temperature Service, The American Society of Mechanical Engineers, N. Y. (1981) pp. 1-83

[39] Hoeppner, D. W., , "*Parameters that Input to Application of Damage Tolerance Concepts to Critical Engine Components*," AGARD Conference, San Antonio, Texas, April, 1985, Published in Conference Proceedings AGARD-CP 393, Damage Tolerance Concepts for Critical Engine Components, pp. 4-1 to 4-16, NATO-AGARD, France, (August, 1985) invited keynote paper.

[40] Metals Handbook - Ninth Edition, Corrosion, Vol. 13, 1987, Publ: American Society for Metals (ASM), Metals Park, OH.

[41] Alvarez, A., "Corrosion on aircraft in marine-tropical environments: a technical analysis", *Material Performance*, May 1997, pp. 33-38.

[42] Suyitno, B. M. and Sutarmadji, T. "Corrosion control assessment for Indonesian aging aircraft", *Anti-corrosion Methods and Materials*, Vol. 44, No. 2, November 1997, pp. 115-122.

[43] Groner, D. J., "US Air Force aging aircraft corrosion", *Current Awareness Bulletin*, Structures Division, Wright Laboratory, Spring 1997.

[44] Piascik, R. S., Kelly, R. G., Inman, M. E., and Willard, S. A., "Fuselage lap splice corrosion", *WL-TR-96-4094*, Vol. II, ASIP, 1996.

[45] McIntyre, J. F. and Dow, T. S., "Intergranular corrosion behavior of aluminum alloys exposed to artificial seawater in the presence of nitrate anion", *Corrosion*, Vol. 48, No. 4, pp. 309-319, 1992.

[46] Thompson, J. J., Tankins, E. S., and Agarwala, V. S., “A heat treatment for reducing corrosion and stress corrosion cracking susceptibilities in 7xxx aluminum alloys”, *Materials Performance*, June 1987, pp. 45-52.

[47] Rinnovatore, J. V., Lukens, K. F., and Corrie, J. D., “Exfoliation corrosion of 7075 aluminum die forgings”, *Corrosion*, Vol. 29, No. 9, 1973, pp. 364-372.

[48] Mills, T. B., “The combined effects of prior-corrosion and aggressive chemical environments on fatigue crack growth behavior in aluminum alloy 7075-T651”, *Ph.D. Dissertation*, University of Utah, 1997.

[49] Mills, T. B., “The effects of exfoliation corrosion on the fatigue response of 7075-T651 aluminum plate,” *M.S. Thesis*, University of Utah, 1994.

[50] Chubb, J. P., Morad, T. A., Hockenhull, B. S., and Bristow, J.W., “The effect of exfoliation corrosion on the fatigue behavior of structural aluminum alloys”, in Structural Integrity of Aging Airplanes, 1991, pp. 87-97.

[51] Op. cit. 7.

[52] Swartz, D. D., Miller, M. and Hoeppner, D. W., "Chemical Environments in Commercial Transport Aircraft and Their Effect on Corrosion Fatigue Crack Propagation", in *Estimation, Enhancement and Control of Aircraft Fatigue Performance*, Vol. I, J.M. Grandage and G.S. Jost, Eds., The proceedings of the 14th symposium of the International Committee on Aeronautical Fatigue, 3-5 May, 1995, Melbourne, Australia, pp. 353-364.

[53] Kramer, J., and Hoeppner, D. W., “Effects of Cyclic Immersion in 3.5% NaCl Solution on Fatigue Crack Propagation Rates in Aluminum 2024-T351”, *Proceedings of the 1995 USAF Structural Integrity Program Conference*, WL-TR-96-4093, Vol. II, pp. 1089-1112.

[54] Mills, T. B., Magda, D. J., Kinyon, S. E., and Hoeppner, D. W., “Fatigue crack growth and residual strength analyses of service corroded 2024-T3 aluminum fuselage panels, Report to Oklahoma City Air Logistics Center and Boeing Defense and Space Group, University of Utah, 1995.

[55] Komorowski, J. P., Bellinger, N. C., and Gould, R. W., “The role of corrosion pillowing in NDI and in the structural integrity of fuselage joints”, in Fatigue in New and Aging Aircraft, Proceedings of the 19th Symposium of ICAF 1997.

[56] op-cit. ref. 55.

[57] Bellinger, N. C., Komorowski, J. P., and Gould, R.W., “Damage Tolerance Implications of Corrosion Pillowing on Fuselage lap joints”, *AIAA journal*, Vol. 35, No. 3, 1997

[58] Op. cit. 57

[59] Jayalakshmi, M., and Muralidharan, “Empirical and deterministic models of pitting corrosion - an overview”, *Corrosion Reviews*, Vol. 14, Nos. 3-4, 1996, pp. 375-402.

[60] Evans, V. R., *J. Chem. Soc*., 92, 1929.

[61] Hoar, T. P., “The Production and Breakdown of the Passivity of Metals”, *Corrosion Science*, Vol. 7, 1967, pp. 341-355.

[62] Hoar, T. P and Wood, “The sealing of porous anodic oxide films on aluminum,” *Electrochemica Acta*, 7, 1962, pg. 333

[63] Bohni and Uhlig, H. H., “Environmental Factors Affecting the Critical Pitting Potential of Aluminum,” *Journal of the Electrochemical Society*, Vol. 116, 1969, pp. 906-910.

[64] Kolotyrkin, Ya, M., “Effects of Anions on the Dissolution Kinetics of Metals,” *Journal of the Electrochemical Society,* Vol. 108, No. 3, 1961, pp. 209-216.

[65] Sato, N., *Electrochemica Acta*, 16, 1971, pg. 1683.

[66] Sato, N., “Anodic Breakdown of Passive Films on Metals”, and “The Stability of Pitting Dissolution of Metals in Aqueous Solution,” *Journal of the Electrochemical Society*, Vol. 129, No. 2, 1982, pp. 255-260 and 260-264.

[67] Lin, Chao, and Macdonald, “A point defect model for anodic passive films II. Chemical breakdown and pit initiation,” *Journal of the Electrochemical Society*, Vol. 128, No. 6, 1981, pp. 1194-1198.

[68] Hoeppner, D. W., Mann, D., and Weekes, J., “Fracture mechanics based modeling of corrosion fatigue process,” in Corrosion Fatigue: Proceedings of the 52nd meeting of the AGARD Structural and Materials Panel held in Turkey, 5-10 April, 1981.

[69] Hoeppner, D. W., Corrosion fatigue considerations in materials selections and engineering design”, Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, 1972, pp. 3-11.

[70] McAdam, D. J., and Gell, G. W., “Pitting and its effect on the fatigue limit of steels corroded under various conditions”, *Journal of the Proceedings of the American Society for Testing Materials*, Vol. 41, 1928, pp. 696-732.

[71] Goto, M., and Nisitani, H., “Crack initiation and propagation behavior of a heat treated carbon steel in corrosion fatigue”, *Fatigue Fracture Engineering Material Structure*, Vol. 15, No. 4, 1992, pp. 353-363.

[72] Muller, M., "Theoretical considerations on corrosion fatigue crack initiation", *Metallurgical Transactions*, Vol. 13A, 1982, pp. 649-655.

[73] Mehdizadeh, P., et al., "Corrosion fatigue performance of a carbon steel in brine containing air, H2S, CO2", *Corrosion*, Vol. 22, 1966, pp. 325-335.

[74] Corsetti, L. V., and Duquette, D. J., "The effect of mean stress and environment on corrosion fatigue behavior of 7075-T6 aluminum", *Metallurgical Transactions*, Vol. 5, 1974, pp. 1087-1093.

[75] Hoeppner, D. W., "Model for Prediction of Fatigue Lives Based Upon a Pitting Corrosion Fatigue Process," Fatigue Mechanisms, Proceedings of an ASTM-NBS-NSF Symposium, J.T. Fong, Ed., ASTM STP 675, American Society for Testing and Materials, 1979 pp. 841-870.

[76] Lindley, T. C., McIntyre, P., and Trant, P. J., "Fatigue Crack Initiation at Corrosion Pits," *Metals Technology*, Vol. 9, 1982, pp. 135-142.

[77] Kawai, S. and Kasai, K., "Considerations of Allowable Stress of Corrosion Fatigue (Focused on the Influence of Pitting)," *Fatigue Fracture of Engineering Materials Structure*, Vol. 8, No. 2, 1985, pp. 115-127.

[78] Kondo, Y., "Prediction of Fatigue Crack Initiation Life Based on Pit Growth," *Corrosion Science*, Vol. 45, No. 1, 1989, pp. 7-11.

[79] Hoeppner, D. W., Mechanisms of fretting fatigue, Keynote Paper, in Fretting Fatigue, ESIS 18, Mechanical Engineering Publications, London, (1994) 3-19.

[80] Hoeppner, D. W., Goss, G. L., A fretting fatigue damage threshold concept, *Wear*, 27, (1974) 61-70.

[81] Hoeppner, D. W., Adibnazari, S., Fretting fatigue in aircraft joints, in Durability and Structural Integrity of Airframes, International Committee of Aeronautical Fatigue (ICAF), (1993) 191-207.

[82] Hoeppner, "Fretting of aircraft control surfaces," in AGARD Conference Proceedings No. 161, Specialists Meeting on Fretting in Aircraft Systems, (1974), 1.1-1.7.

[83] Hoeppner, D. W., Adibnazari, S., Moesser, M. W., "Literature review and preliminary studies of fretting and fretting fatigue including special applications to aircraft joints," *DOT/FAA/CT-93/2*, (1994).

[84] Jones, D., Principles and Prevention of Corrosion, Macmillan Publishing Co., N.Y., 1992, pg. 198.

[85] Szklarska, S., Pitting Corrosion of Metals, published by National Association of Corrosion Engineers (NACE), Houston, Texas, 1986, pg. 1.

[86] Aluminum Properties and Physical Metallurgy, Ed., J.E. Hatch, American Society for Metals (ASM), Metals Park, Ohio, 1984, pg. 253.

[87] McAdam, D. J. and Gell, G. W., "Pitting and its Effect on the Fatigue Limit of Steels Corroded Under Various Conditions," *Journal of the Proceedings of the American Society for Testing Materials*, Vol. 41, 1928, pp. 696-732.

[88] Foley, R. T., "Localized Corrosion of Aluminum Alloys - A Review," *Corrosion*, Vol. 428, No. 5, 1986, pp. 277-288.

[89] Grimes, L., A Comparative Study of Corrosion Pit Morphology in 7075-T6 Aluminum Alloy, *M.S. Thesis*, University of Utah, 1996.

[90] Liversidge, "On the Corrosion of Aluminum," *Chemical News*, LXXI, 1895.

[91] Bengough and Hudson, "Aluminum, Fourth Report to the Corrosion Committee," *Journal of the Institute of Metals*, Vol. 21, No. 1, 1919, pg. 105.

[92] Barnes and Shearer, "A Hydrogen Peroxide Cell," *Journal of physical chemistry*, Vol. 12, 1908, pg. 155.

[93] Dunstan and Hill, "The Passivity of Iron and Certain Other Metals," *Journal of the Chemical Society*, Vol. 99, 1911, pg. 1853.

[94] Godard, the Corrosion of Light Metals, John Wiley and Sons, N.Y., 1967.

[95] Hart, "The Oxidation of Aluminum in Dry and Humid Oxygen Atmospheres," *The Proceedings of the Royal Society*, A236, 1956, pg. 68.

[96] Thompson, Shimizu, and Wood, "Observation of Flaws in Anodic Films on Aluminum," *Nature*, Vol. 286, 1980, pg. 471.

[97] Hoar and Wood, "The Sealing of Porous Anodic Oxide Films on Aluminum," *Electrochemica Acta*, Vol. 7, 1962, pg. 333.

[98] Seligman and Williams, "The Action on Aluminum of Hard Industrial Waters," *Journal of the Institute of Metals*, 23, 1920.

[99] Alwitt, "The Growth of Hydrous Oxide Films on Aluminum," *Journal of the Electrochemical Society*, Vol. 121, No. 10, 1974, pp. 1322-1328.

[100] Graedel, "Corrosion Mechanisms for Aluminum Exposed to the Atmosphere," *Journal of the Electrochemical Society*, Vol. 136, No. 4, 1989, pg. 204C.

[101] Rozenfield and Danilov, “Electrochemical Aspects of Pitting Corrosion,” *Corrosion Science*, Vol. 7, 1967, pg. 129.

[102] Broli, A. and Holtan, H., “Use of Potentiokinetic Methods for the Determination of Characteristic Potentials for Pitting Corrosion of Aluminum in a Deaerated Solution of 3% NaCl,” *Corrosion Science*, Vol. 13, 1973, pp. 237-246.

[103] Hoar, T. P., “The Production and Breakdown of the Passivity of Metals”, *Corrosion Science*, Vol. 7, 1967, pp. 341-355.

[104] Godard, the Corrosion of Light Metals, John Wiley and Sons, N.Y., 1967.

[105] Dallek, S. and Foley, R. T., “Propagation of Pitting on Aluminum Alloys”, *Journal of the Electrochemical Society*, Vol. 125, No. 5, 1978, pp. 731-733.

[106] Nguyen, T. H. and Foley, R. T., “On the Mechanism of Pitting of Aluminum,” *Journal of the Electrochemical Society*, Vol. 126, No. 11, 1979, pp. 1855-1860.

[107] Baumgartner and Kaesche, “Aluminum Pitting in Chloride Solutions: Morphology and Pit Growth Kinetics,” *Corrosion Science*, Vol. 31, 1990, pp. 231-236.

[108] Ma, L., Pitting Effects on the Corrosion Fatigue Life of 7075-T6 Aluminum Alloy, *Dissertation*, University of Utah, 1994.

[109] Chen, G. S., Liao, C., Wan, K., Gao, M., and Wei, R. P., “Pitting Corrosion and Fatigue Crack Nucleation,” Effects of the Environment on the Initiation of Crack Growth, ASTM STP 1298, W. A. Van Der Sluys, R. S. Piascik, and R. Zawierucha, Eds., American Society for Testing and Materials, 1997, pp. 18-33.

[110] Uhlig, H.H., “Adsorbed and Reaction-Product Films on Metals,” *Journal of the Electrochemical Society*, Vol. 97, No. 11, 1950, pp. 215c-220c.

[111] Bohni, H. and Uhlig, H. H., “Environmental Factors Affecting the Critical Pitting Potential of Aluminum,” *Journal of the Electrochemical Society*, Vol. 116, 1969, pp. 906-910.

[112] Leckie, H. P. and Uhlig, H. H., “Environmental Factors Affecting the Critical Potential for Pitting in 18-8 Stainless Steel,” *Journal of the Electrochemical Society*, Vol. 113, No. 2, 1966, pp. 1262-1267.

[113] Hoar, T. P. and Jacob, W.R., *Nature*, 216, 1967, pg. 1299.

[114] Kolotyrkin, Ya, M., “Effects of Anions on the Dissolution Kinetics of Metals,” *Journal of the Electrochemical Society*, Vol. 108, No. 3, 1961, pp. 209-216.

[115] Strehblow, H.H., Titze, B., and Loechel, B.P., “The Breakdown of Passivity of Iron and Nickel by Flouride”, *Corrosion Science*, Vol. 19, 1979, pp. 1047-1057.

[116] Bohni, H., "Localized corrosion," in Corrosion Mechanisms, Ed., F. Mansfeld, Marcel Dekker, Inc., N.Y., 1987, pp. 285-328.

[117] Sato, N., "Anodic Breakdown of Passive Films on Metals", and "The Stability of Pitting Dissolution of Metals in Aqueous Solution," *Journal of the Electrochemical Society*, Vol. 129, No. 2, 1982, pp. 255-260 and 260-264.

[118] Richardson and Wood, "A Study of the Pitting Corrosion of Al by Scanning Electron Microscopy," *Corrosion Science*, Vol. 10, 1970, pp. 313-323.

[119] Nilsen, N. and Bardal, E., "Short Duration Tests and a New Criterion for Characterization of Pitting Resistance of Al Alloys," *Corrosion Science*, Vol. 17, 1977, pp. 635-646.

[120] Hoar, T. P. and Jacob, W.R., *Nature*, 216, 1967, pg. 1299.

[121] Chao, Lin, and Macdonald, "A Point Defect Model for Anodic Passive Films I. Film Growth Kinetics," *Journal of the Electrochemical Society*, Vol. 128, No. 6, 1981, pp. 1187-1194.

[122] Lin, Chao, and Macdonald, "A Point Defect Model for Anodic Passive Films II. Chemical Breakdown and Pit Initiation," *Journal of the Electrochemical Society*, Vol. 128, No. 6, 1981, pp. 1194-1198.

[123] Sato, N., "Anodic Breakdown of Passive Films on Metals", and "The Stability of Pitting Dissolution of Metals in Aqueous Solution," *Journal of the Electrochemical Society*, Vol. 129, No. 2, 1982, pp. 255-260 and 260-264.

[124] Richardson and Wood, "A Study of the Pitting Corrosion of Al by Scanning Electron Microscopy," *Corrosion Science*, Vol. 10, 1970, pp. 313-323.

[125] Galvele, "Transport Processes and the Mechanism of Pitting of Metals," *Journal of the Electrochemical Society*, Vol. 123, No. 4, 1976, pp. 464-474.

[126] Akid, R., "The role of stress-assisted localized corrosion in the development of short fatigue cracks," Effects of the Environment on the Initiation of Crack Growth, ASTM STP 1298, W. A. Van Der Sluys, R. S. Piascik, and R. Zawierucha, Eds., American Society for Testing and Materials, 1997, pp. 3-17.

[127] Hoeppner, D. W., "Corrosion Fatigue Considerations in Materials Selections and Engineering Design," in Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, O. Devereux, A. J. McEvily, R. W. Staehle, Eds., NACE-2, National Association of Corrosion Engineers, 1972, pp. 3-11.

[128] Hoeppner, D. W., "Model for Prediction of Fatigue Lives Based Upon a Pitting Corrosion Fatigue Process," Fatigue Mechanisms, Proceedings of an ASTM-NBS-NSF

Symposium, J.T. Fong, Ed., ASTM STP 675, American Society for Testing and Materials, 1979 pp. 841-870.

[129] Lindley, T. C., McIntyre, P., and Trant, P. J., “Fatigue Crack Initiation at Corrosion Pits,” *Metals Technology*, Vol. 9, 1982, pp. 135-142.

[130] Kawai, S. and Kasai, K., “Considerations of Allowable Stress of Corrosion Fatigue (Focused on the Influence of Pitting),” *Fatigue Fracture of Engineering Materials Structure*, Vol. 8, No. 2, 1985, pp. 115-127.

[131] Kondo, Y., “Prediction of Fatigue Crack Initiation Life Based on Pit Growth,” *Corrosion Science*, Vol. 45, No. 1, 1989, pp. 7-11.

[132] Rebiere, M. and Magnin, T., *Materials Science and Engineering*, Vol. A128, 1990, pg. 99.

[133] Chen, G. S. and Duquette, D. J., “Corrosion Fatigue of a Precipitation-Hardened Al-Li-Zr Alloy in a 0.5 M Sodium Chloride Solution,” *Metallurgical Transactions*, Vol. 23, 1992, pp. 1563-1572.

[134] Chen, G. S. et al., *Corrosion*, Vol. 52, 1996, pg. 8.

[135] Hoeppner, D.W., Mann, and Weekes, “Fracture mechanics based modeling of corrosion fatigue process,” in Corrosion Fatigue: Proceedings of the 52nd meeting of the AGARD Structural and Materials Panel held in Turkey, 5-10 April, 1981.

[136] Ma, L., and Hoeppner, D. W., “The Effects of Pitting on Fatigue Crack Nucleation in 7075-T6 Aluminum Alloy,” *Proceedings of the FAA/NASA International Symposium on Advanced Structural Integrity Methods for Airframe Durability and Damage Tolerance*, NASA Conference Publication 3274, Part 1, 1994, pp. 425-440.

[137] AGARD Conference Proceedings No. 328, Behavior of Short Cracks in Airframe Components, Papers presented at the 55th Meeting of the AGARD Structures and Materials Panel in Toronto, Canada on 19-24 September(1983),.

[138] Akid, R. and Murtaza, G., "Environment assisted short crack growth behavior of a high strength steel", Short Fatigue Cracks, K.J. Miller and E.R. de los Rios, Eds, Mechanical Engineering Publications Limited, (1992), pp. 193-208.

[139] Bolinbroke, R. K., King, J. E., "The growth of short fatigue cracks in titanium alloys IMI550 and IMI318", Small Fatigue Cracks, Ritchie, R. O. and Lankford, J., Eds., A Publication of The Metallurgical Society, Inc., (1986), pp. 129-144.

[140] Boukerrou, A., Cottis, R.A., "The influence of corrosion on the growth of short fatigue cracks in structural steels", Short Fatigue Cracks, K.J. Miller and E.R. de los Rios, Eds, Mechanical Engineering Publications Limited, (1992), pp. 209-217.

[141] Breat, J. L., Mudry, F. Pineau, A., "Short crack propagation and closure effects in A508 steel", Fatigue Fracture of Engineering Materials Structures, 6, (1983), pp. 349-358

[142] Brown, C. W., King, J. E., Hicks, M. A., "Effects of microstructure on long and short crack growth in nickel base super alloys", Metal Science, 18, (1984), pp. 374-380.

[143] Brown, C. W., Taylor, D., "The effects of texture and grain size on the short fatigue crack growth rates in Ti-6Al-4V", Fatigue Crack Threshold Concepts, D.L. Davidson and S. Suresh, Eds, AIME, (1984), pp. 433-446.

144] Cameron, D. W., Perspectives and insights on the cyclic response of metal, Ph.D. Dissertation, University of Toronto (1984),

145] Chan, K. S. and Lankford, J., "The role of microstructural dissimilitude in fatigue and fracture of small cracks", Acta Metallurgica, (1988) pp. 193-206.

146] Clement, P., Angeli, J. P. and Pineau, A., "Short crack behavior in nodular cast iron", Fatigue Fracture of Engineering Materials and Structures, 7, (1984), pp. 251-265.

[147] Davidson, D. L., "Small and large fatigue cracks in aluminum alloys", Acta Metallurgica, 36, (1988) pp. 2275-2282.

[148] Davidson, D. L., Campbell, J. B., and Page, R. A., "The initiation and growth of fatigue cracks in a titanium aluminide alloy", Metallurgical Transactions, 22A, (1991)pp. 377-391.

[149] De Los Rios, E. R., Tang, Z. and Miller, K. J., "Short crack fatigue behavior in a medium carbon steel", Fatigue Fracture of Engineering Materials and Structures, 7, (1984), pp. 97-108.

[150] De Los Rios, E. R., Mohamed, H. J., and Miller, K. J., "A micro-mechanic analysis for short fatigue crack growth", Fatigue Fracture of Engineering Materials and Structures, 8, (1985), pp. 49-63.

[151] De Los Rios, E. R., Navarro, A., Hussain, K., "Microstructural variations in short fatigue crack propagation of a C-Mn steel", Short Fatigue Cracks, K.J. Miller and E.R. de los Rios, Eds, Mechanical Engineering Publications Limited, (1992), pp. 115-132.

[152] Dutta, V. B., Suresh, S., and Ritchie, R. O., "Fatigue crack propagation in dual-phase steels: effects of ferritic-martensitic microstructures on crack path morphology", Metallurgical Transactions, 15A, (1984) pp. 1193-1207.

[153] Eastabrook, J. N., "A dislocation model for the rate of initial growth of stage I fatigue cracks", International Journal of Fracture, 24, (1984), pp. 43-49.

[154] El Haddad, M. H., Dowling, N.E., Topper, T. H., Smith, K. N., "J-integral applications for short fatigue crack at notches", International Journal of Fracture, 16, pp. 15-30.

[155] Forsyth, P. J. E., the Physical Basis of Metal Fatigue, Blackie and Son Limited. . (1969).

[156] Gangloff , R. P., "Crack size effects on the chemical driving force for aqueous corrosion fatigue", Metallurgical Transactions, 16A, (1985), pp. 953-969.

[157] Gangloff , R. P., Wei, R. P. , "Small crack-environment interaction: The hydrogen embrittlement perspective", Small Fatigue Cracks, R.O. Ritchie and J. Lankford, Eds., A Publication of The Metallurgical Society, Inc., (1986), pp. 239-264.

[158] M. Goto, "Scatter in small crack propagation and fatigue behavior in carbon steels", Fatigue Fracture of Engineering Materials and Structures, 16, (1993), pp. 795-809.

[159] M. Goto, "Statistical investigation of the behavior of small cracks and fatigue life in carbon steels with different ferrite grain sizes", Fatigue Fracture of Engineering Materials and Structures, 17, (1994), pp. 635-649.

[160] Healy, J. C., Grabowski, L., Beevers, C. J., "Short-fatigue-crack growth in a nickel-base superalloy at room and elevated temperature", International Journal of Fatigue, 13, (1991), pp. 133-138.

[161] M. A. Hicks, Brown, C. W., "A comparison of short crack growth behavior in engineering alloys", Fatigue 84, C.J. Beevers, Ed., EMAS, Warley, U.K. (1984), pp. 1337.

[162] Hirose, S., Fine, M. E., "Fatigue crack initiation and microcrack propagation in X7091 type aluminum P/M alloys", Metallurgical Transactions, 14A, (1983), pp. 1189-1197.

[163] Hobson, P. D., "The formulation of a crack growth equation for short cracks", Fatigue Fracture of Engineering Materials and Structures, 5(1982) pp. 323-327.

[164] Hoeppner, D. W., "The effect of grain size on fatigue crack propagation in copper," Fatigue Crack Propagation, ASTM 415, American Society for Testing and Materials, (1967), pp. 486-504.

[165] Op. cit. 38.

[166] Hoeppner, D. W., "Application of Damage Tolerance concepts to "short cracks" in safety critical components", in Industrial Applications of Damage Tolerance

[167] Concepts, *Proceedings of the Twelfth ICAF Symposium*, ICAF Doc. No. 1336, (1983), pp. 2.1/1 - 2.2/20

[168] Hoeppner, A.M. (now A. Taylor), The effect of prior corrosion damage on the short crack growth rates of two aluminum alloys, M.S. Thesis, (1996) University of Utah.

[169] Hoshide, T., Yamada, T., Fujimura, S., "Short crack growth and life prediction in low-cycle fatigue and smooth specimens", Engineering Fracture Mechanics, 21, (1985), pp. 85-101.

[170] Hyspecky, P., Stranadel, B., "Conversion of short fatigue cracks into a long crack", Fatigue Fracture of Engineering Materials and Structures, 15, (1992), pp. 845-854.

[171] Kawachi, S., Yamada, K., Kunio, T. "Some aspects of small crack growth near threshold in dual phase steel", Short Fatigue Cracks, K.J. Miller and E.R. de los Rios, Eds, Mechanical Engineering Publications Limited, (1992), pp. 101-114.

[172] Kim, Y. H., Mura, T., Fine, M.E., "Fatigue crack initiation and microcrack growth in 4140 steel", Metallurgical Transactions, 9A, (1978), pp. 1679-1683.

[173] Kim, Y. H., Fine, M.E., "Fatigue crack initiation and strain-controlled fatigue of some high strength low alloy steels", Metallurgical Transactions, 13A, (1982), pp. 59-71.

[174] Kumai, S., Kino, J. E., Knott, J. F. "Short and long fatigue crack growth in a SiC reinforced aluminum alloy", Fatigue Fracture of Engineering Materials and Structures, 13, (1990), pp. 511-524.

[175] Kung, C. Y., Fine, M.E. "Fatigue crack initiation and microcrack growth in 2024-T4 and 2124-T4 aluminum alloys", Metallurgical Transactions, 10A, (1979) pp. 603-610.

[176] Kunio, T., Yamada, K. "Microstructural aspects of the threshold condition for non-propagating fatigue cracks in martensitic-ferritic structures", Fatigue Mechanisms, J.T. Fong, Ed., ASTM STP 675, (1979), pp. 342-370.

[177] Kwun, S. I., Fournelle, R. A. "Fatigue crack initiation and propagation in a quenched and tempered niobium bearing HSLA steel", Metallurgical Transactions, 13A, (1982), pp. 393-399.

[178] Lankford, J., Cook, T. S., Sheldon, G. P., "Fatigue microcrack growth in nickel-base superalloy", International Journal of Fracture, 17, (1981), pp. 143-155.

[179] Lankford, J. "The growth of small fatigue cracks in 7075-T6 aluminum", Fatigue Fracture of Engineering Materials and Structures, 5, (1982), pp. 233-248.

[180] Lankford, J., "The effect of environment on the growth of small fatigue cracks", Fatigue Fracture of Engineering Materials and Structures, 6, (1983), pp. 15-31.

[181] Lankford, J., Davidson, D. L. "The role of metallurgical factors in controlling the growth of small fatigue cracks", Small Fatigue Cracks, R.O. Ritchie and J. Lankford, Eds., A Publication of The Metallurgical Society, Inc., (1986), pp. 51-72.

[182] Mahajan, Y. Margolin, H. "Low cycle fatigue behavior of Ti-6Al-2Sn-4Zr-6Mo: Part I. The role of microstructure in low cycle crack nucleation and early crack growth", Metallurgical Transactions, 13A, (1982), pp. 257-267.

[183] McClung, R. C., Chan, K. S., Hudak, S. J., Davidson, D. L. "Analysis of small crack behavior for airframe applications", FAA/NASA International Symposium on Advanced Structural Integrity Methods for Airframe Durability and Damage Tolerance. (1994).

[184] McEvily, A. J. Minakawa, S., "Crack closure and the conditions for crack propagation", Fatigue Crack Growth Threshold Concepts, D.L. Davidson and S. Suresh, Eds., TMS-AIME, (1984), pp. 517-530.

[185] Mei, Z., Morris, J. W., "The growth of small fatigue cracks in A286 steel", Metallurgical Transactions, 24A, (1993), pp. 689-700.

[186] Mei, Z., Krenn, C. R. Morris, J. W., "Initiation and growth of small fatigue cracks in a Ni-base superalloy", Metallurgical Transactions, 26A, (1995), pp. 2063-2073.

[187] Miller, K. J., "The short crack problem", Fatigue and Fracture of Engineering Materials and Structures, 5, (1982), pp. 223-232

[188] Minakawa, K., Matsuo, Y., and McEvily, A., "The influence of a duplex microstructure in steels on fatigue crack growth in the near-threshold region", Metallurgical Transactions, 13A, (1982), pp. 439-445.

[189] Morris, W. L., Buck, O., Marcus, H. L., "Fatigue crack initiation and early propagation in Al 2219-T851", Metallurgical Transactions, 7A, (1976), pp. 1161-1165.

[190] Morris, W. L. Buck, O., "Crack closure load measurements for microcracks developed during the fatigue of Al 2219-T851", Metallurgical Transactions, 8A, (1977), pp. 597-601.

[191] Murakami, Y., Endo, M., “Quantitative evaluation of fatigue strength of metals containing various small defects or cracks”, Engineering Fracture Mechanics, 17, No. 1, (1983), pp. 1-15.

[192] Nicholls, D. J., Martin, J. W., "A comparison of small fatigue crack growth, low cycle fatigue and long fatigue crack growth in Al-Li alloys", Fatigue Fracture of Engineering Materials and Structures, 14, (1991), pp. 185-192.

[193] Newman, J. C., Edwards, P. R., "Short crack growth behavior in an aluminum alloy", An AGARD cooperative test Programme, NATO-AGARD report, (1988).

[194] Okazaki, M. Tabata, T., Nohmi, S., "Intrinsic Stage I crack growth of directionally solidified Ni-Base superalloys during low-cycle fatigue at elevated temperature", Metallurgical Transactions, 21A, (1990) pp. 2201-2208.

[195] Pan, J. Z., De Los Rios, E. R, Miller, K. J., "Short fatigue crack growth in plain and notched specimens of an 8090 Al-Li alloy", Fatigue Fracture of Engineering Materials and Structures, 16, (1993), pp. 1365-1379.

[196] Pearson, S. "Initiation of fatigue cracks in commercial aluminum alloys and the subsequent propagation of very short cracks", Engineering Fracture Mechanics, 7, (1975), pp. 235-247.

[197] Petit, J., Zeghloul, A., "Environmental and Microstructural influence on fatigue propagation of small surface cracks", Environmentally Assisted Cracking: Science and Engineering, ASTM STP 1049, W. B. Lisagor, T.W. Crooker, and B. N. Leis, Eds., American Society for Testing and Materials, Philadelphia, (1990), pp. 334-346.

[198] Petit, J., Mendez, J., Berata, Legendre, W. L., Muller, C., "Influence of environment on the propagation of short fatigue cracks in a titanium alloy", Short Fatigue Cracks, K.J. Miller and E.R. de los Rios, Eds, Mechanical Engineering Publications Limited, (1992) pp. 235-250.

[199] Petit, J. and Zeghloul, A., "On the effect of environment on short crack growth behavior and threshold", The Behavior of Short Fatigue Cracks, K.J. Miller and E.R. de los Rios, Eds, Mechanical Engineering Publications Limited, (1986), pp. 163-178.

[200] Petit, J., Kosche, K., "Stage I and Stage II propagation of short and long cracks in Al-Zn-Mg alloys", Short Fatigue Cracks, K. J. Miller and E. R. de los Rios, Eds, Mechanical Engineering Publications Limited, (1992), pp. 135-151.

[201] Piascik, R. S., Willard, S.A., “The growth of small corrosion fatigue cracks in alloy 2024,” Fatigue Fracture of Engineering Materials and Structures, Vol. 17, (1994), pp. 1247-1259.

[202] Plumtree, A., O'Connor, B. P. D., "Influence of microstructure on short fatigue crack growth", Fatigue Fracture of Engineering Materials and Structures, 14, (1991) pp. 171-184.

[203] Polak, J. P. Laskutin, T., "Nucleation and short crack growth in fatigued polycrystalline copper", Fatigue Fracture of Engineering Materials and Structures, 13, (1990), pp. 119-133.

[204] Potter, J. M., Yee, B. G. W., "Use of small crack data to bring about and quantify improvements to aircraft structural integrity", in Behavior of Short Cracks in Airframe Components, NATO-AGARD (1983).

[205] R .O. Ritchie and J. Lankford, "Small fatigue cracks: A statement of the problem and potential solutions", Materials Science and Engineering, 84, (1986) pp. 11-16.

[206] Ritchie, R. O. and Suresh, S. "Mechanics and physics of the growth of small cracks", A University of California, Berkeley report (1995),.

[207] Schijve, J., "Fatigue crack closure, observations and technical significance", NLR TR-679, National Aerospace Laboratory NLR, Amsterdam (1986).

[208] Schijve, J., "Multiple-site-damage fatigue of riveted joints", International Workshop On Structural Integrity Of Aging Airplanes, Atlanta, 31 March-2 April (1992),.

[209] Shang, J. K., Tzou, J. L., and Miller, K. J., "Role of crack tip shielding in the initiation and growth of long and small fatigue cracks in composite microstructures", Metallurgical Transactions, 18A, (1987), pp. 1613-1627.

[210] Sheldon, G. P., Cook, T. S., Jones, J. W., Lankford, J., "Some observations on small fatigue cracks in a superalloy", Fatigue Fracture of Engineering Materials and Structures, 3, (1981), pp. 219-228.

[211] D. Sigler, M.C. Montpetit, and W.L. Haworth (1983), "Metallography of fatigue crack initiation in an overaged high-strength aluminum alloy", Metallurgical Transactions, 14A, pp. 931-938.

[212] Stephens, R. R., Grabowski, L., Hoeppner, D. W. "The effect of temperature on the behavior of short fatigue cracks in Waspaloy using an in situ SEM fatigue apparatus", International Journal of Fatigue, 15, (1993), pp. 273-282.

[213] Suh, C. M., Lee, J. J., Kang, Y. G., "Fatigue microcracks in type 304 stainless steel at elevated temperature", Fatigue Fracture of Engineering Materials and Structures, 13, (1990) pp. 487-496.

[214] Suresh, S. "Crack Deflection: Implications For The Growth Of Long And Short Fatigue Cracks", Metallurgical Transactions, 14A, (1983), pp. 2375.

[215] Suresh, S. "Fatigue crack deflection and fracture surface contact: Micromechanical model", Metallurgical Transactions, 16A, (1985), pp. 249-260.

[216] Taira, S., Tanaka, K., Hoshina, M. "Grain size effect on crack nucleation and growth in long-life fatigue of low-carbon steel", Fatigue Mechanisms, J.T. Fong, Ed., ASTM STP 675, Philadelphia, (1979), pp. 135-173.

[217] Taylor, D. and Knott, J. F. "Fatigue crack propagation behavior of short cracks; the effect of microstructure", Fatigue Fracture of Engineering Materials and Structures, 4, (1981), pp. 147-155.

[218] Tokaji, K., Ogawa, T., Harada, Y. "The growth of small fatigue cracks in a low carbon steel; the effect of microstructure and limitations of linear elastic fracture mechanics", Fatigue Fracture of Engineering Materials and Structures, 9, (1986), pp. 205-217.

[219] K. Tokaji, T. Ogawa, Y. Harada, and Z. Ando (1986), "Limitations of linear elastic fracture mechanics in respect of small fatigue cracks and microstructure", Fatigue Fracture of Engineering Materials and Structures, 9, pp. 1-14.

[220] Tokaji, K., Ogawa, T., Harada, Y. "Evaluation on limitation of linear elastic fracture mechanics for small fatigue crack growth", Fatigue Fracture of Engineering Materials and Structures, 10, (1987), pp. 281-289.

[221] Tokaji, K., Ogawa, T., Osako, S. Harada, Y., "The growth behavior of small fatigue cracks; the effect of microstructure and crack closure", Fatigue '87, Vol. 2, (1988), pp. 313-322.

[222] Tokaji, K., Ogawa, T. "The growth of microstructurally small fatigue cracks in a ferritic-pearlitic steel", Fatigue Fracture of Engineering Materials and Structures, 11, (1988), pp. 331-342.

[223] Tokaji, K., Ogawa, T., Aoki, T., "Small fatigue crack growth in a low carbon steel under tension-compression and pulsating-tension loading", Fatigue Fracture of Engineering Materials and Structures, 13, (1990), pp. 31-39.

[224] Tokaji, K., Ogawa, T. "The effects of stress ratio on the growth behavior of small fatigue cracks in an aluminum alloy 7075-T6 (with special interest in Stage I crack growth", Fatigue Fracture of Engineering Materials and Structures, 13, (1990), pp. 411-421.

[225] Tokaji, K., Ogawa, T., Kameyama, Y., Kato, Y. "Small fatigue crack growth behavior and its statistical properties in a pure titanium", Fatigue '90, Vol. 2, (1990), pp. 1091-1096.

[226] Tokaji, K. Ogawa, T. "The growth behavior of microstructurally small fatigue cracks in metals", Short Fatigue Cracks, K.J. Miller and E.R. de los Rios, Eds, Mechanical Engineering Publications Limited, (1992), pp. 85-100.

[227] K. T. Venkateswara Rao, W. Yu, and R.O. Ritchie (1988), "Fatigue crack propagation in aluminum-lithium alloy 2090: Part II. Small crack behavior", Metallurgical Transactions, 19A, pp. 563-569.

[228] Wagner, L., Gregory, J. K., Gysler, A., Lutjering, G., "Propagation behavior of short cracks in a Ti-8.6Al alloy", Small Fatigue Cracks, R.O. Ritchie and J. Lankford, Eds., A Publication of The Metallurgical Society, Inc., (1986), pp. 117-128.

[229] Wood, H. A. Rudd, J. L., "Evaluation of small cracks in airframe structures". (1983) personal communication.

[230] Wu, D. C., An investigation into the fatigue crack growth characteristics of a single crystal nickel-base superalloy, Ph. D. Dissertation, (1986), University of Toronto.

[231] Yates, J. R., Zhang, W., Miller, K .J., "The initiation and propagation behavior of short fatigue cracks in Waspaloy subjected to bending", Fatigue Fracture of Engineering Materials and Structures, 16, (1993), pp. 351-362.

[232] Zeghloul, A., Petit, J., "Environmental sensitivity of small crack growth in 7075 aluminum alloy", Fatigue Fracture of Engineering Materials and Structures, 8, (1985), pp. 341-348.

[233] Zurek, A. K., James, M. R., and Morris, W. L., "The effect of grain size on fatigue growth of short cracks", Metallurgical Transactions, 14A, (1982), pp. 1697-1705.

[234] Aircraft Structural Fatigue, Hoeppner, D. W. et al., four volumes of notes, Course sponsored by the US FAA, 1979-92.

[235] Structural Integrity of New and Aging Metallic Aircraft, with M. Creager, T.R. Brussat, D. W. Hoeppner, and T. Swift, Short Course by UCLA Extension, Department of Engineering, Information Systems and Technical Management, Los Angeles, CA, 1970-current.

[236] Practical Considerations in Structural Fatigue and Damage Tolerant Design of New and Aging Aircraft, D. W. Hoeppner, Course offered by FASIDE International Inc., in conjunction with the Division of Continuing Education, University of Utah, and the Quality and Integrity Design Engineering Center (QIDEC), Department of Mechanical Engineering, University of Utah, Salt Lake City, UT.

[237] Zheng, X., “Corrosion Growth in Lap Joint Crevice,” Presented at the First Technical Interchange Meeting on Corrosion Modeling, Organized by NCI, 15-16 October, 1997.

[238] Roberge, Pierre, R., Handbook of Corrosion Engineering, McGraw Hill Book Co., New York, N.Y., 1999.

[239] Roberge, Pierre, R., Corrosion Engineering: Principles and Practice, McGraw Hill Book Co., New York, N.Y., 2008.

[240] Roberge, Pierre, R., Corrosion Inspection and Monitoring, Wiley-Interscience, John Wiley and Sons, Hoboken, N. J., 2007.

[241] Bloomberg Business Week, June 12, 2011, page 37.

[242] Hoeppner**,** D. W., "A Review of Corrosion Fatigue and Corrosion/Fatigue Considerations in Aircraft Structural Design", Invited paper presented at International Conference on Fatigue of Aircraft, Lucerne, SW, May, 2003, **ICAF 2003-Fatigue of Aeronautical Structures as an Engineering Challenge**, Vol. 1, Edited by M. Guillaume, Proceedings of the 22nd Symposium of the International Committee of Aeronautical Fatigue, EMAS Publishing, Sheffield, England, 2004, pp 425-438.

[243] Swift, S., "Rusty Diamond", ICAF 2007 Durability and Damage Tolerance of Aircraft Structures: Metals vs. Composites, Proceedings of the 24th Symposium of the International Committee on Aeronautical Fatigue 16-18 May 2007, Naples, Italy Ed. L Lazzeri and A. Salvetti.

CHAPTER 3

CORROSION FATIGUE MODELING OF ALUMINUM ALLOY 7075-T6

Abstract

Corrosion fatigue experiments were conducted on specimens of aluminum alloy 7075-T6. Such specimens were precorroded with an acidified saline solution of 3.5% NaCl. The effect of corrosion time and stress magnitude on the specimen's fatigue life was studied. A statistical factorial model was used to setup the protocol for testing. Two levels of corrosion time, and stress magnitude were chosen to be evaluated based on assessed criticality from other related studies and the literature. Specimens were simultaneously exposed to the saline solution and cyclic loading, until failure by fracture was observed.

Analysis of variance was done on the results from the experiments to evaluate the effects of maximum stress and corrosion time on the fatigue life of the specimens. Results of such analysis indicated that stress magnitude had greater deleterious impact when compared with corrosion time. A statistical factorial model was developed by stabilizing the variance with a transformation. The model provides prediction of failure with statistical confidence for the conditions previously defined. Data were fitted to several distribution functions including, normal, lognormal, exponential and the Weibull distribution fits the data with 95% confidence. Localized pitting corrosion was observed in the specimens exposed to the acidified saline solution. In addition, fractographic

analysis revealed formation/nucleation of cracks from discontinuities caused by pitting. Finally, intergranular attack, subsurface pitting and tunneling were also observed and played a role in the formation of fatigue cracks.

Key Words: A. Aluminum; B. SEM; C. Corrosion fatigue; D. Pitting corrosion.

Introduction

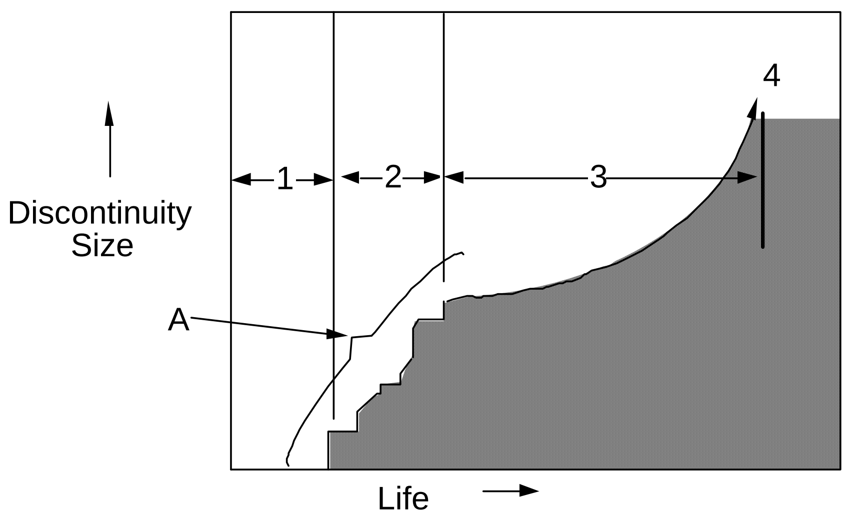
Corrosion and fatigue are mechanisms of degradation of engineering materials and structures which have deleterious effects on the integrity of structures. The synergistic effect of these mechanisms is a serious concern particularly to the aerospace industry. With an increasing number of aging aircraft in service, understanding the combined effects of corrosion and fatigue is critical to the maintenance of structural integrity and associated safety of flight. Corrosion has multiple forms including, but not limited to, general corrosion, pitting, filiform, exfoliation, crevice, intergranular, fretting and corrosion fatigue. These forms of corrosion are commonly found on all aircraft, regardless of efforts to minimize corrosive environmental effects [1].

Aluminum alloys such as 2024-T3 and 7075-T6 are extensively used in aircraft structures and have a heterogeneous microstructure which renders them highly susceptible to corrosion [2]. It is well known that such microstructure creates galvanic cells due to the difference in chemical nature between the matrix and the constituent particles, and it is this difference in electrochemical potential that causes pitting [3]. A large number of chemical, mechanical and electrochemical factors affect pitting. Some of these factors include chemical potential, passive film, pH, composition of environment, type of alloy, composition, integrity of oxide film, loading environment, manufacturing induced discontinuities, etc.

It has been established that corrosion produces accelerated fatigue crack formation/nucleation [4-12]. Hoeppner proposed that the phases of life of a structure include the following [13, 14] (Fig. 3.1): phase 1, the formation or nucleation of damage by specific internal or external factors occurs during the fatigue process. Thus, from the literature this author has indicated numerous times the importance of differentiating the physics of the formation or nucleation phase, from the word initiation [15-17]. Phase 2, “short” crack propagation which is microstructurally dominated crack propagation. Phase 3 is “long” crack propagation, which can be characterized by linear-elastic fracture mechanics (LEFM), elastic-plastic fracture mechanics (EPFM) and fully plastic fracture mechanics (FPFM). Phase 4 is final failure which leads to ultimate fracture or some other instability. Understanding each of these phases, including the transition from one phase to the next, is crucial for developing models to predict with confidence the life of a structure.

Models based on pitting corrosion fatigue (PCF) mechanisms have been proposed. Such models assume hemispherical pit shapes and stress intensity relationships are used to determine the critical pit depth using the crack growth threshold that is found empirically. Multiple engineers and scientists have proposed models for several materials, environments and applications [18-24]. Some of these models include the following: Hoeppner (1971 - current) [25-27]; Lindley et al. (1982) [28]; Kawai and Kasai (1985) [8]; and Kondo (1989) [7]. Due to the numerous factors and variability that are involved in these mechanisms, modeling becomes a complex and challenging endeavor.

The degradation process



A= "FIRST" detectable crack

1. Nucleation phase, "NO CRACK"

2. "SMALL CRACK" phase-steps related to local structure (Anisotropy)

3. Stress dominated crack growth, LEFM, EPFM

4. Crack at length to produce instability

Fig. 3.1: Phases of Life (after Hoeppner, 1971[13], 1985 [14]).

The purpose of the research reported herein was to examine and characterize the effects of different levels of prior corrosion and stress magnitude on the fatigue life of the specimens. Some effort is placed upon minimizing the effect of corrosion fatigue in aircraft structural integrity programs depending on the company and regulating body approach. Some do only a minimum as specified in a CPCP (Corrosion Prevention and Control Program). Research focusing on statistical modeling, such as reported herein, will increase the understanding of a structure through the phases of life and diminishing the effects of corrosion fatigue in structural integrity. Thus, it is envisioned that this work is one of the steps needed to continue to make aircraft structures safe relative to the potential degradation from corrosion fatigue.

Experimental Procedures

Center-pin-loaded dogbone specimens were designed and machined from 7075-T6 aluminum alloy sheet of thickness 1.600 mm (0.063 in.). The impact of different levels of stress magnitude and exposure time to the corrosive solution, into the fatigue life of aluminum alloy 7075-T6 specimens, was evaluated. Basis for the corrosion fatigue protocol were taken from previous studies performed at the University of Utah's Structural Integrity Laboratory. In addition, ASTM standards were reviewed and adapted to the protocol, with some modifications.

An important assumption for this study is that surfaces are homogeneous and free of discontinuities. To achieve this state, a rigorous regime of surface polishing was followed. Specimen preparation involved polishing the side of interest to a 0.3 μm mirror finish. The final surface appearance was mirror-like, which was assumed free of imperfections. This was verified by confocal microscopy, and no significant pits were found in the surface. After polishing, specimens were cleaned with acetone in an ultrasonic bath for 5 minutes. Specimens were weighed in an analytical high precision balance and stored in a vacuum dessicator.

Two levels of prior-corrosion time were evaluated, 24 and 48 hours. Pre-corrosion was performed to nucleate discontinuities and accelerate short crack growth. A 3.5% NaCl solution was prepared to simulate the salinity of sea water, which was acidified to a pH of three, by addition of 1M HCl. Such pH was chosen based on electrochemical principles which indicate that Al^{3+} ions are stable at low pH values. The corrosion area was set to 3 mm by 10 mm. Pits were characterized with a metallurgical microscope that allowed measuring pit depth, as a function of time. Specimens were exposed simultaneously to the saline acidic environment and cyclic loading. Prior to exposure, the solution was aerated for 1 hour. The flow rate was approximately 1 ml/min. Fatigue was performed utilizing an electro-hydraulic, servo-controlled MTS 3.3 kip capacity load frame. The loading was controlled by a MTS TestStar system. Two levels of stress were used, σ_{max} = 120.6 MPa (17.5 ksi) and σ_{max} = 241.3 MPa (35 ksi). Stress ratio was R = +0.1. The waveform was sinusoidal. The frequency was 10 Hz, with reduction to 0.5 Hz during inspection intervals. The inspection system was setup to record every 3985 cycles, where the frequency was reduced to 0.5 Hz, for 15 cycles. Two levels of corrosion time and stress were chosen according to the proposed matrix based on statistical factorial design with two levels. Specimens were exposed to corrosion-fatigue conditions until fracture, and then were cleaned with HNO_3 and acetone ultrasonic bath. Pitting characterization was done using a Scanning Electron Microscope provided by FASIDE international. The randomized experiments are shown in Table 3.1.

Table 3.1: DOE Matrix for Corrosion Fatigue Experiments.

Standard Order	Run Order	Blocks	Prior Corrosion Time (hr)	Stress (MPa)
3	1	Block 1	48	121
5	2	Block 1	24	241
1	3	Block 1	24	121
7	4	Block 1	48	241
4	5	Block 2	48	121
8	6	Block 2	48	241
2	7	Block 2	24	121
6	8	Block 2	24	241

Results

In this study, the process of pitting induced crack formation/nucleation for a 7075-T6 aluminum alloy cyclically stressed in an acidified saline solution is quantitatively demonstrated by varying the corrosion time and maximum stress. Pitting depths were obtained by using a metallurgical microscope; however an important factor to consider is that this technique does not allow detection of subsurface tunneling and subsurface pitting, which were proven to be critical factors in this study. SEM analysis allowed subsurface pit characterization, and it was evident that subsurface tunneling and pitting were present. In addition, cracks were originated from each of the pits analyzed, including the formation of subsurface cracks.

Specimens were weighed with a high precision analytical balance prior and post corrosion. This approach enabled the measurement of mass loss by corrosion as a function of time for each specimen. However, this technique may not be accurate for rate determination, due to the presence of corrosion byproducts. In addition, inductively couple plasma (ICP) techniques were used to quantitatively show the content of aluminum which dissolved into the solution by pitting.

Design of experiments (DOE) was used to setup the protocol for testing. Data were analyzed with statistical techniques including analysis of variance (ANOVA) and Weibull distributions. Several Box-Cox transformations were evaluated to stabilize the variance and to develop statistical significant models. Table 3.2 contains the results for the corrosion fatigue experiments, including the exposure time, the stress magnitude and the cycles to failure.

Table 3.2: Summary of Results of Corrosion Fatigue Experiments.

Factor Cor Time (hr)	Stress (MPa)	Cycles to Failure Replicate I	 II	 Average
24	121	1,026,642	1,264,086	1,145,364
48	121	884,865	1,041,949	963,407
24	241	64,281	57,486	60,884
48	241	38,461	41,507	39,984

Specimens were pre-exposed to an acidic saline environment for 24 and 48 hours. Two blocks were used, the first one with agitation of solution using a magnetic Fisher stirring plate, at a speed of three; and the second block with a stagnant solution. Agitation of the solution increases the removal of aluminum from the pits, and prevents the accumulation of corrosion products at the pit mouth, which could potentially act as a block for direct attack of chloride anions into the pit. Intergranular attack is evident at these conditions. Specimens exposed to the stagnant solution showed additional damage, which is caused by the hydrogen evolved by the reaction of aluminum and the acidified saline solution. Hydrogen evolving from the aluminum reaction, accumulated at the surface. Aluminum was removed leaving “rings” impressed at the surface as the accumulation of hydrogen increased. Such rings measured up to 5 μm in depth. Additional mechanisms observed included subsurface pitting, tunneling and intergranular attack. Specimens were analyzed with Scanning Electron Microscope to identify the origin of failure.

A fraction of the specimens were pre-exposed to the saline acidic solution for 48 hours, followed by simultaneous corrosion and cyclic loading with maximum stress of 241 MPa, a stress ratio of 0.1 and frequency of 10 Hz.

One of the specimens fractured at 38461 cycles, due to a crack that originated from a 50 μm pit, which extended through subsurface tunneling about 140 μm. Fig. 3.2 shows an overview of the fracture surface. Fig. 3.3 show an overview of the surface exposed to the corrosive medium. Damage at the surface is caused by pitting and intergranular mechanisms. Additional damage is caused by the accumulation of hydrogen, which accelerates aluminum removal from the surface leaving "rings" impressed in the specimen. Figs. 3.4 and 3.5 show SEM micrographs of pitting. It is evident from these images that pits propagated through subsurface tunneling, and intergranular attack.

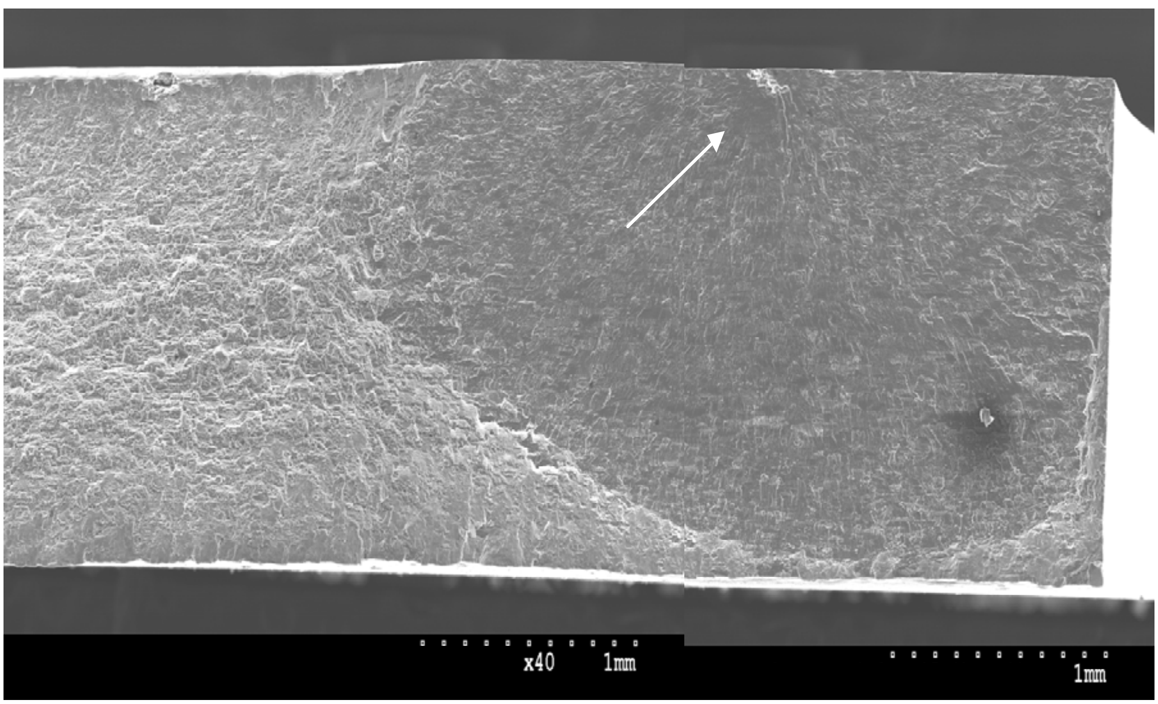


Fig. 3.2: Fracture Surface Overview showing a pit which extended by subsurface mechanisms. The arrow shows a pit at the fracture surface.

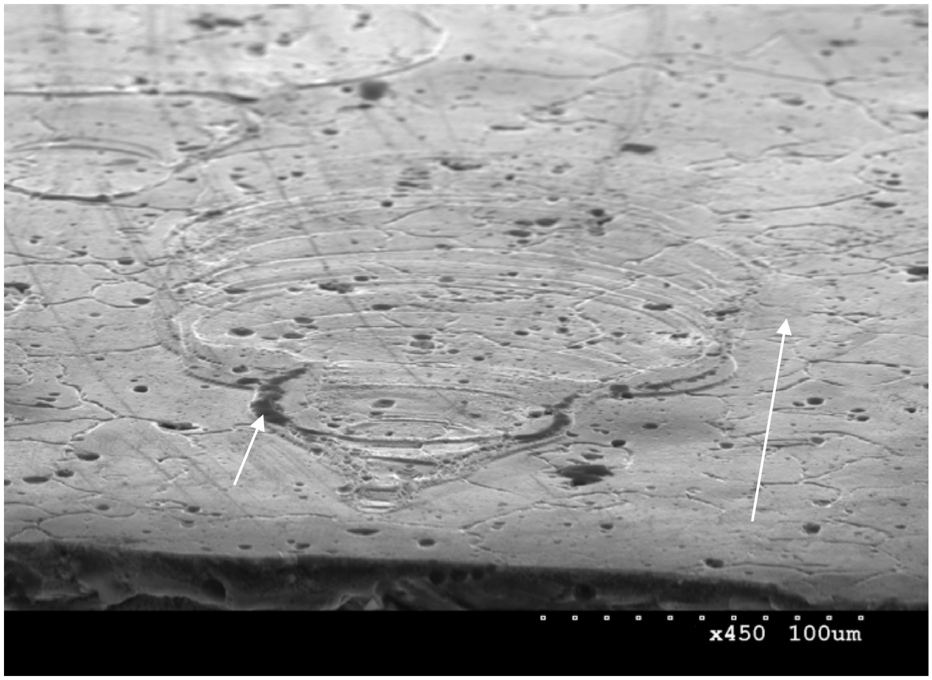


Fig. 3.3: Damage Caused by Hydrogen Formation at the Surface.
Arrows indicate direction of hydrogen bubble, and pitting at the surface.
“Rings” represent damage by Hydrogen formation at the surface.

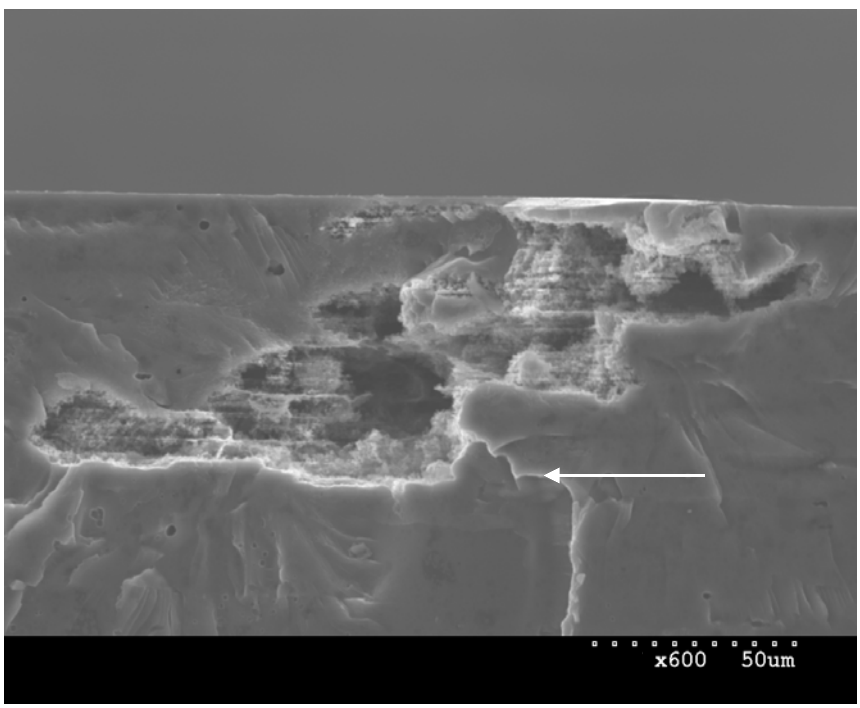


Fig. 3.4: Pitting and Subsurface Tunneling.
Arrow indicates direction of pit growth by tunneling.

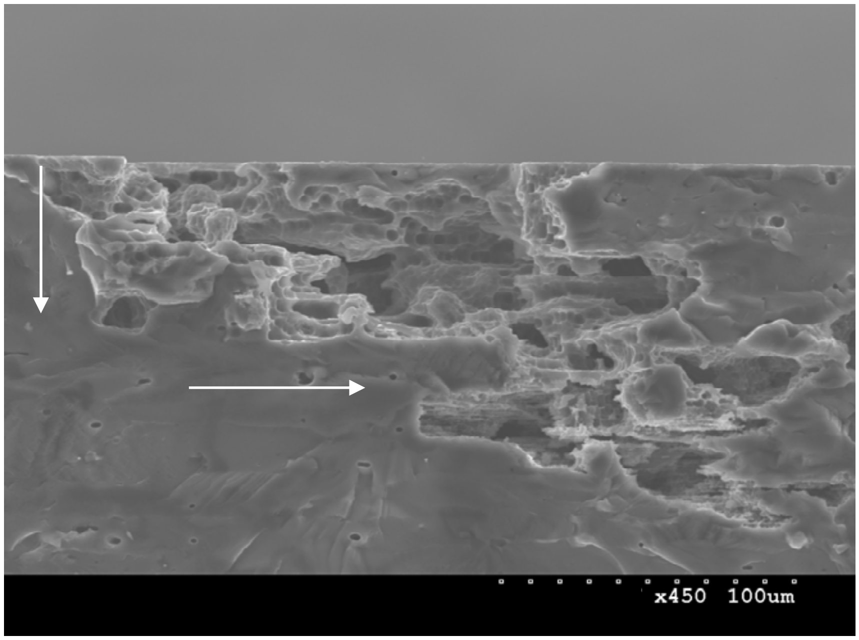


Fig. 3.5: Subsurface Pitting, Tunneling and IGA.
Arrows indicate direction of pit growth by tunneling and subsurface pitting.

The cycles to failure of each of the specimens were used to develop a corrosion fatigue model for the conditions used during testing. Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response. For the purpose of this study a 2^2 factorial design was used with two variables, which included corrosion time, and stress magnitude. In this study, the two levels of interest included, corrosion time 24 and 48 hours, and stress magnitude 120.6 MPa and 241.3 MPa. The experiments were replicated two times, with two blocks. Several Box-Cox transformations were investigated to develop the corrosion fatigue model. Generally, transformations are used for stabilizing response variance, making the distribution of the response variable closer to the normal distribution, and improving the fit of the data. A natural log transformation fits the data with statistical confidence.

Using this transformation, the effects of the two factors are estimated with a half normal probability plot (Fig.3.6).

It is evident from such analysis that stress has the major effect in the response, as compared with corrosion time. Interaction between the two factors is expected to be minimum at these conditions. In a factorial design, it is convenient to express the results of the experiment in terms of a regression model. For the corrosion fatigue experiments, the regression model is given by

$$\ln(Nf) = \beta_0 + \beta_{stress} \cdot A + \beta_{cor} \cdot B + \beta_{stress\_cor} \cdot A \cdot B \quad (1)$$

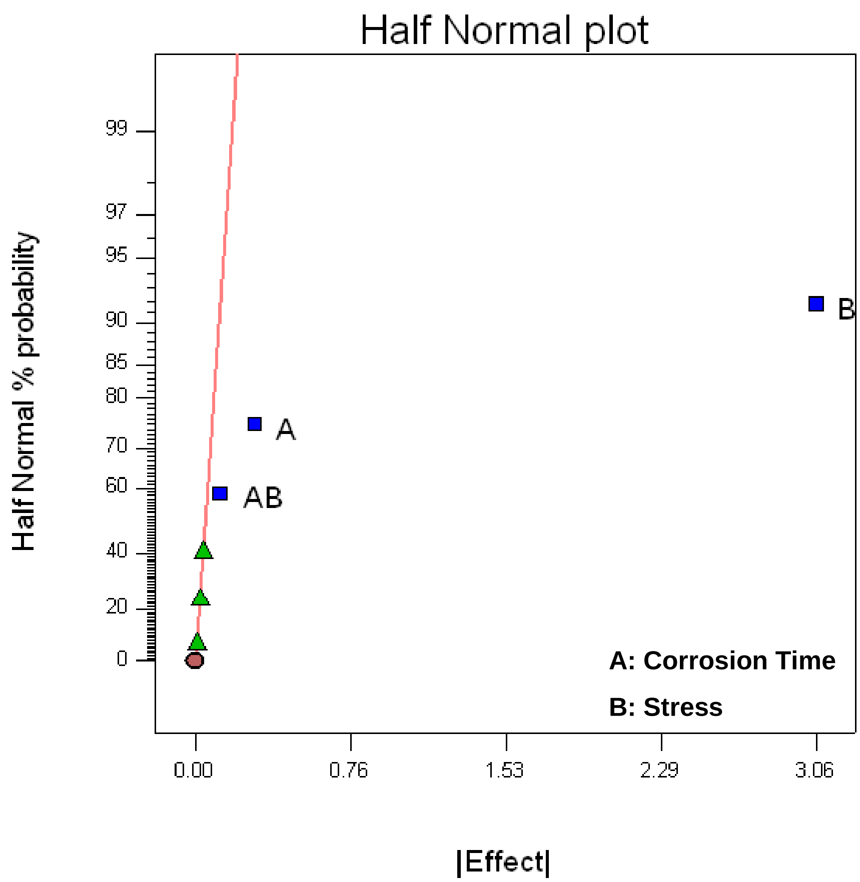


Fig. 3.6: Half Normal Plot of the Factors – Corrosion Time and Stress Magnitude

where A is a coded factor that represents the stress factor and B is a coded factor that represents the corrosion time. In order to convert the coded factors into natural variables, the following relationships are used, where A is converted by

$$A = \frac{\mathrm{Corr} - \left(\frac{\mathrm{Corr}_{low} + \mathrm{Corr}_{high}}{2}\right)}{\frac{\mathrm{Corr}_{high} - \mathrm{Corr}_{low}}{2}} \tag{2}$$

and B is converted by

$$B = \frac{\mathrm{Stress} - \left(\frac{\mathrm{Stress}_{low} + \mathrm{Stress}_{high}}{2}\right)}{\frac{\mathrm{Stress}_{high} - \mathrm{Stress}_{low}}{2}} \tag{3}$$

substituting into equation (1) and after some algebraic manipulation, yields the final solution and proposed model which is given by the following relationship

$$\ln(Nf) = a + b \cdot \tau_c - c \cdot \sigma - d \cdot \tau_c \cdot \sigma \tag{4}$$

where τ_c is the corrosion time, and σ is the maximum stress. Finally, Fig. 3.7 shows a Pareto chart of the standardized effects, which indicates that stress magnitude, had the major impact in the life of the specimens, as compared with corrosion time.

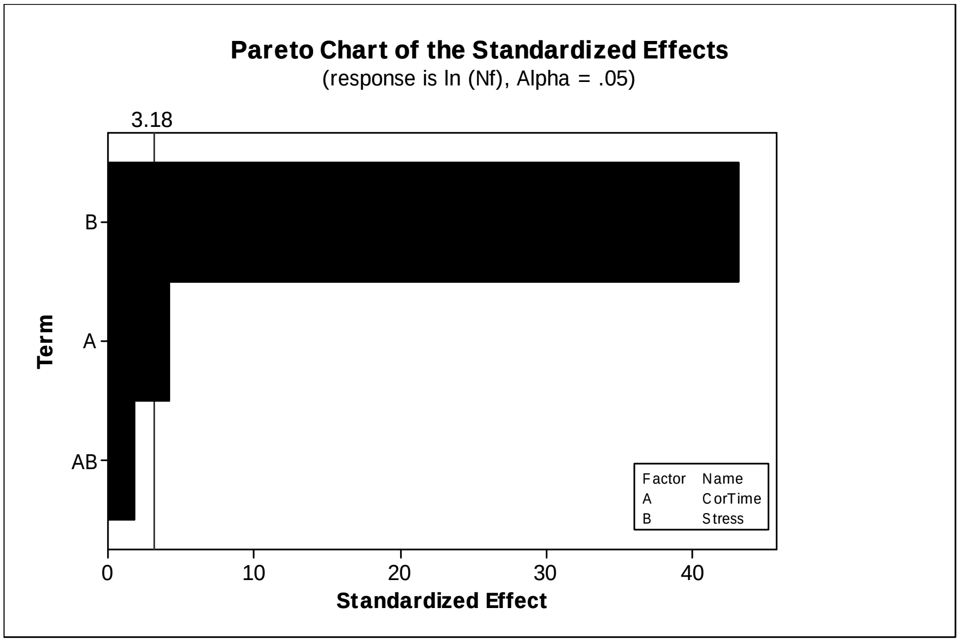


Fig. 3.7: Pareto Chart of the Standardized Effects.

For the conditions specified in Table 3.1, the resulting model is

$$Nf(\sigma, \tau_c) = e^{a + b \cdot \tau_c - c \cdot \sigma - d \cdot \tau_c \cdot \sigma} \tag{5}$$

where the constants a, b c and d are material and environment dependent.

A useful way to represent the previous model, is by two-dimensional and three-dimensional surface plots of the cycles to failure. Fig. 3.8 presents a contour plot of this model. A linear relationship results by plotting the cycles to failure in a natural log scale. It is evident that the life of the specimen is reduced as stress increases. Although corrosion time has minimum impact at low stresses, at higher stresses this factor has a more detrimental effect in the residual life of the specimens.

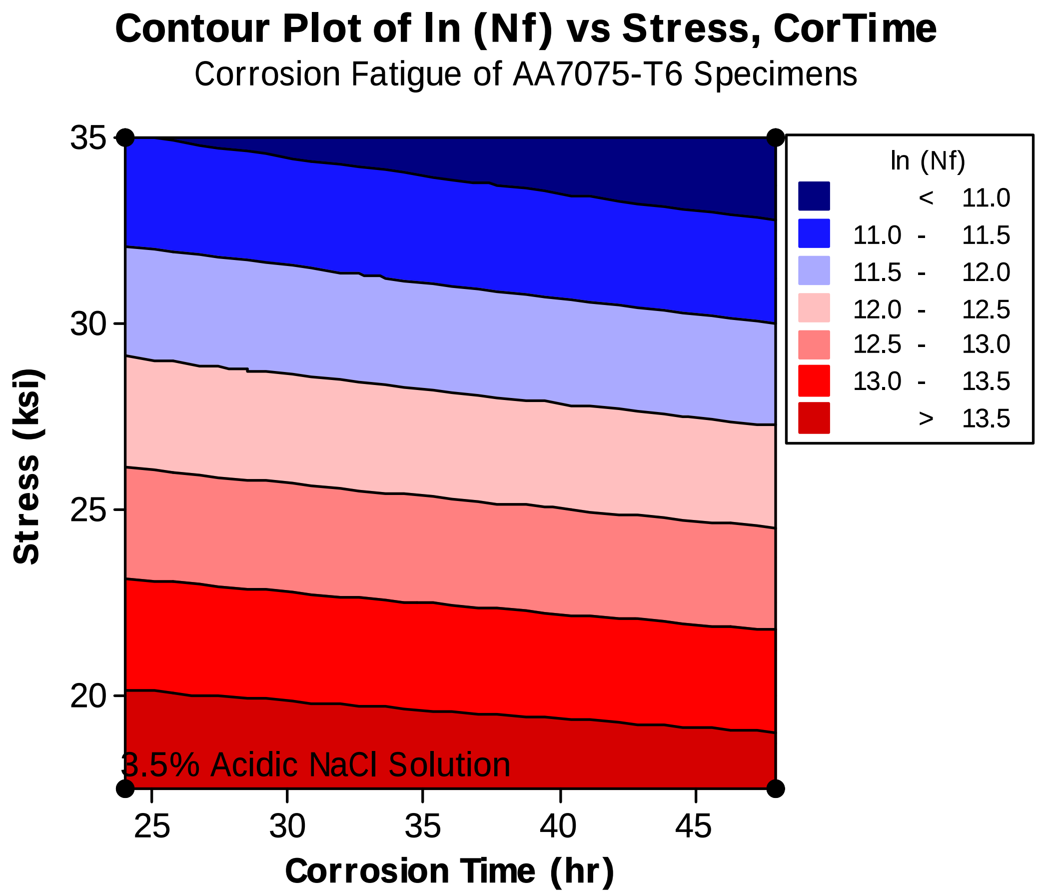


Fig. 3.8: Contour Plot of Cycles to Failure versus Stress and Corrosion Time.

Another way to express the previous model is by taking the exponential in the expression, which transforms the response into millions of cycles to failure as a function of corrosion time and stress magnitude. Fig. 3.9 represents the surface plot with the exponential transformation. Fig. 3.10 shows both a contour plot and a surface plot of the model.

Finally, data obtained from the residual life experiments were used to fit different functions including normal, lognormal, exponential and Weibull distributions.

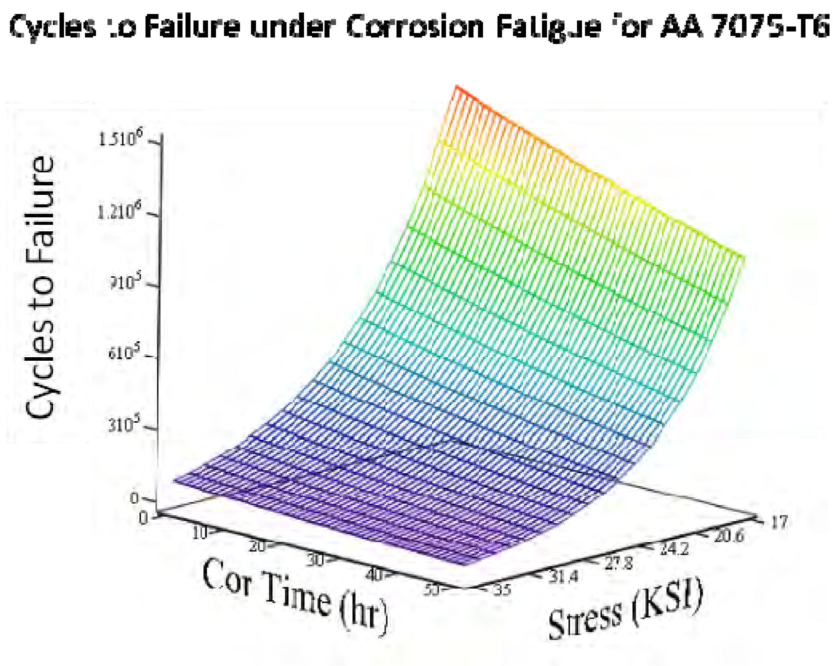


Fig.3.9: Surface Plot of the Corrosion Fatigue Model

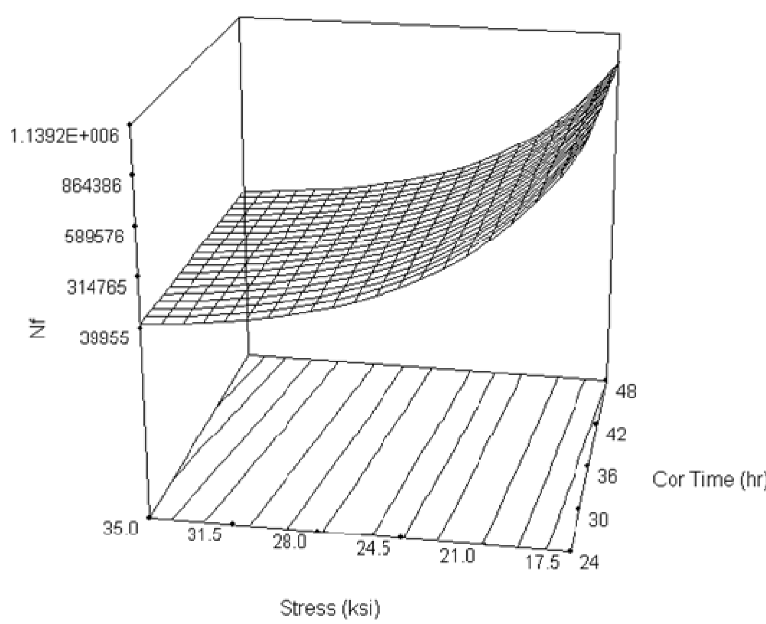


Fig. 3.10: Surface Plot and Contour Plot for Corrosion Fatigue Model.

Data fit a Weibull distribution within 95% confidence interval, with correlation coefficients greater than 0.9 and with P value of less than 0.01, which is less than the risk factor of 5 %. Probability plots with 95% confidence intervals are shown in Fig. 3.11. This plot uses stress magnitude as differentiating variable. From this plot, it is evident that the stress magnitude has a major impact in the life of the specimens. When stress is 241.3 MPa, (35 Ksi) only 64,000 cycles are required to reach 90% of the life of the specimen. However, when 120.6 MPa (17.5 Ksi) is applied, 1.2 million cycles are needed to reach 90% of the life of the specimens.

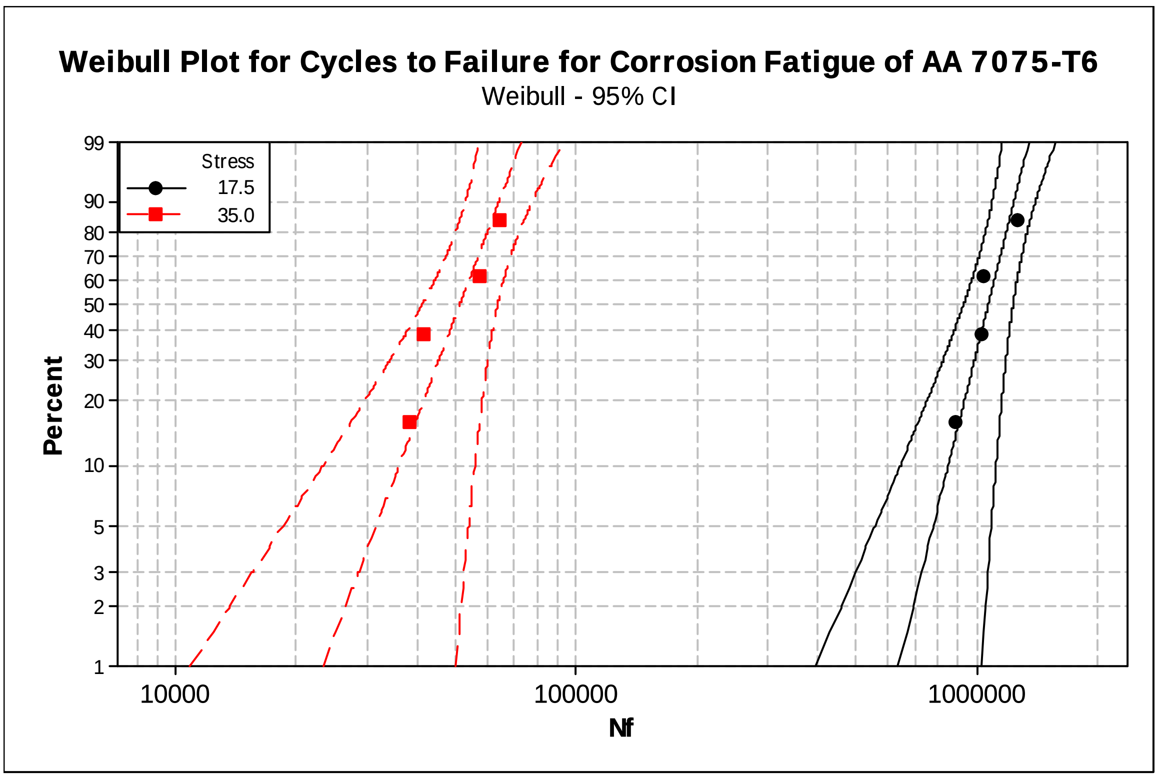


Fig. 3.11: Weibull Probability Plot with Stress Magnitude.

It can be shown using a Weibull probability plot with corrosion time as principle variable that at 24 and 48 hours, the impact in the life of the specimen is very similar or minimal impact. Approximately 1.3 million cycles are required to reach 90% of the life of the specimens at 24 hours, and at 48 hours it takes 1.5 million cycles.

Damage tolerance handbooks provide fatigue data for metals including aerospace alloys. Typically, such data are obtained at standard laboratory conditions, at different levels of stress ratio. Fig. 3.12 shows a comparison of data obtained at laboratory air conditions [29], against the results obtained from this study with an acidified 3.5% solution. It is evident from the plot that exposure of specimens to acidic saline solutions, reduces significantly the fatigue life as compared to lab air conditions.

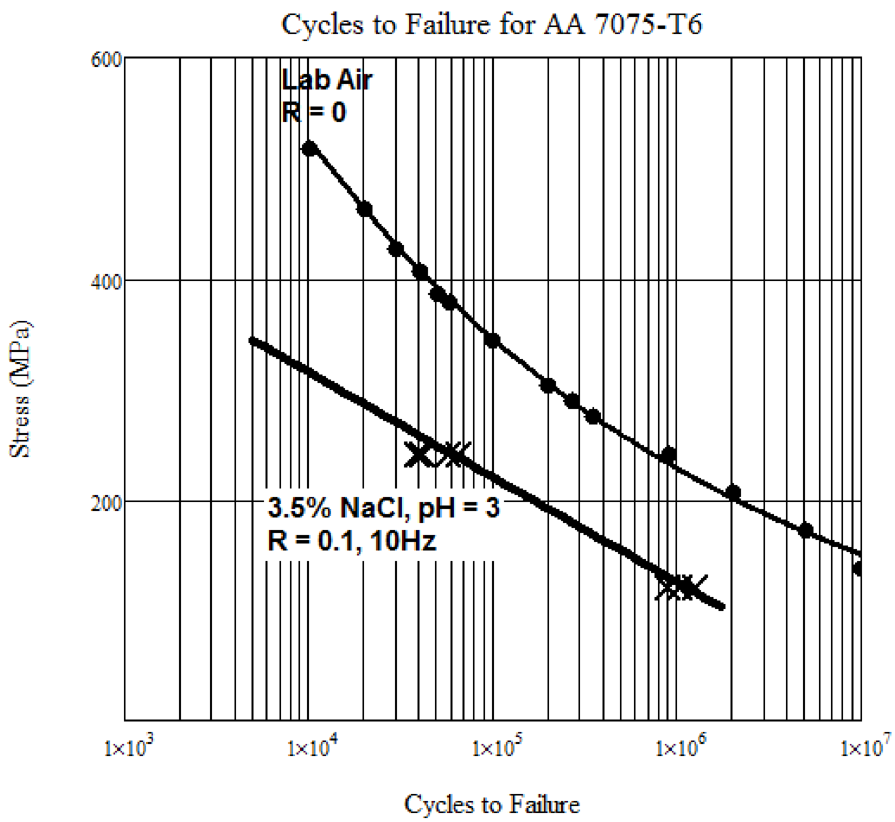


Fig. 3.12: Corrosion Fatigue Comparison with Laboratory Air.
Data for Lab Air Conditions were obtained from Damage Tolerance Handbook [29].
Trend line for 3.5% NaCl was obtained from equation (5).

Discussion

An acidic chloride environment caused aluminum alloy 7075-T6 to dissolve by pitting into the solution. Pitting was confirmed by several techniques including metallurgical microscope, and SEM. Scanning electron micrographs revealed that cracks nucleated from each of the pits analyzed, which caused failure by fracture. In addition, the solution used to pre-corrode the specimens was analyzed by inductively couple plasma (ICP) methods, which revealed that aluminum had dissolved into the solution.

Hydrogen evolved from the reaction of aluminum with the acidic chloride environment, which accelerated structural damage by anodic dissolution. This was qualitatively observed by SEM and confocal methods. Chlorine ions are adsorbed at discontinuities in the oxide film, causing the formation of pits. Inspection revealed the formation of hydrogen which accelerated anodic dissolution. As hydrogen accumulated at the surface, aluminum was dissolved into the solution, leaving “rings” impressed in the specimen. SEM analysis revealed that hydrogen damage accelerated the removal of metal from the surface, nucleating pits up to 5 μm in depth. Pits nucleated by dissolution of the metal into the corrosive environment, and continued to grow by subsurface pitting, tunneling and intergranular mechanisms. These mechanisms may have a detrimental impact in the life of structures since they are difficult to detect by conventional inspection methods.

Stress magnitude has greater impact than corrosion time, in the residual life of specimens, under acidic chloride environment. Statistical techniques were utilized during this study including DOE to setup the protocol, and ANOVA to determine the effect of stress magnitude and corrosion time, in the fatigue life of the specimens. A natural log transformation was used that reduced the variance, fitting the model within the expected statistical confidence. A model was developed to predict the cycles to failure as a function of corrosion time and stress.

The model and analysis were effective predicting the life of the specimens with statistical confidence within the limits of the variables set by the DOE matrix. Weibull probability plots indicated that stress magnitude had significant greater impact in the fatigue life of the specimens compared with corrosion time.

Conclusions

Pits were identified as crack origins for all specimens in this study. Fractographic examinations revealed that pits propagated by subsurface tunneling, subsurface pitting and intergranular attack. Formation of subsurface cracks competes with pits in propagating damage to the specimens. Aluminum was dissolved by the acidified saline solution, and hydrogen attack was evident in the surface of the specimens. The acidified saline solution accelerated fatigue crack propagation decreasing the cycles to failure for up to 10 times, as compared to specimens exposed to lab air.

Statistical planned experiments provide a solid background to establish models to predict with confidence the life of specimens/structures exposed to several variables. In this study a DOE matrix was setup with a full factorial design. Results indicated that stress magnitude had higher detrimental impact as compared with corrosion time, for the conditions defined. ANOVA was utilized to evaluate the effects of the variables in the response, and natural log transformations were used to minimize the variance. A model was proposed to estimate the cycles to failure for the conditions of interest. Weibull distributions fit the data within 95% statistical confidence.

Corrosion fatigue modeling is an inherently challenging undertaking, due to the many factors that are involved in this process. In addition, conventional inspection methods may be limited and inadequate for critical components since, as shown in this study, significant damage to the structures occur at the subsurface level. Development of statistical based models to predict with confidence the behavior of materials will increase our ability to predict and prevent catastrophic structural failures thereby increasing the safety of our aircraft structures.

In this chapter a testing methodology was established and a statistical model has been developed. The next chapter expands statistical modeling to several Box-Cox transformations, and presents contour and surface plots as potential means to present the results of these models. The following chapter has been **accepted** for publication **by Corrosion - The Journal of Science and Engineering** (NACE).

Acknowledgements

The authors wish to acknowledge FASIDE International Inc. for their financial support and use of FASIDE facilities and the University of Utah for the use of their facilities. Sincere thanks are offered to Ms. Amy Hoeppner Taylor and Mr. Larry Smiltneek for their assistance related to fatigue test setup, calibration, and to fractographic examination of the specimens post fracture.

References

[1] K. Jones, D.W. Hoeppner, The interaction between pitting corrosion, grain boundaries, and constituent particles during corrosion fatigue of 7075-T6 aluminum alloy. Int. J. Fatigue 31 (2009) 686-692.

[2] K.K. Sankaran, R.Perez, R.V.Jata, Effects of pitting corrosion on the fatigue behavior of aluminum alloy 7075-T6: modeling and experimental studies. Materials Science and Engineering. A297 (2001) 223-229.

[3] R.P. Wei, G.S.Chen, K.C. Wan, M. Gao, T.H. Flournoy. Transition from pitting to fatigue crack growth-modeling of corrosion fatigue crack nucleation in a 2024-T3 aluminum alloy. Material Science and Engineering. A219 (1996) 126-132.

[4] C.L.Harmsworth, Effect of corrosion on the fatigue behavior of 2024-T3 aluminum alloy, in : ASD Technical Report 61-121, 1961, pp.1-7.

[5] G.S. Chen, C.M. Liao, K.C. Wan, M.Gao, R.P.Wei, Pitting corrosion and fatigue crack nucleation, in W.W. Van Der Sluys R.S. Pisacik R. Zawierucha (Eds.) Effects of the environment on the initiation crack of growth, ASTM STP 1298, American Society for Testing and Materials, Philadelphia, 1997, pp. 18-31

[6] T.C. Lindley, P. McIntyre, P.J. Trant, Fatigue-crack initiation at corrosion pits, Met. Technol. 9 (1982) 135-142.

[7] Y. Kondo, Prediction of fatigue crack initiation life based on pit growth. Corrosion 45 (1989) 7-11.

[8] S. Kawai, K. Kasai, Consideration of allowable stress of corrosion fatigue (focused on the influence of pitting), Fatigue Fract. Eng. Mater. Struct. 8 (2) (1985) 115-127

[9] D.W. Hoeppner, Model for prediction of fatigue lives based upon a pitting corrosion fatigue process, in J. Long (Ed.), Fatigue Mechanisms, ASTM STP 675, American Society for Testing and Materials, Philadelphia, 1979, pp. 841-870.

[10] T. Goswami, D.W. Hoeppner, Transition Criteria – from a pit to a crack, J. Mech. Behavior Mater. 10 (1999) 261-278.

[11] P.N. Clark, D.W. Hoeppner, Pitting behavior and residual fatigue life of 2024-T3 aluminum considering the loading and sheet thickness. J. Mech. Behav. Mater. 13 (2) (2002) 91-105.

[12] K.M. Gruenberg, B.A. Craig, B.M. Hillberry, R.J. Bucci, A.J. Hinkle, Predicting fatigue life of pre-corroded 2024-T3 aluminum. Int. J. Fatigue 26 (2004) 629-640.

[13] D.W. Hoeppner. Corrosion Fatigue considerations in materials selection and design, invited keynote paper, International conference on Corrosion Fatigue, June 1971, published in the Conference Proceedings, NACE, 1972, pp. 3-11.

[14] D.W. Hoeppner, Parameters that input to application of damage tolerance concepts to critical engine components, AGARD Conference, San Antonio Texas, April 1985, Published in conference proceedings, AGARD-CP 393, pp. 4-1 to 4-16, NATO-AGARD, France, August, 1985, invited keynote paper.

[15] D.W. Hoeppner, Initiation of Fatigue in aluminum alloys, American Institute of Mining, Metallurgical and Petroleum Engineers, Symposium on Fatigue of Metals, Atlanta GA, April 1971.

[16] D.W Hoeppner, W. Krupp, Prediction of component life by application of fatigue crack growth knowledge, Eng Frac. Mech., (1974) vol. 6, pp. 47-70.

[17] D.W. Hoeppner, The formation/nucleation of fatigue cracks in aircraft structural materials. ICAF Symposium, Montreal, Canada, June 2011. Keynote speaker

[18] D.G. Harlow, R.P. Wei. Probability modeling and material microstructure applied to corrosion and fatigue of aluminum and steel alloys. Eng. Fract. Mech. 76 (2009) 695-708.

[19] D.G. Harlow, R.P. Wei. Probability approach for corrosion and corrosion fatigue life. AIAA J 1994; 32(10) 2073-2079.

[20] D.G. Harlow, R.P. Wei. A probability model for the growth of carrion pits in aluminum alloys induced by constituent particles. Eng Fract Mech. 1998; 59(3) 305-325

[21] R.S. Piascik, S.A. Willard. The growth of small corrosion fatigue cracks in alloy 2024. Fatigue Fract. Eng Materl Struct (1994); 17, 1247-1259.

[22] J.C. Newman. A review of modeling small-crack behavior and fatigue life predictions for aluminum alloys. Fatigue Fract Eng Mater Struct (1994); 17 (4) 429-439.

[23] N.R. Cawley. D.G. Harlow. Spatial statistics of constituent particles and corrosion pits in 2024 aluminum alloys. J Mater Sci (1996) 31, 5127-5134.

[24] P. Shi, S. Mahadevan. Damage tolerance approach for probabilistic pitting corrosion fatigue life prediction. Eng Fract Mech 68 (2001) 1493-1507.

[25] D.W. Hoeppner, Model for prediction of fatigue lives based upon a pitting corrosion fatigue process. American Society for Testing and Materials, (1979) pp. 841-869.

[26] D. W. Hoeppner, V. Chandrasekaran, A. Taylor., "Review of Pitting Corrosion Fatigue Models", Structural Integrity for the Next Millennium, Editors J. Rudd, R. Bader, Proceedings of the 20th Symposium of the International Committee on Aeronautical Fatigue, ICAF, Electronic Print Imaging Corp., Dayton, OH, 1999, pp 253-277.

[27] D.W. Hoeppner, "A Review of Corrosion Fatigue and Corrosion/Fatigue Considerations in Aircraft Structural Design", Invited paper presented at International Conference on Fatigue of Aircraft, Lucerne, SW, May, 2003, ICAF 2003-Fatigue of Aeronautical Structures as an Engineering Challenge, Vol. 1, Edited by M. Guillaume, Proceedings of the 22nd Symposium of the International Committee of Aeronautical Fatigue, EMAS Publishing, Sheffield, England, 2004, pp 425-438.

[28] T.C Lindley, P. McIntyre, P.J. Trant, Fatigue crack initiation at corrosion pits. Metals Technology, Vol. 9, 1982, pp.135-142.

[29] Military Standardization Handbook 5E (1986) *Bes-fit S/N curves for unnotched 7075-T6 aluminum alloy sheet.* Vol. 1, Department of Defense.

CHAPTER 4

EFFECTS OF PRIOR CORROSION AND STRESS IN CORROSION FATIGUE OF ALUMINUM ALLOY 7075-T6

Abstract

The nucleation of fatigue cracks from corrosion pits was investigated by evaluating the effects of two variables on the fatigue life of dog-bone specimens of aluminum alloy 7075-T6. The specimens were exposed to different levels of corrosion in an acidified saline solution of 3.5% NaCl. In addition, the specimens were exposed to concomitant fatigue and corrosion until failure by fracture occurred. SEM analysis indicated that fatigue cracks formed/nucleated from each pit, and subsurface mechanisms of degradation were identified associated with the pitting nucleation sites including subsurface pitting, cracking, tunneling and intergranular attack.

Failure data were analyzed by ANOVA methods and three transformations were evaluated to minimize the variance, including natural log, inverse square root and power with a lambda of 1/3. These transformations were selected after evaluation of several Box-Cox transformations and these resulted in the best combination of F-values and p-values. Contour and surface plots were developed to show how these variables impact the response of cycles to failure for the conditions evaluated. Results indicate that p-values (called the significance level) for these models are statistically significant. The

effect of stress is more detrimental than corrosion time on the fatigue life of the specimens for the values previously defined by the matrix.

Introduction

Many industries rely on the reliability of their structures to provide safe and high quality products that will not undergo premature development of degradation that may cause an excessive maintenance burden or fail prematurely and cause loss of equipment and injury or death to users. The aircraft industry in particular faces many challenges as their aircraft age in both the commercial and military fleets. It is well known that aircraft structures deteriorate over time due to both mechanical and chemical degradation. Some of these mechanisms are designed for and some are not in the current state of the art. Mechanisms that are well known to accelerate structural damage of airframes include fatigue, fretting, corrosion, and a combination of these such as corrosion fatigue. These mechanisms can lower the overall structural integrity and reduce the reliability and expected life, especially with aircraft intended to stay in service for long periods of time [1]. The adverse effects of corrosion on structural integrity of aircraft have been a concern for some time [2-38].

Multiple failure investigations have been documented where corrosion pitting was found to affect the reliability, maintainability, and safety (RMS) of aircraft (1, 2). Incidents and accidents of aircraft and helicopters were caused by pitting corrosion, where an incident is any damage to the aircraft and/or injuries to passengers and crew, and an accident is loss of the aircraft and/or fatal injuries to passengers and crew. It is essential to recognize the RMS deficiencies that may arise before accidents occur.

Although the aircraft industry focuses its attention to safety concerns, for many years it has limited corrosion to maintenance, economic, and inspection issues. While the industry has developed some corrosion prevention and control programs (CPCP) , much more could be done to quantitatively evaluate the effects of corrosion on structural integrity in the design process itself and the FAA, USN, USA, USCG, and USAF are now mandating much more be done to consider corrosion effects on structural integrity. Corrosion has become such a concern to the US DOD that it has recently established a corrosion office at the Pentagon [40].

Structures that are continuously exposed to fluctuating forces/loads and deleterious chemical environments are at risk of premature failure imposing excessive maintenance burdens and potential catastrophe on the aircraft and passengers including the crews. Structural damage can be introduced by nucleation mechanisms such as corrosion pitting, which act as stress raisers and nucleation sites for premature cracking in the critical structure. A major issue that is concomitant with the occurrence is the potential for changing the site of criticality of the cracking sites and structurally significant items (SSI). Often the SSI are selected based on maximum stress or strain values or in locations where cracks have been observed previously. However, once pitting has been introduced by the chemical environment acting synergistically with applied forces/loads, a combination of metallurgical, electrochemical, mechanical, environmental and even human factors can combine to accelerate structure failure by the mechanism of pitting corrosion fatigue. The number of factors involved in the corrosion fatigue process are numerous, making the prediction of failure a complex challenge but one that can be resolved when enough knowledge is gained from appropriate research on the subject. The complexity of the pitting corrosion fatigue process makes it essential for DOE techniques to be used to study it more appropriately. Due to the nature of the corrosion and fatigue processes, it is necessary to analyze these issues using statistical approaches similar to those presented herein.

In previous studies Harlow and Wei at Lehigh University developed probability models for corrosion fatigue of aluminum and steel alloys and these models have provided important insight and background for these types of studies. They indicated that prognosis and life assessment are highly dependent on probabilistic models which include material microstructural properties. They emphasized that the methodology proposed is highly dependent on accurately estimating the statistical characteristics of the materials properties [41].

Cavanaugh et al. also studied the effects of environmental factors to develop models using artificial neural network approaches (ANN). Variables included during these studies included temperature, pH, [Cl-], exposure time and orientation. The effects of these variables in affecting maximum pit depth and maximum pit diameter for high strength aluminum alloy 7075-T651 were studied and reported. It was found that exposure time and pH, followed by temperature were the most significant variables impacting pit depth. A power “law” relationship successfully modeled the effect of environment on the maximum pit depth [42].

Jones and Hoeppner studied the pit to crack transition in pre-corroded 7075-T6 aluminum alloys under cyclic loading in recent years as part of an extensive program at U of U that continued work originally started at Lockheed Aircraft Corp. in 1969. The background on all of these studies is provided in the reference (43). During this study pits were identified as crack origins in all corroded specimens. However, it was not always the largest pit that formed/nucleated fatigue cracks. The combined effects of pit depth, pit surface area, and proximity to other pits were found to substantially reduce fatigue life [43].

Wei et al. also studied the transition from pitting to fatigue cracks for 2024-T3 aluminum alloys. They observed from fractographic examinations that pitting was responsible for the nucleation of corrosion fatigue cracks. They showed that pit size and stress intensity factor was independent at high frequency (f> 5 Hz), but increased with decreasing frequency at f < 5 Hz [44].

According to Birbilis and Buchheit, high strength aluminum alloys contain heterogeneous microstructures which contain second phase (intermetallic) particles. Such particles have electrochemical characteristics that differ from the matrix, rendering the alloy susceptible to localized corrosion. They observed the following types of pits: circumferential and selective dissolution of the constituent particle. They found a large number of intermetallics showed electrochemical activity. Noble particles, e.g., Al_2Cu, with high electrochemical activity have the ability to sustain large cathodic current. Active particles with high self dissolution rates, e.g., $MgZn_2$, have the ability to undergo anodic dissolution at high rates [45]. These authors also showed in another study that evidence of anodic dissolution within peripheral pits in aluminum alloys, is provided by hydrogen bubble evolution, which suggests that overall alloy corrosion proceeds almost self-catalytically. They observed that electrochemical response of intermetallic particles is highly dependent on the pH of the environment, and they also indicted that intermetallics containing Fe are highly susceptible to corrosion [46].

The purpose of the research reported herein was to understand the factors that are involved in the corrosion fatigue of high strength aluminum alloys. Once such variables are understood and defined, it is necessary to develop models to predict with confidence, the life of the structure subjected to such factors. This study concentrates on two variables: stress and corrosion time. A full factorial design is used to setup a testing protocol. A 3.5% NaCl solution acidified with 1 molar HCl was used for the experiments.

Dog-bone specimens were designed to provide a constant stress concentration in the test section area, and to allow for a desired corrosion area as well. Specimens were pre-exposed to the solution and then simultaneously corroded with fatigue loading applied until failure occurred through the critical test section. Analysis of variance was performed to evaluate the effects of stress and corrosion time in the life of the specimens. Box-Cox transformations were used, which stabilized the variance. Models were developed that predict with statistical confidence, the time of failure of the specimens exposed at the predefined conditions.

Fractography revealed formation/nucleation of cracks from the induced pits. Tunneling was observed as a manner by which propagation of these evolving discontinuity states evolved during the experiments. SEM (Scanning Electron Microscopy) evaluation subsequent to the failures suggests that pits propagated by intergranular attack in most cases. Subsurface pitting and cracking also were observed by SEM analysis. Finally, hydrogen damage is evident in the surface of specimens that were exposed to the stagnant corrosive solution for longer periods of time but in order to assure this observation additional studies are needed beyond this work.

The purpose of the research reported herein is to examine and characterize the effects of concomitant fluctuating stresses and an acidic saline environment on the residual life of aluminum alloy 7075-T6. Several hypotheses were tested to establish a correlation between these variables and their effect on the fatigue life of the specimens:

Hypothesis I. Aluminum alloy 7075-T6 will dissolve by pitting when exposed to an acidified saline environment. Furthermore, cracks will nucleate from pits and propagate until failure by fracture is reached.

Hypothesis II. Stress magnitude will have a greater deleterious impact as compared with corrosion exposure time on the fatigue life of the specimens.

Hypothesis III. Statistical models will predict with confidence the life of specimens exposed to stress and an acidified saline environment with limits defined by a DOE matrix.

Research focusing on statistical modeling, such as reported herein, undoubtedly will increase the understanding of an aircraft structure through the phases of life and will assist in diminishing the effects of corrosion fatigue on structural integrity. Thus, it is envisioned that this work is one of the steps needed to continue to make aircraft structures safer relative to the potential degradation from corrosion fatigue. Aspects of this work already are being applied through the HOLSIP activities of numerous agencies (see www.holsip.com). Table 4.1 summarizes some examples that clearly show that degradation originated by corrosion fatigue is a significant issue in the assurance of structural integrity of aircraft [39].

Table 4.1: Aircraft Accidents Related to CF (with permission from D.W. Hoeppner).

Aircraft	**Location of Failure**	**Cause**	**Incident Severity**	**Place**	**Year**	**From**
Bell Helicopter	Fuselage, longeron	Fatigue, corrosion pitting	Serious	AR	1997	NTSB
DC-6	Engine, master connecting rod	Corrosion pitting	Fatal	AK	1996	NTSB
Piper PA-23	Engine, cylinder	Corrosion pitting	Fatal	AL	1996	NTSB
Boeing 75	Rudder control	Corrosion pitting	Substantial damage to plane	WI	1996	NTSB
Embraer 120	Propeller blade	Corrosion pitting	Fatal and loss of plane	GA	1995	NTSB
Gulfstream GA-681	Hydraulic line	Corrosion pitting	Loss of plane, no injuries	AZ	1994	NTSB
L-1011	Engine, compressor, assembly disk	Corrosion pitting	Loss of plane, no injuries	AK	1994	NTSB
Embraer 120	Propeller blade	Corrosion pitting	Damage to plane, no injuries	Canada	1994	NTSB
Embraer 120	Propeller blade	Corrosion pitting	Damage to plane, no injuries	Brazil	1994	NTSB
Mooney 20	Engine, interior	Corrosion pitting	Minor injuries	TX	1993	NTSB
C-130	Bulkhead 'Porkchop' Fitting	Fatigue, corrosion pitting	Pressurization leaks	-	1995	LMAS
C-141	FS998 Main Frame	Corrosion pitting, stress corrosion cracking	Found crack during inspection	-	1991	LMAS

Methodology

The material used for this study was aluminum alloy 7075-T6. This alloy is utilized in aircraft applications including body panels and various skin panels. The major alloying elements added are zinc, magnesium and copper. T6 tempering condition implies solution heat treating and then artificial aging to stabilize it. Table 4.2 summarizes the tensile strength and other relevant properties.

Aluminum attains high resistance to corrosion in many environments because of rapid formation of a thin and tenacious oxide film over the surface that limits further corrosion. Aluminum is an amphoteric metal for which the protective oxide film dissolves at low and high ph. Thus, a Pourbaix diagram shows that the aluminum ion, Al^{3+}, is stable at low pH; the aluminate ion, AlO_2^- , at high pH; and the oxide, Al_2O_3, at intermediate pH. At low nonoxidizing potentials, the metal itself, Al, is stable and immune to corrosion. Although corrosion rates are not derived from the diagram, it is relatively low for aluminum due to kinetic limitations, despite the large driving force for the oxidation-reduction reactions.

Table 4.2: Tensile Properties for AA 7075-T6 at 25^{o}C [47].

Tensile Strength	Yield Strength	Elongation	Modulus of Elasticity
MPa	MPa	%	10^3 MPa
538	469	12	71

Chemical composition: 1.2 to 2.0 Cu, 2.1 to 2.9 Mg, 0.3 Mn, 0.40 Si, 0.50 Fe, 0.18 to 0.28 Cr, 5.1 to 6.1 Zn, 0.20 Ti, 0.05 other (each), 0.15 other (total), bal Al.

A Pourbaix diagram for aluminum can be used to make preliminary predictions of the corrosion as a function of electrode potential and pH. Predictions are very general, and the method has been criticized in leading to incorrect conclusions because the diagram does not recognize the controlling factors of rate of corrosion and nonequilibrium.

In this research, center-pin-loaded dogbone specimens were designed and machined from 7075-T6 aluminum alloy sheet of thickness 1.600 mm (0.063 in.). The impact of different levels of stress magnitude and exposure time to the corrosive solution, into the fatigue life of aluminum alloy 7075-T6 specimens, was evaluated. Basis for the corrosion fatigue protocol were taken from previous studies performed at the University of Utah's Structural Integrity Laboratory. Variables taken from these studies include solution concentration 3.5% NaCl, solution flow rate, frequency, etc. In addition, ASTM standards were reviewed and adapted to the protocol, with some modifications. Some of these modifications included the acidification of the solution to a pH of 3.

Specimen preparation involved polishing the side of interest to a 0.3 μm finish. The final surface appearance was mirror-like, which was assumed free of imperfections. This was verified by use of metallurgical microscope to look for any pits prior to corrosion. After polishing, specimens were cleaned with acetone in an ultrasonic bath for 5 minutes. Specimens were weighed in an analytical high precision balance and stored in a vacuum desiccator.

Two levels of prior-corrosion time were evaluated, 24 and 48 hours. A 3.5% NaCl solution was prepared which was acidified to a pH of three, by addition of 1M HCl. This concentration was chosen to simulate the salinity of sea water, and the pH was chosen based on electrochemical principles which indicate that aluminum is prone to corrode at these conditions. The corrosion area was set to 3 mm by 10 mm. Pits were characterized with a metallurgical microscope that allowed measuring "apparent" pit depth, as a function of time. Specimens were exposed simultaneously to the saline acidic environment and cyclic loading, with an environmental chamber and a servo-hydraulic MTS equipment. Prior to exposure, the solution was aerated for 1 hour, since addition of oxygen accelerates cathodic dissolution of aluminum. The flow rate of the solution was approximately 1 ml/min. Fatigue experiments were performed utilizing an electro-hydraulic, servo-controlled MTS 14.7 kN capacity load frame. The loading was controlled by an MTS TestStar system. Two levels of stress were used, σ_{max} = 120.6 MPa and σ_{max} = 241.3 MPa. Stress ratio was R = +0.1. The waveform was sinusoidal. The frequency was 10 Hz, with reduction to 0.5 Hz during inspection intervals for ease of observation. The inspection system was setup to record every 3,985 cycles, where the frequency was reduced to 0.5 Hz, for 15 cycles.

Specimens were exposed to corrosion-fatigue conditions until fracture, and then were cleaned with HNO_3 and acetone ultrasonic bath. Pitting characterization was done using a Scanning Electron Microscope provided by FASIDE International Inc. The randomized experiments are shown in Table 4.3.

Results

Pitting corrosion

It is well known that pitting of aluminum alloys in chloride-containing solutions produces the formation of acid within the pits that may form. The passivating film of Al_2O_3 surrounding the pit acts as the cathode, but its effectiveness in reducing dissolved

Table 4.3: DOE Matrix for Corrosion Fatigue Experiments.

Standard Order	Run Order	Blocks	Prior Corrosion Time (hr)	Stress (MPa)
3	1	Block 1	48	121
5	2	Block 1	24	241
1	3	Block 1	24	121
7	4	Block 1	48	241
4	5	Block 2	48	121
8	6	Block 2	48	241
2	7	Block 2	24	121
6	8	Block 2	24	241

oxygen is significantly enhanced if copper is either deposited on the surface or enters the lattice of the Al_2O_3, and pitting of aluminum occurs rapidly when the water contains copper ions. Similar considerations apply to phases such as $FeAl_3$ and $CuAl_2$, which can increase the kinetics of oxygen reduction. The microstructure of metals and alloys is made up of grains, separated by grain boundaries. Intergranular corrosion is a localized attack along the grain boundaries, or immediately adjacent to grain boundaries, while the bulk remains unaffected. This form of corrosion is associated with chemical segregation effects, where impurities have a tendency to be enriched at grain boundaries, or specific phases precipitated on the grain boundaries. Such precipitation can produce zones of reduced corrosion resistance in the immediate vicinity.

In the case of aluminum alloys exposed to NaCl solutions, chloride ions attack the imperfections of the oxide film and aluminum starts to dissolve into the solution. Inside the resultant pit an acidic condition occurs and hydrogen is evolved. Attack then propagates through the grains, and is accelerated by additional cathodic reactions by oxygen or other alloying metals.

In this study, specimens were exposed to a 3.5% NaCl solution acidified with 1M HCl to a pH of three. Such environment was chosen to simulate acidic and sea water conditions as a corrosive electrolyte although the properties of seas water as a corrosive medium are primarily determined by its salt content. Table 4.4 summarizes some of the salt concentrations contained in several oceans. The most typical compositions of salt residues in seawater include NaCl, 77.8%; MgCl2, 10.9%; MgSO4, 4.7%; CuSO4, 3.6%; and K2SO4, 2.5% [48].

After several pilot tests, specimens were pre-exposed to an acidified saline solution environment for 24 hours, and 48 hours. Blocking is the arranging of experimental units in groups (blocks) that are similar to one another. Two blocks were used, the first one with a solution that was agitated while the second was a stagnant solution. Specimens with agitation of solution have higher average pit depths compared with those exposed to a stagnant solution, by a factor of two. Agitation of the solution increases the removal of aluminum from the pits, and prevents the accumulation of corrosion products at the pit mouth, which could potentially act as a block for direct attack of chloride anions to the pit. Intergranular attack is evident at conditions were solution was agitated.

Table 4.4: Salinity of Sea Water for Several Oceans.

Ocean	**Salt Concentration (% NaCl)**
Atlantic Ocean	3.54%
Pacific Ocean	3.49%
Mediterranean Sea	3.7-3.9%
Red Sea	Up to 4.1%

Fig. 4.1 shows a specimen that exhibited corrosion damage by pitting, and intergranular attack. Specimens exposed to stagnant solution show additional damage, which is caused by the hydrogen evolved by the reaction of aluminum and the acidified saline solution. Hydrogen evolving from the aluminum reaction accumulated at the surface. As the accumulation of hydrogen increased, aluminum was dissolved leaving "rings" impressed at the surface. Such rings measured approximately 4 μm in depth. Additional mechanisms observed included pitting, and intergranular attack.

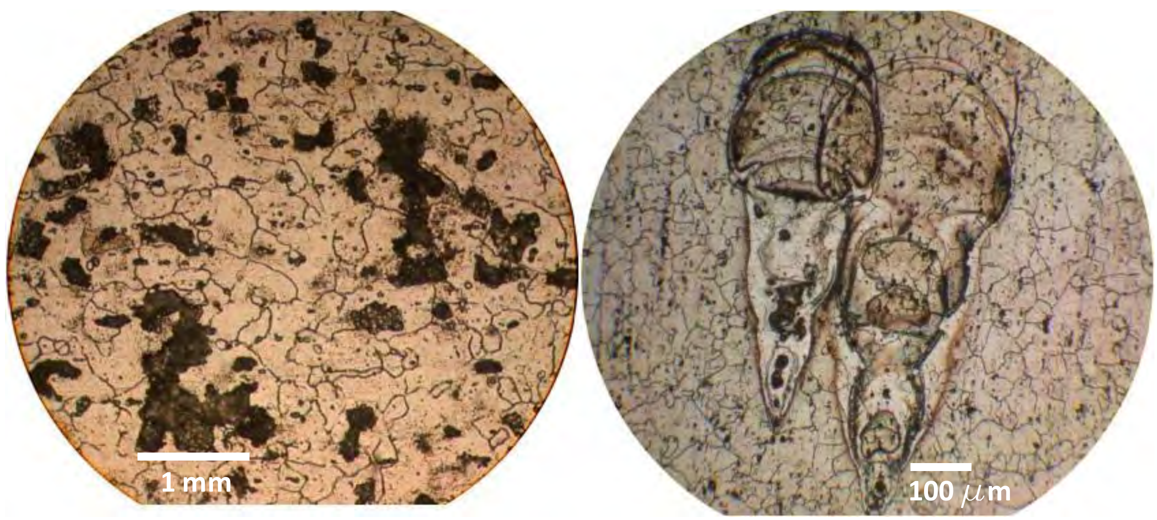


Fig. 4.1: Specimens after 48 hr. exposure, with agitation (left), pitting and IGA are evident; without agitation where hydrogen damage is shown (right).

Fractography

Specimens were analyzed with a scanning electron microscope to identify the origins of failure. For instance, one of the specimens (number CA4) was pre-exposed to the stagnant acidified saline solution for 48 hours, and subsequently exposed to simultaneous corrosion and fatigue at 241 MPa. Fracture occurred after 38,461 cycles due to a crack that originated from a pit, which also presented tunneling. Fig. 4.2 shows an overview of the fracture surface. Multiple pits were found in the fracture surface that extended by subsurface mechanisms including tunneling and subsurface pitting and intergranular attack. Fig. 4.3 shows evidence of these mechanisms.

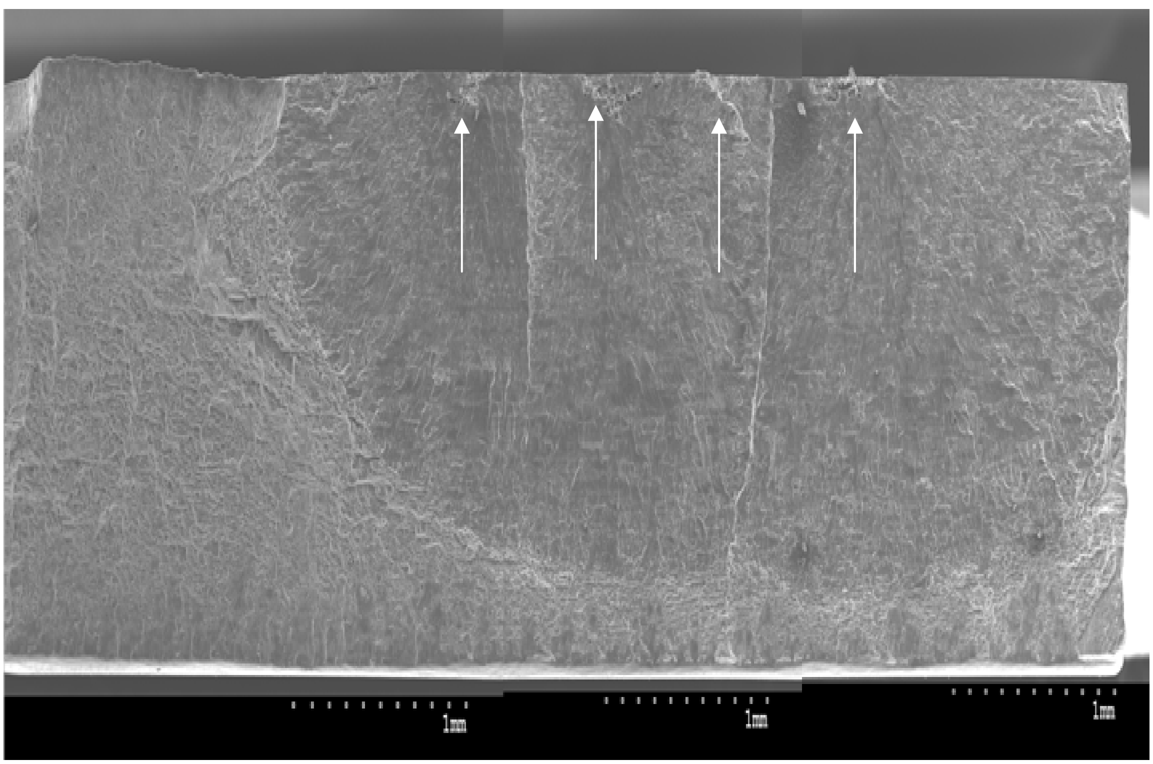


Fig. 4.2: Specimen CA4 Fracture Surface Overview.
Pits are shown in the exposed surface to the acidified corrosive solution.
Arrows indicate location of several pits at the fracture surface.

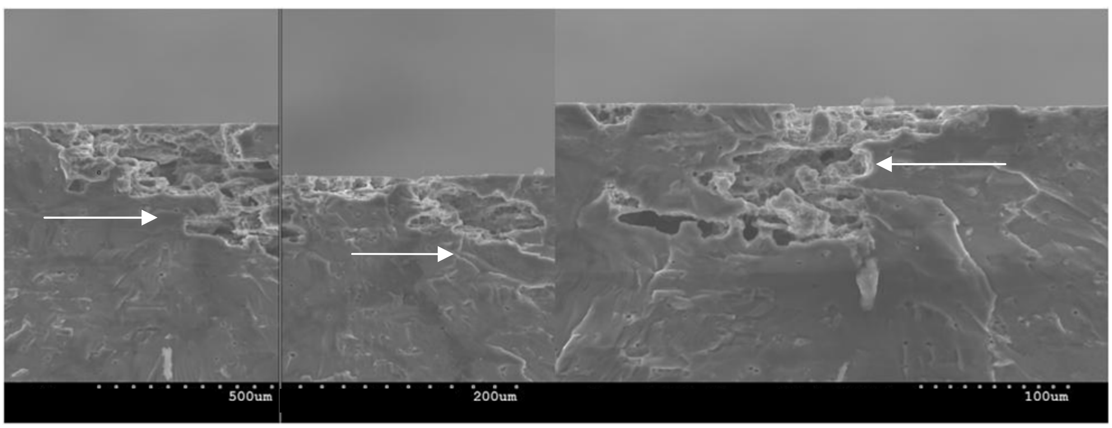


Fig. 4.3: SEM micrographs for Specimen CA4 Showing Tunneling and Subsurface Pitting. Arrows indicate direction of subsurface pit growth by tunneling.

Another set of specimens was pre-exposed to the acidified saline solution for 24 hours without agitation, and then corrosion fatigue at 121 MPa. Specimen CA9 fractured after 1,264,086 cycles due to a crack that originated from a pit. Figs. 4.4-4.6, show severe pitting damage, including sub-surface pitting, tunneling and intergranular attack. The severe detrimental impact that the corrosive solution caused in the structural integrity of the specimens is evident from these micrographs.

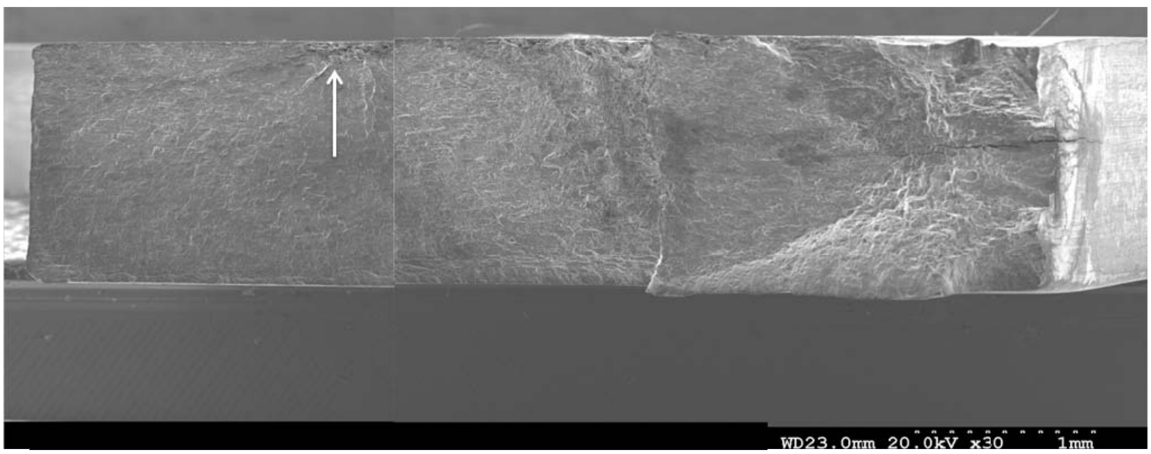


Fig. 4.4: Specimen CA9 Fracture Surface Overview.
Arrow indicates location of critical pit.

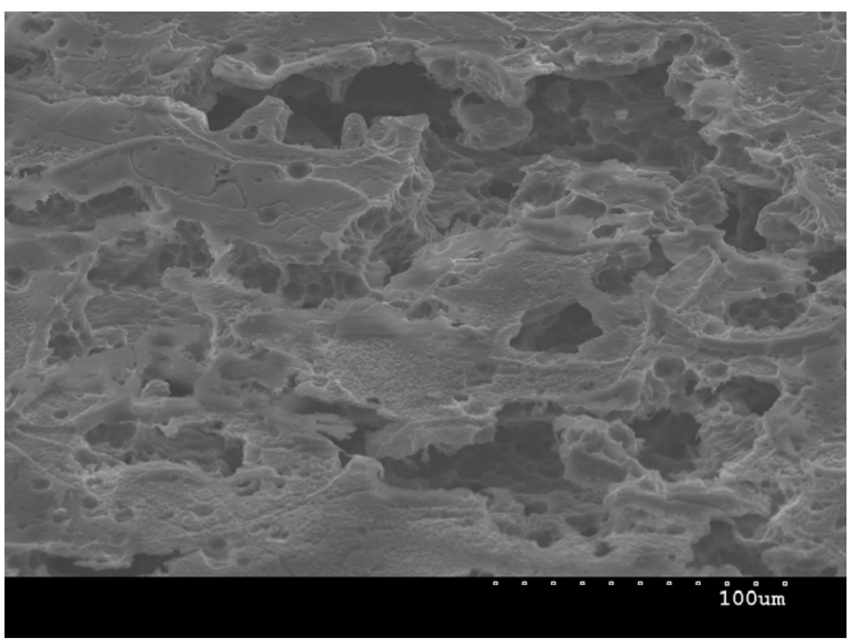


Fig. 4.5: Severe Pitting Damage caused by the acidified saline solution.

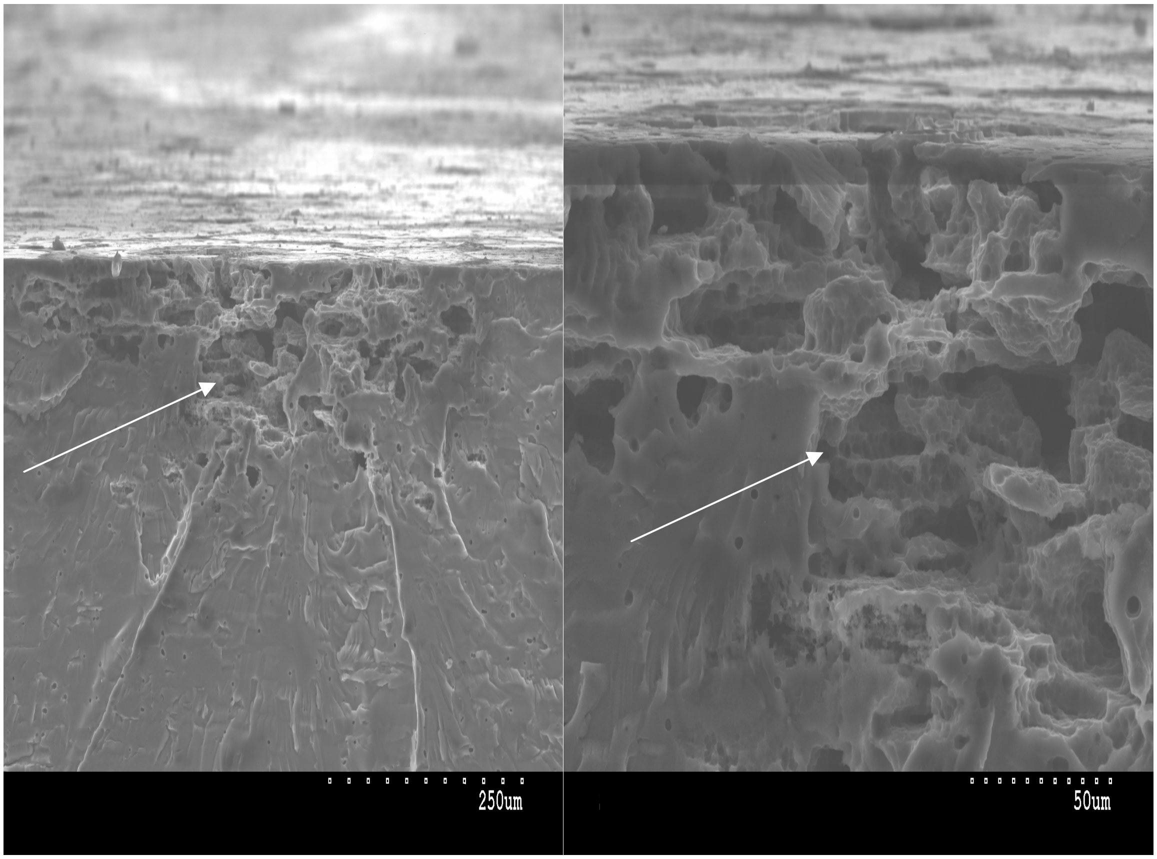


Fig. 4.6: Subsurface Damage on CA9, showing Subsurface Pitting and Severe Tunneling. Arrows indicate pit growth by tunneling.

SEM micrographs for specimen CA5 are shown in Figs. 4.7 and 4.8. This specimen was pre-exposed to the solution for 24 hours with agitation, and then simultaneously exposed to the corrosive solution and cyclic load at 121 MPa. Fracture occurred after 1,026,642 cycles due to a crack that originated from a pit. Fig. 4.7 shows an overview of the fracture surface. Fig. 4.8 shows evidence of pitting, subsurface pitting and subsurface cracking. Subsurface damage was captured by the SEM analysis; however the magnitude of such mechanisms would be difficult to detect by conventional inspection methods used on aircraft with the current state of the art.

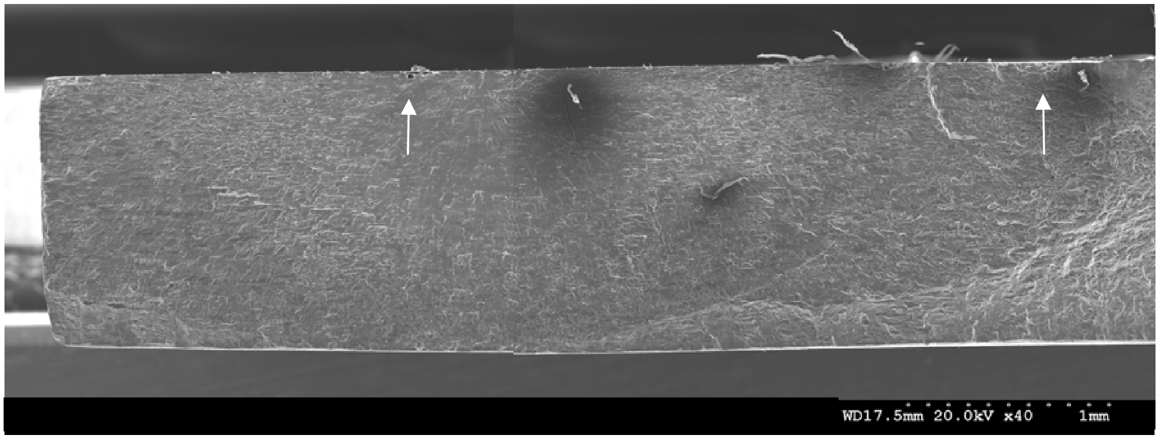


Fig. 4.7: Specimen CA5 Fracture Surface Overview, showing pits at the surface. Arrows show location of pits.

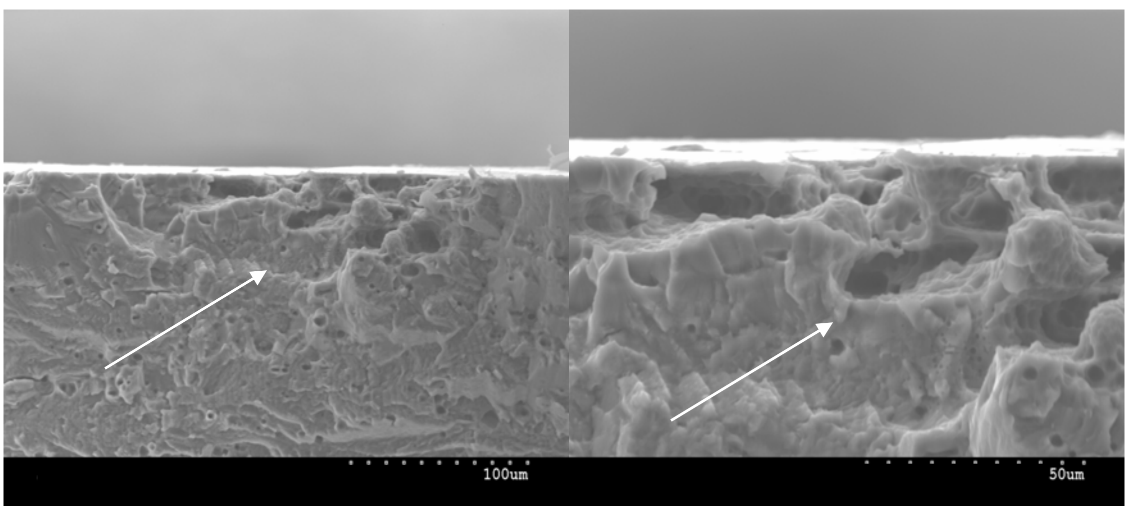


Fig. 4.8: Specimen CA5 Pitting, Tunneling and Subsurface Cracking. Arrows show pit growth by tunneling.

ANOVA –Box-Cox Transformations

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response. Analysis of Variance (ANOVA) is a statistical method that can be used to evaluate the effect(s) of several variables into a response(s). ANOVAs are also useful in comparing the means of several groups. For the purpose of this study a 2^2 factorial design was used with two variables: the effect of corrosion time, and stress magnitude. The two levels of interest for corrosion time are 24 and 48 hours, and for stress magnitude 121 MPa and 241 MPa. The experiment was replicated two times, with two blocks. The data are summarized in Table 4.5.

Several Box-Cox transformations were investigated to develop a statistically significant corrosion fatigue model. Generally, transformations are used for stabilizing response variance, making the distribution of the response variable closer to the normal distribution, and thus improving the fit of the data.

Table 4.5: Results of Corrosion Fatigue Experiments.

Factor Cor Time (hr)	Stress (MPa)	Cycles to Failure Replicate I	II	Average
24	121	1,026,642	1,264,086	1,145,364
48	121	884,865	1,041,949	963,407
24	241	64,281	57,486	60,884
48	241	38,461	41,507	39,984

Natural Log Transformation

Analysis of variance (ANOVA) was performed to evaluate the effects of the variables, corrosion time and stress magnitude, in the response (cycles to failure). Using a natural log transformation, the model F-value is 628, with corresponding 0.01% p-value (significance level), therefore there is only a 0.01% chance that the model F value could occur due to noise. The analysis indicates that factors A, B and the model are statistically significant. Fig. 4.9 shows a graphic representation of the corrosion fatigue model. A natural log transformation fits the data with statistical confidence.

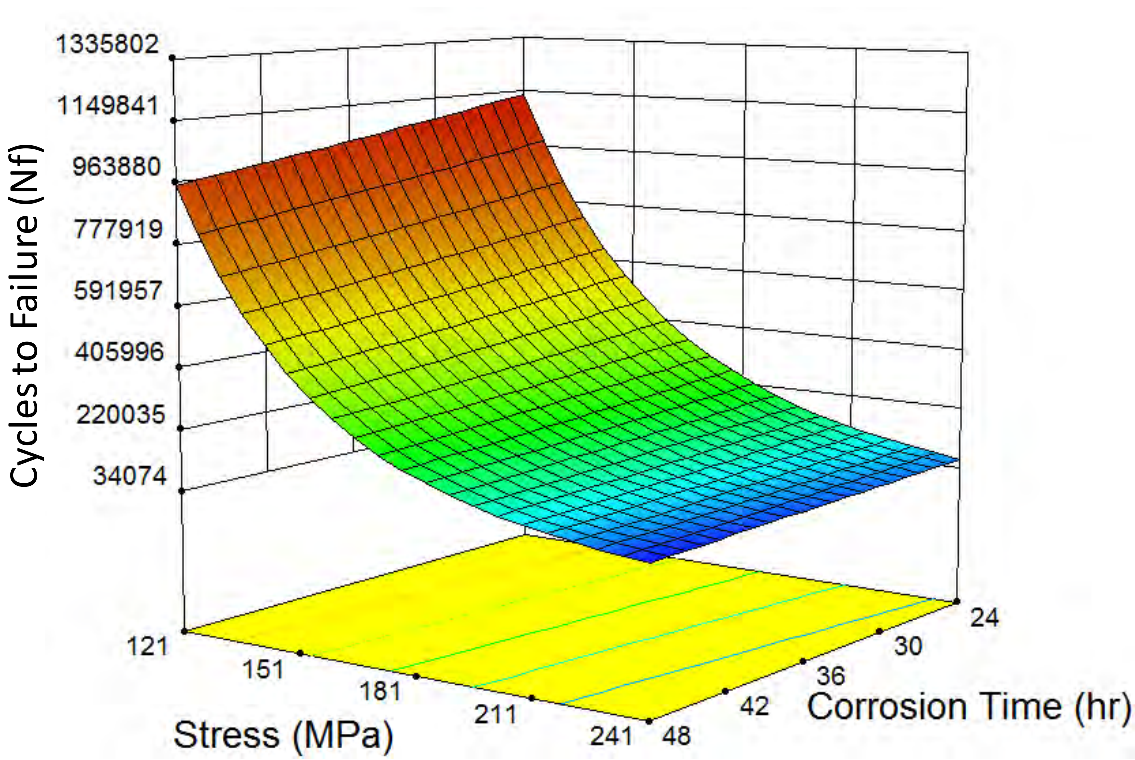


Fig. 4.9: Cycles to Failure for CF 7075-T6, with a Natural Log Transformation

Inverse Square Root Transformation

An inverse square root transformation of cycles to failure (N_f) has the following form

$$\frac{1}{\sqrt{Nf}} = f\,(\text{CorTime}, \text{Stress}) \tag{1}$$

where Nf is cycles to failure, and CorTime is the pre-corrosion time. A contour plot and a surface plot are shown in Figs. 4.10 and 4.11. Analysis of variance yields a model F value of 528, with a p-value (significance level) of 0.01%, which implies the model is statistical significant.

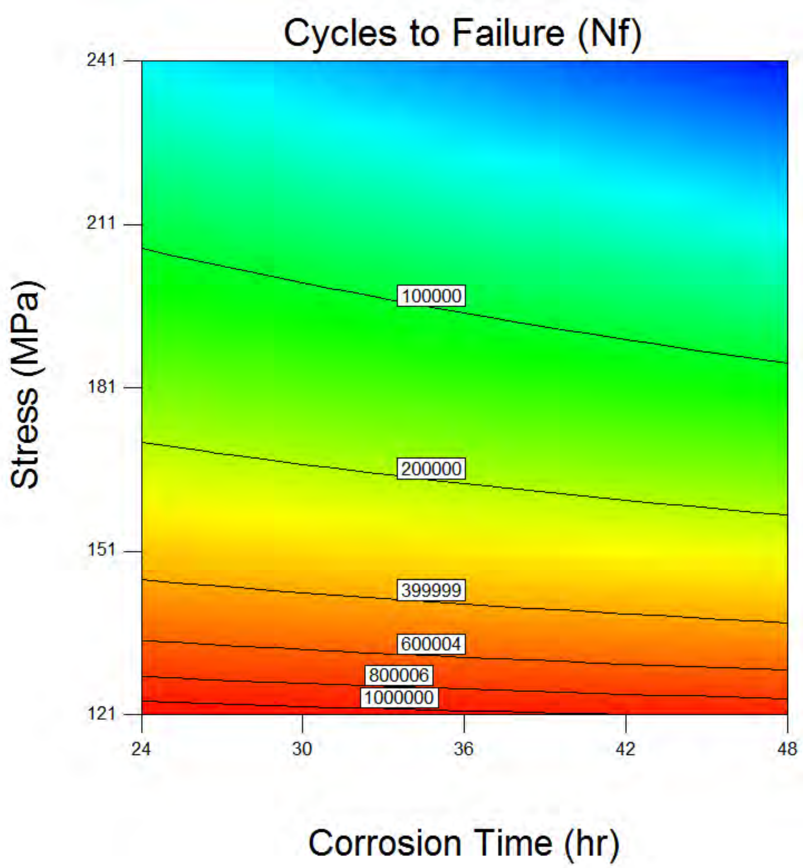
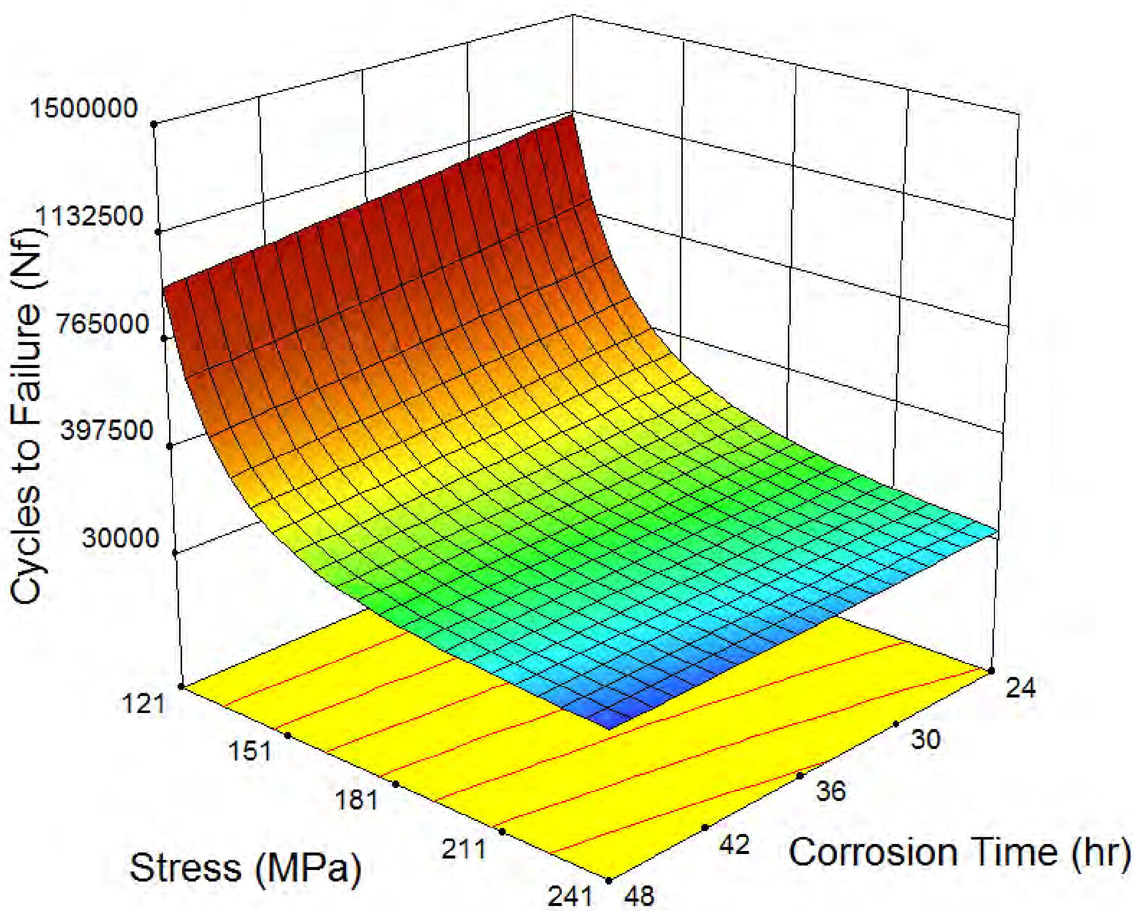


Fig. 4.10: Contour Plot for Inverse Square Root Transformation.



Figs. 4.11: Surface Plot for Inverse Square Root Transformation.

Power Transformation

A Box-Cox power transformation with a lambda value of 1/3 was used to minimize the variance as follows

$$Nf^{\frac{1}{3}} = f(\text{CorTime}, \text{Stress}) \tag{2}$$

The corresponding contour and surface plots are shown in Fig. 4.12 and 4.13.

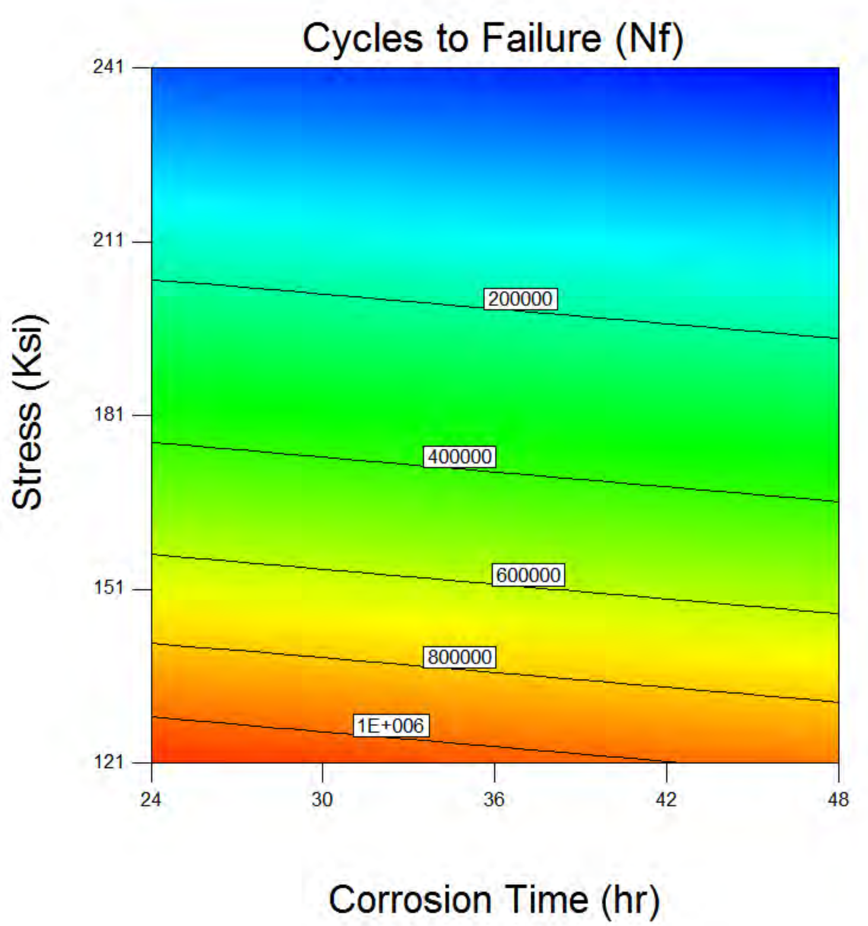
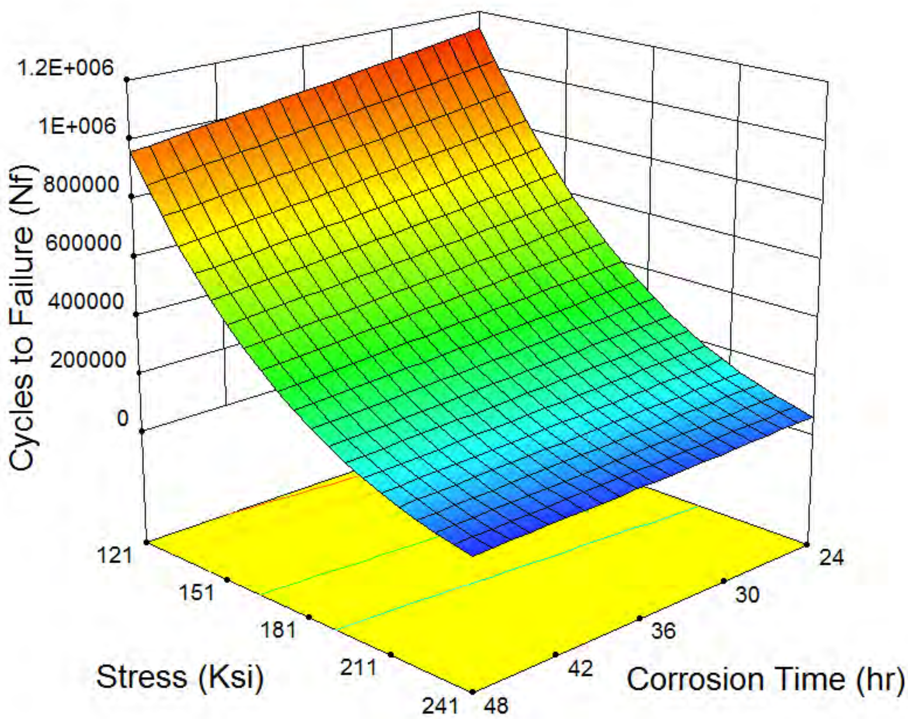


Fig. 4.12: Contour Plot for Power Transformation.



Figs. 4.13: Contour and Surface Plot for Power Transformation

The model F-value of 754 implies the model is significant. There is only a 0.01% chance that this model could occur due to noise. In this model no interaction between corrosion time and stress was considered, since the p-value was higher than the 5% expected.

Discussion

In this study, the process of pitting induced crack formation/nucleation for 7075-T6 aluminum alloy cyclically stressed in an acidified 3.5% NaCl solution is quantitatively demonstrated by varying the corrosion time and the stress. Fractured specimens were analyzed by scanning electron microscopy postfracture, and it was found that cracks nucleated from each of the pits analyzed. In addition, subsurface damage also was observed, including tunneling, subsurface cracking, and subsurface pitting. Design of experiments (DOE) was used to setup the protocol for testing. Two variables were evaluated, corrosion time and stress. The response evaluated was the effect of these variables on the cycles to failure. Data were analyzed by ANOVA methods, and Box-Cox transformations were evaluated to minimize the variance. Three transformations were evaluated in this study, natural log, inverse square root and power function with a lamba of 1/3. Such transformations fit the data with statistical confidence, however, as shown in Table 4.6, the transformation that yields the best statistical significant model is the inverse square root. This can be shown by the higher p-values (significance level) obtained in the other two models. For natural log a value of 17% was obtained for the interaction between the two variables. For power with lambda of 1/3, there is a 3% p-value for the corrosion variable, which is not unacceptable, however is higher than the inverse square root model.

Table 4.6: Analysis of Variance

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob >F		
Block	2.63×10^{-9}	1	2.63×10^{-9}			Std. Dev.	1.28×10^{-4}
Model	2.61×10^{-5}	3	8.71×10^{-6}	528.1	0.0001	Mean	2.76×10^{-3}
A-CorTime	5.30×10^{-7}	1	5.3×10^{-7}	32.1	0.0109	C.V.	4.66
B-stress	2.52×10^{-5}	1	2.52×10^{-5}	1529.7	< 0.0001	R-Squared	0.998
AB	3.72×10^{-7}	1	3.72×10^{-7}	22.6	0.0177		
Residual	4.95×10^{-8}	3	1.65×10^{-8}				
Cor Total	2.62×10^{-5}	7					

Response Nf
Transform: Inverse Square Root

The proposed model is given by

$$\frac{1}{\sqrt{Nf}} = a + b \cdot \tau_c + c \cdot \sigma + d \cdot \tau_c \cdot \sigma \qquad (3)$$

where Nf represents the cycles to failure, τ_c is the corrosion time and σ is the stress. Coefficients a, b, c and d are material dependent.

From the previous analysis is evident from the contour and surface plots that the prediction of cycles to failure is dependent upon the model utilized. Both the Natural Log and inverse square root transformations have different surface curves compared with the power transformation. This may represent more aggressive or conservative predictions depending on the model chosen.

Conclusions

In this study, specimens of aluminum alloy 7075-T6 were pre-exposed to an acidified saline solution. Pits nucleated by the acidified saline solution, and cracks originated from each of the pits for all specimens. Such cracks propagated until failure was reached by fracture. SEM analysis revealed additional mechanisms including subsurface pitting, subsurface cracking, tunneling and intergranular attack.

The protocol for testing was based on full factorial design with two variables and two blocks. The variables studied were corrosion time and stress, and the response was cycles to failure. ANOVA was used to develop models by using transformations to stabilize the variance. Three Box-Cox transformations were chosen, natural log, inverse square root, and power with lambda of 1/3. Analysis revealed that these models fit the data with statistical confidence; however the square root transformation had the lowest p-values for corrosion time, stress and the interaction between these two factors. Such p-values (significance level) are below the risk value of 5%. The proposed correlation has a CV of 4.66 with an R-squared of 0.998. Finally, such analysis suggests that stress has a higher detrimental impact in the fatigue life of the specimens as compared with corrosion time.

The last two chapters have established the foundation for a robust testing methodology which, if applied effectively, may result in statistical significant models. Two manuscripts have been submitted for publication, one has been accepted by **Corrosion - The Journal of Science and Engineering, by NACE**, and the other was submitted at **Corrosion Science**. The next chapter expands the study to another common aircraft material AA20224-T3. The same methodology is applied but stresses are used to simulate a current world's aircraft application such as the F-16. In addition, to increase statistical significance replicate experiments are increased as well.

Acknowledgements

The authors wish to acknowledge FASIDE International Inc. for their financial support and use of FASIDE facilities and the University of Utah for the use of their facilities. Sincere thanks are offered to Ms. Amy Hoeppner Taylor and Mr. Larry Smiltneek for their assistance related to fatigue test setup, calibration, and to fractographic examination of the specimens post fracture.

References

[1] W. Wallace, D.W. Hoeppner, Advisory Group for Aerospace Research and Development (AGARD) Corrosion Handbook. Vol. 1. Aircraft Corrosion: Causes and Case Histories. 1985.

[2] Corrosion Fatigue and Environmental Assisted Cracking in Aging Military Vehicles. North Atlantic Treaty Organization (NATO) March 2011.

[3] K. Jones, S.R. Shinde, P.N. Clark, D.W. Hoeppner, Effect of prior corrosion on short crack behavior in 2024-T3 aluminum alloy, Corrosion Science 50 (2008) 2588-2595.

[4] Editors: R.W. Staehle, A.J. Forty, D. van Rooyen .Fundamental Aspects of Stress Corrosion Cracking, Proceedings of a conference held at the Ohio State University, 11-15Sept. 1967, NACE-1, National Association of Corrosion Engineers, Houston, TX, 1969.

[5] Editors: M. Rosenfeld, D.W. Hoeppner, and R.I. Stephens, Effects of Environment and Complex Load History on Fatigue Life, ASTM STP 462, Proceedings of the Symposium on Effects of Environment and Complex Load History on Fatigue Life held in Atlanta, GA, 29Sept. -4Oct., 1968, ASTM, Philadelphia, PA., 1970.

[6] Editors: O. Devereux, A.J. McEvily, R.W. Staehle. Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, Proceedings of the Conference held at the University of Connecticut, 14-18 June1971, NACE-2, National Association of Corrosion Engineers, Houston, TX, 1973.

[7] Brown, B.F., Stress-Corrosion Cracking in High Strength Steels and in Titanium and Aluminum Alloys, Naval Research Laboratory, Washington, D.C., 1972.

[8] L.R. Hall, R.W. Finger, W.F. Spurr, “Corrosion Fatigue Crack Growth in Aircraft Structural Materials”, AFML-TR-73-204, Boeing Company, September, 1973.

[9] D. Pettit, J. Ryder, W. Krupp, D.W. Hoeppner. “Investigation of the Effects of Stress and Chemical Environments on the Prediction of Fracture in Aircraft Structural Materials”, AFML-TR-74-183, Lockheed California Company, December, 1974.

[10] Editors: H.L. Craig, T.W. Crooker, and D.W. Hoeppner. Corrosion-Fatigue Technology, ASTM STP 642, Proceedings of a Symposium held in Denver, CO, 14-19 Nov.1976, ASTM, Philadelphia, PA, 1978.

[11] Aircraft Corrosion, AGARD Conference Proceedings No. 315, Papers presented at the 52nd Meeting of the AGARD Structures and Materials Panel Meeting held in Cesme, Turkey, 5-10 April 1981, , NATO-AGARD, 64 Rue De Varenne, Paris,France, 1981.

[12] Corrosion Fatigue, AGARD Conference Proceedings No. 316, Papers presented at the 52nd Meeting of the AGARD Structures and Materials Panel Meeting held in Cesme, Turkey, 5-10 April 1981, , NATO-AGARD, 64 Rue De Varenne, Paris, France, 1981.

[13] Corrosion Fatigue, ASTM STP 801, Proceedings of the Symposium on Corrosion Fatigue: Mechanics, Metallurgy, Electrochemistry, and Engineering held in St. Louis, MO21-22 OCT. 1981, Edited by T.W. Crooker, B.N.Leis, ASTM, Philadelphia, PA., 1983.

[14] G.S. Campbell, R. Lahey, Int. J. Fatigue, Vol. 6, No. 1, 1984, pp. 25-30. Metals Handbook, 9th ed., Vol. 13, Corrosion, American Society for Metals, Metals Park, Ohio, 1985, pp. 584-609

[15] W. Wallace, D.W. Hoeppner, P.V. Kandachar. “Aircraft Corrosion: Causes and Case Histories”, AGARD Corrosion Handbook, Vol. 1, AGARD-AG-278-Vol. 1,1985.

[16] ASM Handbook, Vol. 13, Corrosion, ASM International, Metals Park, Ohio, 1987.

[17] The Boeing Company, Corrosion Prevention and Control, Manual for Training Operators of Boeing Commercial. Aircraft, Seattle, WA, 1988.

[18] Kawai S., Kasai K., Fatigue Fract. Engng. Mater. Struct. 8 (2) (1985) 115–127

[19] Environment Induced Cracking of Metals, Editors: Gangloff, R.P., Ives, M.B., Proceedings of the conference held in Kohler, WI, 2-7Oct. 1988, NACE-10, National Association of Corrosion Engineers, Houston, TX, 1990

[20] ASM Handbook, Volume 18, Friction, Lubrication, and Wear Technology, ASM International, Metals Park, Ohio, 1992.

[21] Naval Aviation Safety Program, US Navy, OPNAVINST 3750.6Q CH-1, OP-05F, March 1991.

[22] Federal Aviation Administration, Aircraft Accident and Incident Synopses Related to Corrosion, Fretting, and Fatigue for the Period 1976-1993, obtained July1994.

[23] National Transportation Safety Board, Aircraft Accident and Incident Synopses

Related to Corrosion, Fretting, and Fatigue for the Period 1975-1993, obtained July1994.

[24] Federal Aviation Administration, Aircraft Accident and Incident Synopses Related to Corrosion, Fretting, and Fatigue for the Period 1976-1993, obtained July1994.

[25] P.N. Clark, D.W. Hoeppner, J. Mech. Behavior Mater. 13 (2) (2002) 91–105

[26] United States Air Force, Navy, and Army, Aircraft Accident and Incident Synopses Related to Corrosion, Fretting, and Fatigue, obtained June-August 1994.

[27] P.N. Clark, D.W. Hoeppner, Corrosion pitting behavior of 2024-T3 aluminum considering the effects of loading and sheet thickness, (2001) ASC 01-2552.

[28] W. Schütz, "Corrosion Fatigue-The Forgotten Factor in Assessing Durability", ICAF 95, Estimation, Enhancement and Control of Aircraft Fatigue Performance, Vol. 1, Edited by J.M. Grandage, G.S. Jost, Proceedings of the 18th Symposium on the International Committee of Aeronautical Fatigue, 3-5 May, 1995, Melbourne, Australia, EMAS, Warley, West Midlands, U.K., 1995, pp 1-52.

[29] S.J. Swift, "The Aero Commander Chronicle", ICAF 95, Estimation, Enhancement and Control of Aircraft Fatigue Performance, Vol. 1, Edited by J.M. Grandage, G.S. Jost, Proceedings of the 18th Symposium on the International Committee of Aeronautical Fatigue, 3-5 May, 1995, Melbourne, Australia, EMAS, Warley, West Midlands, U.K., 1995, pp 507-530..

[30] D.W. Hoeppner, L. Grimes, A.Hoeppner, J. Ledesma, T. Mills, A. Shah, " Corrosion and Fretting as Critical Aviation Safety Issues", ICAF 95, Estimation, Enhancement and Control of Aircraft Fatigue Performance, Vol. 1, Edited by J.M. Grandage, G.S. Jost, Proceedings of the 18th Symposium on the International Committee of Aeronautical Fatigue, 3-5 May, 1995, Melbourne, Australia, EMAS, Warley, West Midlands, U.K., 1995, pp 87-106..

[31] C.L Brooks, K. Liu, R.G. Eastin, "Understanding Fatigue Failure Analyses Under Random Loading Using a C-17 Test Article", ICAF 95, Estimation, Enhancement and Control of Aircraft Fatigue Performance, Vol. 1, Edited by J.M. Grandage, G.S. Jost, Proceedings of the 18th Symposium on the International Committee of Aeronautical Fatigue, 3-5 May, 1995, Melbourne, Australia, EMAS, Warley, West Midlands, U.K., 1995, pp 449-468.

[32] ASM Handbook, Vol. 19, Fatigue and Fracture, ASM International, Metals Park, Ohio, 1996.

[33] R. P. Gangloff, S. Kim, J. T. Burns, Fatigue crack formation and growth from localized corrosion in Al-Zn-Mg-Cu, Eng Fracture Mech 76 (2009) 651-667.

[34] G.K. Cole, G. Clark, P.K. Sharp, Implications of Corrosion With Respect to Aircraft Structural Integrity, DSTO –RR-0102, AMRL, Melbourne, Australia, March, 1997.

[35] D.W. Hoeppner, The formation/nucleation of fatigue cracks in aircrafts structural materials, 26th ICAF Symposium Montreal (2011).

[36] K. Jones, D.W. Hoeppner, The interaction between pitting corrosion, grain boundaries, and constituent particles during corrosion fatigue of 7075-T6 aluminum alloy, Int J Fatigue 31 (2009) 686-692.

[37] K. Sankaran, R. Perez, K.V. Jata, Effects of pitting corrosion on the fatigue behavior of aluminum alloy 7075-T6: modeling and experimental studies, Materials Science and Eng A297 (2001) 223-229.

[38] Fatigue in the Presence of Corrosion, RTO Proceedings 18, Papers Presented at the Workshop of the RTO Applied Technology (AVT) Panel, held in Corfu, Greece, 7-9 October, 1998, AC/323(AVT) TP/8, NATO, Research and Technology Organization, BP 25, 7 Rue Ancelle, F-92201, Neully-Sur-Seine, Cedix, France, 1999.

[39] D.W. Hoeppner, V. Chandrasekaran, A.M.H.Taylor, Review of Pitting Corrosion Fatigue Models. Proceedings of 20th ICAF Symposium, Structural Integrity for the Next Millenium, Electronic Printing Services, Dayton OH, 2000, pp 253-276.

[40] https://www.corrdefense.org/default.aspx

[41] D.G. Harlow, R.P.Wei, Probability modeling and material microstructure applied to corrosion and fatigue of aluminum and steel alloys. Engineering Fracture Mechanics 76 (2009) 695-708.

[42] M.K Cavanaugh., R.G. Buchheit, N. Birbilis, Modeling the environmental dependence of pit growth using neural network approaches. Corrosion Science 52 (2010) 3070-77.

[43] K. Jones and D.W Hoeppner, Pit-to-crack transition in pre-corroded 7075-T6 aluminum alloy under cyclic loading. Corrosion Science 47 (2005) 2185-98.

[44] G.S. Chen, K.C. Wan, M. Gao, R.P. Wei, Flournoy T.H. Transition from pitting to fatigue crack growth-modeling of corrosion fatigue crack nucleation in a 2024-T3 aluminum alloy. Material Science and Engineering A219 (1996) 126-132.

[45] N. Birbilis, R.G. Buchheit. Electrochemical characteristics of intermetallic phases in aluminum alloys. Journal of Electrochemical Society 152 (4) B140-B151 (2005).

[46] N. Birbilis, R.G. Buchheit, Investigation and discussion of characteristics for intermetallic phases common to aluminum alloys as a function of solution pH. Journal of Electrochemical Society 155(3) C117-C126 (2008).

[47] J. G. Kaufman, Properties of Aluminum Alloys; Tensile, Creep, and Fatigue Data at High and Low Temperatures, 1999, ASM International.

[48] N.D. Tomashov, Theory of Corrosion and Protection of Metals, The Science of Corrosion, The MacMillan Company, 1965, pp 455-456.

CHAPTER 5

EFFECTS OF PRIOR CORROSION AND STRESS IN CORROSION FATIGUEOF ALUMINUM ALLOY 2024-T3

Abstract

The effects of prior corrosion and maximum stress on the fatigue behavior of 2024-T3 aluminum alloy were investigated. Dog bone specimens were pre-exposed to an acidic saline environment of 3.5 % NaCl. Subsequently, specimens were exposed to a saline solution and cyclic loading concomitantly until failure by fracture was observed. Two levels of corrosion time and maximum stress were chosen to be evaluated based on Design of Experiments (DOE) and on assessed criticality from other related studies and the literature.

ANOVA was done to evaluate the effects of both the corrosion time and maximum stress on the fatigue life of the specimens. Results indicate that maximum stress had greater deleterious impact in the fatigue life compared with corrosion time. Statistical factorial models are proposed based on Box-Cox transformations including natural log and power with lambda of 1/3. In addition, data were fitted to several distribution functions and the Weibull distribution fits the data with 95% confidence. Finally, SEM analysis revealed that all pre-corroded specimens tested in this study fractured from fatigue cracks that formed from corrosion induced pits. Moreover, these initial pits also were associated with intergranular attack, subsurface pitting and tunneling

which played a significant role in the both the formation and propagation of the pits and also the formation of fatigue cracks.

Introduction

Environmental degradation and fatigue are known to adversely impact the structural integrity of aircraft as well as many other components of systems. Recently, on April 2011, a Boeing 737 operated by Southwest Airlines had to make an emergency landing after a 5-feet hole opened on top of the aircraft while cruising at 36,000 feet. Initial inspection found ‘clear evidence that the skin separated at the lower rivet line’, in addition ‘widespread cracking’ was found at the origin of the hole. Fortunately the pilot was able to land the aircraft in a military base in Yuma Arizona, without major consequences [1]. Boeing indicated that they did not expect cracks in 737s so soon [2]. The Federal Aviation Administration issued Emergency Airworthiness Directive to inspect certain Boeing 737-300, 400 and 500 aircraft, for cracking in the lower skin of the lap joint of the airplanes. Four of these airplanes were found to have crack indications at a single rivet and one airplane was found to have crack indications at two rivets. These aircraft had accumulated between 40,000 and 45,000 total cycles. The lap joints from these areas of the subjected airplanes were removed [3]. Although no signs of corrosion have been reported by the NTSB in this incident, it is expected that this aircraft was exposed to corrosion fatigue.

The previous scenario sounds similar if not identical to the Aloha Airlines accident of 1988, where a Boeing 737-200 lost a major portion of the fuselage at 24,000 feet while in route to Maui. Unfortunately in this case, a flight attendant was killed during decompression. Corrosion issues combined with multiple site fatigue damage were identified as the root cause of that catastrophe, and a deficient corrosion control program also was identified as part of the problem at that time. Subsequent to the AA accident extensive commercial fleet surveys were conducted and they showed how extensive the challenge of corrosion was on the commercial fleets of operating aircraft. Regulations have been put in place to rectify this situation including more rigor into the design for corrosion prevention and control including the potential deleterious effects of corrosion fatigue.

From 1910 to around 1980 there was limited research and development on corrosion effects on structural integrity-especially related to corrosion fatigue. In 1971 NACE co-sponsored the first international symposium on corrosion fatigue and many papers were presented that were a definition of the state of the art on corrosion fatigue and suggested areas for future R and D on the subject [4]. The lead paper of that symposium presented how to deal with the issues of corrosion fatigue in materials selection and engineering design [5]. In the 1980's there appeared to be an overall recognition of the challenges related to corrosion and fatigue, however there were just a few systematic programs in the world dealing with these issues. The North Atlantic Treaty Organization (NATO) had as a primary goal to alert those involved with the operation and maintenance of aircraft to the dangers of corrosion and corrosion fatigue [6]. This was accomplished by sharing their experiences through case histories of structural failures and explaining the corrective actions taken on each case. Initially, the approach was to increase an understanding of the mechanisms and consequences of corrosion mechanisms, including pitting, and recognizing that such discontinuities could act as a stress riser where cracks can be formed/nucleated. Formation/nucleation of cracks from corrosion pits was observed by many researchers [7-22], including the works of Hoeppner [23], McAdam [24], and Goto [25] in heat treated carbon steel and Muller [26] in several steels. As well, in NaCl environment, lowering of the fatigue life due to generation of pits in carbon steel [27] and 6076-T6 Aluminum alloy [28] under corrosion fatigue conditions. Research indicated that corrosive environments accelerated fatigue crack growth rates. When dealing with the issue of corrosion and its effect on structural integrity of aircraft it became necessary for the design community (including maintenance) and operation community of aircraft to accept that corrosion was not just an economic problem but was very directly related to airworthiness and a potential safety threat. Investigation of several accidents revealed the challenges of detection and quantification of damage that resulted from corrosion and corrosion fatigue. It was recognized that in addition to metal dissolution, conversion of metal to metal oxides or hydroxides increased volume causing metal separation constrained only by rivets or bolts holding the sheets together. This represented new complex stress distributions not considered in early assessments. In recent years, it has been recognized the need of integrating several approaches, and not isolating to a single corrosion mechanism. Programs such as Holistic Integrity (HOLSIP) combine environmental effects and elastic and plastic fracture mechanics with the concepts of damage tolerance in a probabilistic and deterministic approach [29].

Considering corrosion as deterioration of metal, the damage tolerance approach can be implemented. A model has been proposed based on five factors: 1) site – where will corrosion grow; 2) scenario - how will it grow; 3) detectable – what can be reliably found (or what can be sometimes is missed); 4) dangerous – what can be safely born by the aircraft in question? And 5) duration – what is the time to go from one state to the other state. Such a model known as ‘Rusty diamond’ is shown in Fig. 5.1 [30].

Many researchers including Hoeppner [31], Schütz [32] and Wei [33], have proposed mechanisms to understand the interaction between corrosion and fatigue. The synergistic effects of these mechanisms and the multiple mechanical, chemical and metallurgical variables involved, make determination of the three D’s of the “rusty diamond” (detectable, duration and dangerous) a very challenging endeavor.

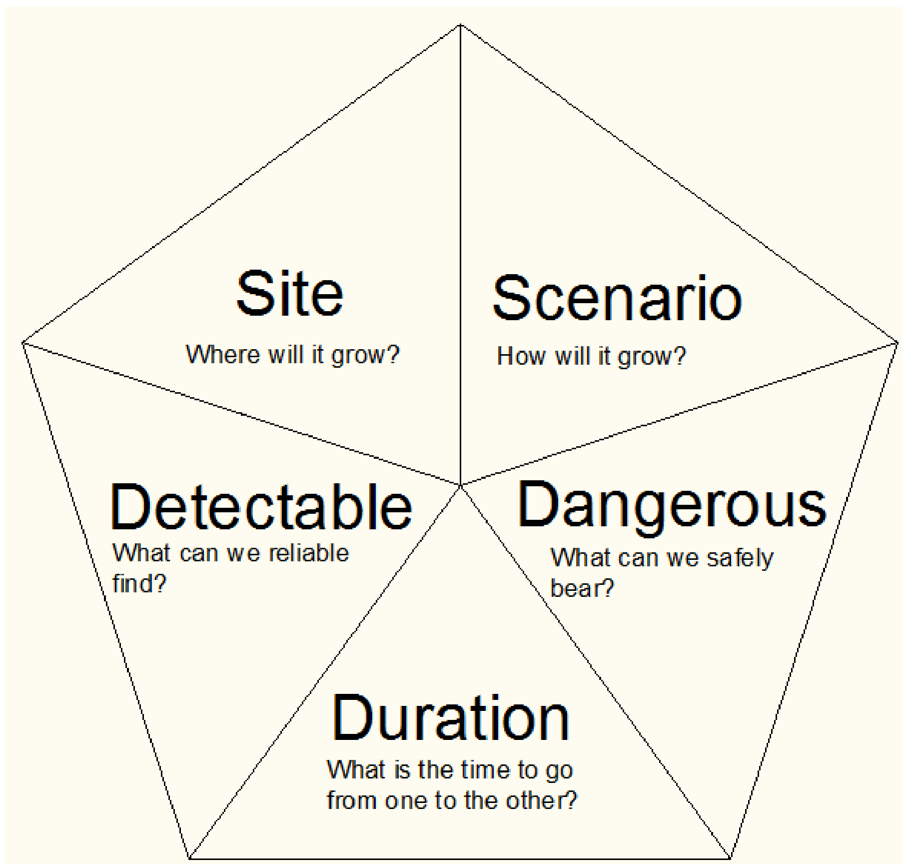


Fig. 5.1: Damage Tolerance for Corrosion – Rusty Diamond [after 30].

Other researchers such as Cavanaugh et al. studied the effects of environmental factors to develop models using artificial neural network approaches (ANN) [34]. Jones and Hoeppner studied the pit to crack transition in pre-corroded 7075-T6 aluminum alloys under cyclic loading [31]. According to Birbilis and Buchheit, high strength aluminum alloys contain heterogeneous microstructures which contain second phase (intermetallic) particles. Such particles have electrochemical characteristics that differ from the matrix, rendering the alloy susceptible to localized corrosion [35]. Wei et al. studied the transition from pitting to fatigue cracks for 2024-T3 aluminum alloys. They observed from fractographic examinations that pitting was responsible for the nucleation of corrosion fatigue cracks [36].

The purpose of the research reported herein is to examine and characterize the effects of concomitant fluctuating stresses and an acidic saline environment on the residual life of aluminum alloy 2024-T3. Several hypotheses were tested to establish a correlation between these variables and their effect on the fatigue life of the specimens:

Hypothesis I. Aluminum alloy 2024-T3 will dissolve by pitting when exposed to an acidified saline environment. Furthermore, cracks will form/nucleate from pits and propagate until failure by fracture occurs.

Hypothesis II. Stress magnitude will have a greater deleterious impact as compared with corrosion exposure time on the fatigue life of the specimens.

Hypothesis III. Statistical models will predict with confidence the life of specimens exposed to stress and an acidified saline environment with limits defined by a DOE matrix. Weibull functions will fit the corrosion fatigue data with statistical confidence.

Experimental Procedures

Center-pin-loaded dogbone specimens were designed and machined from 2024-T3 aluminum alloy sheet of thickness 1.600 mm. This alloy has a nominal composition of 4.4% copper, 0.6% manganese, and 1.5% magnesium with aluminum as reminder. Therefore, constituent particles in 2024 aluminum include copper, manganese, iron, magnesium and aluminum [37].

The impact of different levels of stress magnitude and exposure time to an acidified saline solution on the fatigue life of the specimens was evaluated in this study. The basis for the corrosion fatigue protocol was taken from previous studies performed at the University of Utah's Structural Integrity Laboratory. In addition, ASTM standards were reviewed and adapted to the protocol with some modifications. Some of these modifications included acidifying the solution to a pH of 3, since aluminum alloy is prone to corrode at these conditions.

An important assumption in this study is that surfaces are homogeneous and free of any manufacturing or processing discontinuities. To achieve this state, a rigorous regime of surface polishing was followed. Specimen preparation involved polishing the side of interest to a 0.3 µm finish. The final surface appearance was mirror-like, which was assumed free of imperfections and this was confirmed by microscopic examination for each specimen. This was verified by examining the surface with metallurgical microscope prior to corrosion. After polishing, specimens were cleaned with acetone in an ultrasonic bath for 5 minutes. Specimens were stored in a vacuum dessicator.

Two levels of prior-corrosion time were evaluated, viz. 24 and 72 hours. These levels were chosen after several pilot tests were run, which indicated that after 72 hours no significant difference was noted in the life of the specimens during simultaneous corrosion fatigue. A 3.5% NaCl solution was prepared which was acidified to a pH of three, by addition of 1M HCl. The corrosion area was set to 3 mm by 10 mm. Pits were characterized with a metallurgical microscope that allowed measuring “apparent” pit depth. Specimens were exposed simultaneously to the saline acidic environment and cyclic loading. The flow rate of the solution through the chamber was approximately 1 ml/min.

It is known that aircraft such as the F-16 operate with stresses between 117 and 152 MPa, including critical areas such as the fuselage bulkheads. Based on this, two levels of stress were used, viz. σ_{max} = 117 MPa and σ_{max} = 151.7 MPa. This was done to assure that the stress levels used had some degree of validity related to an operating fleet of aircraft. Fatigue loading was performed utilizing an electro-hydraulic closed loop, servo-controlled MTS 5 kip capacity load frame. The loading was controlled by a MTS TestStar system. A stress ratio R = +0.1 was used for all experiments which were performed at constant load amplitude using a sinusoidal waveform with a frequency of 10 Hz.

Specimens were exposed to corrosion-fatigue conditions until fracture occurred, and then were cleaned with HNO_3 and acetone ultrasonic bath. Pitting characterization was done using a Scanning Electron Microscope provided by FASIDE International Inc. The randomized experiments are shown in Table 5.1. Redundancy of experiments in statistical factorial design increases the statistical confidence in the results. Two levels of stress and corrosion time were chosen according to 2^2 factorial design.

Table 5.1: DOE Matrix for Corrosion Fatigue Experiments.

Standard Order	Run Order	Block	Prior Corrosion Time (hr)	Stress (MPa)
6	1	Block 1	72	117
11	2	Block 1	24	151.7
1	3	Block 1	24	117
16	4	Block 1	72	151.7
17	5	Block 2	72	151.7
7	6	Block 2	72	117
2	7	Block 2	24	117
12	8	Block 2	24	151.7
3	9	Block 3	24	117
18	10	Block 3	72	151.7
13	11	Block 3	24	151.7
8	12	Block 3	72	117
19	13	Block 4	72	151.7
4	14	Block 4	24	117
14	15	Block 4	24	151.7
9	16	Block 4	72	117
20	17	Block 5	72	151.7
15	18	Block 5	24	151.7
10	19	Block 5	72	117
5	20	Block 5	24	117

Results and Discussion

In this study, the process of pitting induced crack formation/nucleation for a 2024-T3 aluminum alloy cyclically stressed in an acidified saline solution is quantitatively demonstrated by varying the corrosion time and maximum stress. Specimens were pre-exposed to the acidified saline solution at two intervals, 24 and 72 hours. Specimens were pre-corroded, and then were exposed simultaneously to the acidic saline solution, and cyclic loading of 117 MPa and 151.7 MPa, according to a statistical based protocol. SEM analysis allowed subsurface pit characterization, and it was evident that subsurface tunneling and pitting were present. In addition, cracks were originated from each of the pits analyzed, including the formation of subsurface cracks.

Design of experiments (DOE) was used to set up the protocol for testing. Data were analyzed with statistical techniques including analysis of variance (ANOVA) and Weibull distributions. Several transformations were evaluated to stabilize the variance and to develop statistical significant models. Table 5.2 contains the results for the corrosion fatigue experiments, including exposure time, stress magnitude and cycles to failure. Not shown in the table are specimens exposed only to cyclic fatigue at both levels, which did not fracture and were stopped after 10 million cycles.

Table 5.2: Summary of Results of Corrosion Fatigue Experiments.

Factor		Replicate - Cycles to Failure					
Cor Time (hr)	Stress (MPa)	I	II	III	IV	V	Average
24	117	303,607	271,018	382,711	252,739	303,471	302,709
72	117	437,605	464,665	261,141	506,632	229,925	379,994
24	151.7	148,906	93,558	87,926	119,734	82,883	106,601
72	151.7	101,843	160,577	114,169	121,425	39,876	107,578

Analysis of Variance (ANOVA)

Analysis of variance is a useful mathematical approach designed to verify if there is a statistical difference between various factors of interest. A typical application is to determine which factor has more impact on the output or response. In this study, two variables were investigated, viz. pre-corrosion time and maximum stress. Their impact on the fatigue life of the specimens was investigated. In order to normalize the variance, several transformations were identified. As demonstrated in the following sections, the natural log transformation and the power transformation reduce the variance. Box-Cox transformations were selected from the following equation:

$$\left(y_i\right)^{(\lambda)} = \left| \begin{array}{l} \dfrac{\left(y_i\right)^{\lambda} - 1}{\lambda} \leftarrow \text{when\_}\lambda \neq 0 \\ \log\left(y_i\right) \leftarrow \text{when\_}\lambda = 0 \end{array} \right. \tag{1}$$

where Y is the response variable and λ is the transformation parameter. Several λ values were evaluated and a natural log. The results are presented in the following sections.

Natural Log Transformation

Experiments were executed in five blocks. The sum of the squares for the blocks is given by

$$\text{Blocks} := \frac{1}{a \cdot b} \cdot \sum_{i=1}^{5} \left(Nf_{ts_i}\right)^2 - \frac{\left(\displaystyle\sum_{i=1}^{2} \sum_{j=1}^{10} Nf_{t_{i,j}}\right)^2}{a \cdot b \cdot n} \tag{2}$$

where a represents the number of variables, b the number of levels, and n the number of repetitions. The sum of the squares for factor A, corresponding to corrosion time is given by

$$SS_A = \frac{1}{b \cdot n} \cdot \sum_i {y_{i..}}^2 - \frac{{y_{...}}^2}{a \cdot b \cdot n} \qquad (3)$$

and for factor B, stress is given by

$$SS_B = \frac{1}{a \cdot n} \cdot \sum_j {y_{.j.}}^2 - \frac{{y_{...}}^2}{a \cdot b \cdot n} \qquad (4)$$

In the case of interaction between variables, the sum of the factors is given by

$$SS_{AB} = \frac{1}{n} \cdot \left(\sum_i \sum_j {y_{.j.}}^2 \right) - \frac{{y_{...}}^2}{a \cdot b \cdot n} - SS_A - SS_B \qquad (5)$$

and the total sum of the squares

$$SS_T := \sum_{i=1}^{2} \sum_{j=1}^{10} \left(Nf_{t_{i,j}} \right)^2 - \frac{\left(\sum_{i=1}^{2} \sum_{j=1}^{10} Nf_{t_{i,j}} \right)^2}{a \cdot b \cdot n} \qquad (6)$$

Following the previous equations, the analysis of variance Table 5.3 is generated. This table also includes the F-values and corresponding p-values (significance level) for each variable as indicated previously. The p-value for the model is 0.01%, therefore there is only 0.01% chance that this model is due to noise. However corrosion time has an undesirable high p-value.

It is evident from the table that corrosion time is not a significant variable for this model, as shown by the high p-value. This may indicate that for the conditions of interest as specified in the DOE matrix, maximum stress has higher detrimental impact in the fatigue life of the specimens, as compared with corrosion time.

Since the probability values for stress are within expected values of less than 5%, additional models are generated in the following sections with only maximum stress as variable.

Figs. 5.2 and 5.3 are contour and surface plots corresponding to the natural log transformation as indicated in the previous table.

Table 5.3: ANOVA for Natural Log Transformation with Two Variables

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F		
Block	0.85	4	0.21				
Model	7.01	2	3.50	37.46	< 0.0001	R-Sqr	0.85
A-cor time	0.02	1	0.02	0.22	0.65	Std. Dev.	0.31
B-stress	6.99	1	6.99	74.70	< 0.0001	Mean	12.11
Residual	1.22	13	0.09			C.V. %	2.52
Cor Total	9.07	19					
Response	Nf						
Transform:	Natural Log						

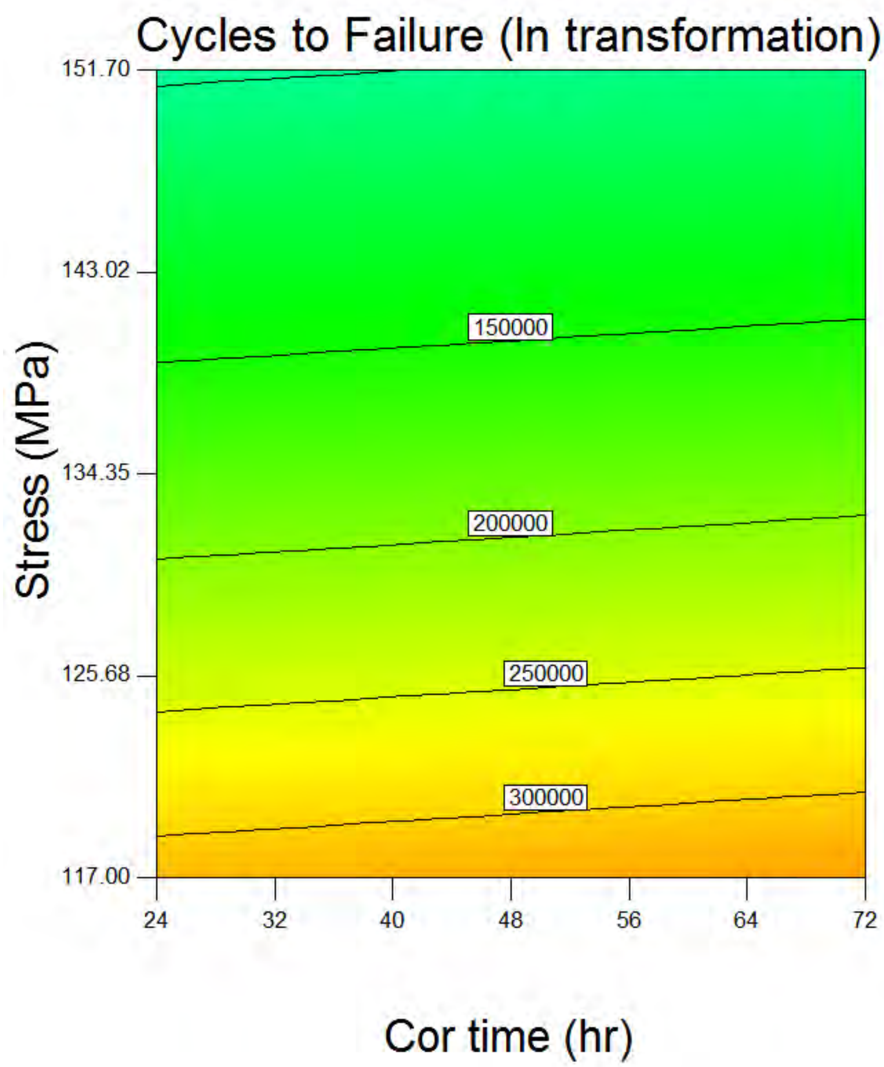


Fig. 5.2: Contour Plot for Natural Log Transformation

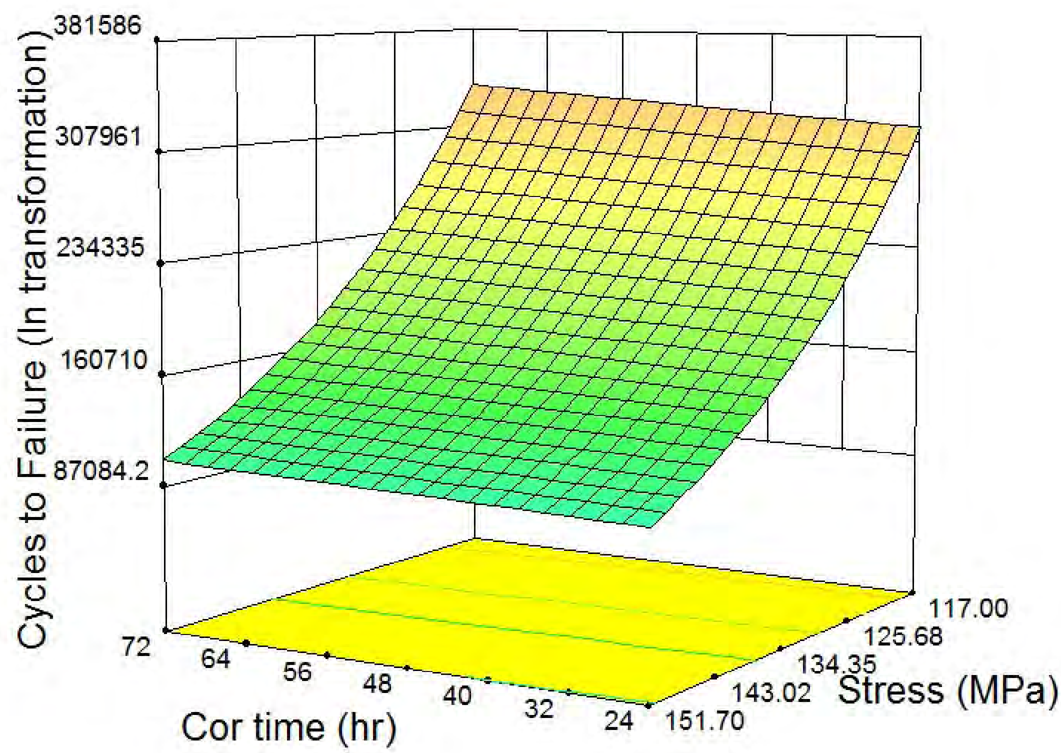


Fig. 5.3: Surface Plots of Natural Log Transformation

.

Power Transformation with Lambda = 1/3

Another transformation of interest is the power function with a lambda of 1/3, which can be represented by

$$Nf^{\frac{1}{3}} = f(CorTime, Stress) \tag{7}$$

Such transformation gives a model with a corresponding R^2 of 0.86 and a P-value for the model of 0.01%, which indicates the model is statistical significant. Figs. 5.4 and 5.5 represent such model in a contour plot and surface plot respectively.

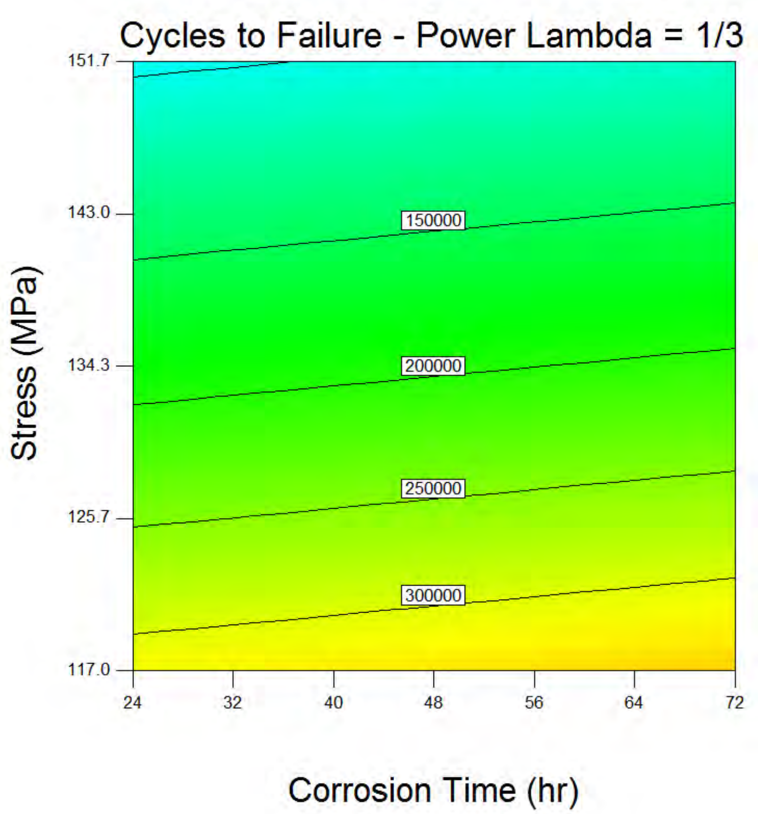


Fig. 5.4: Contour Plot for Power Function with Lambda = 1/3.

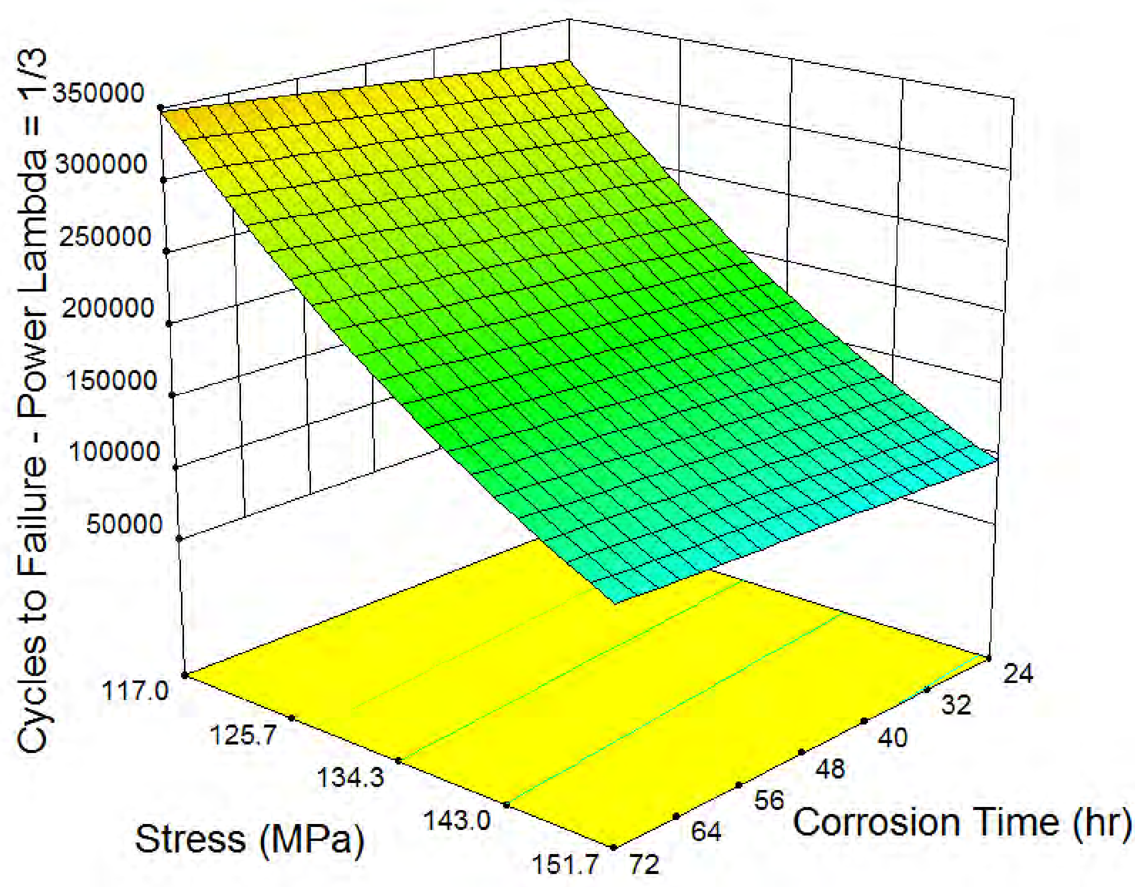


Fig. 5.5: Surface Plot with a Power transformation with a Lambda = 1/3**.**

Natural Log Transformation – Stress Only

As indicated in the previous section corrosion time is not a statistically significant variable in this model, therefore ANOVA was done without considering this variable. The results are compiled in Table 5.4, which shows for a natural log transformation a statistical significant model with an R^2 value of 0.85.

The following equation represents the model with a natural log transformation, and stress only as variable. The parameters alpha and beta are material and environment dependent. Figs. 5.6 and 5.7 show graphically the results of this analysis.

$$\ln(Nf) = \alpha - \beta \cdot (\sigma) \tag{8}$$

Table 5.4: ANOVA for Natural Log Transformation with Stress only

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F		
Block	0.85	4	0.21			R-Squared	0.85
Model	6.99	1	6.99	79.1	< 0.0001	Std. Dev.	0.30
B-stress	6.99	1	6.99	79.1	< 0.0001	Mean	12.11
Residual	1.24	14	0.09			C.V. %	2.45
Cor Total	9.07	19					

Response Nf
Transform: Natural Log

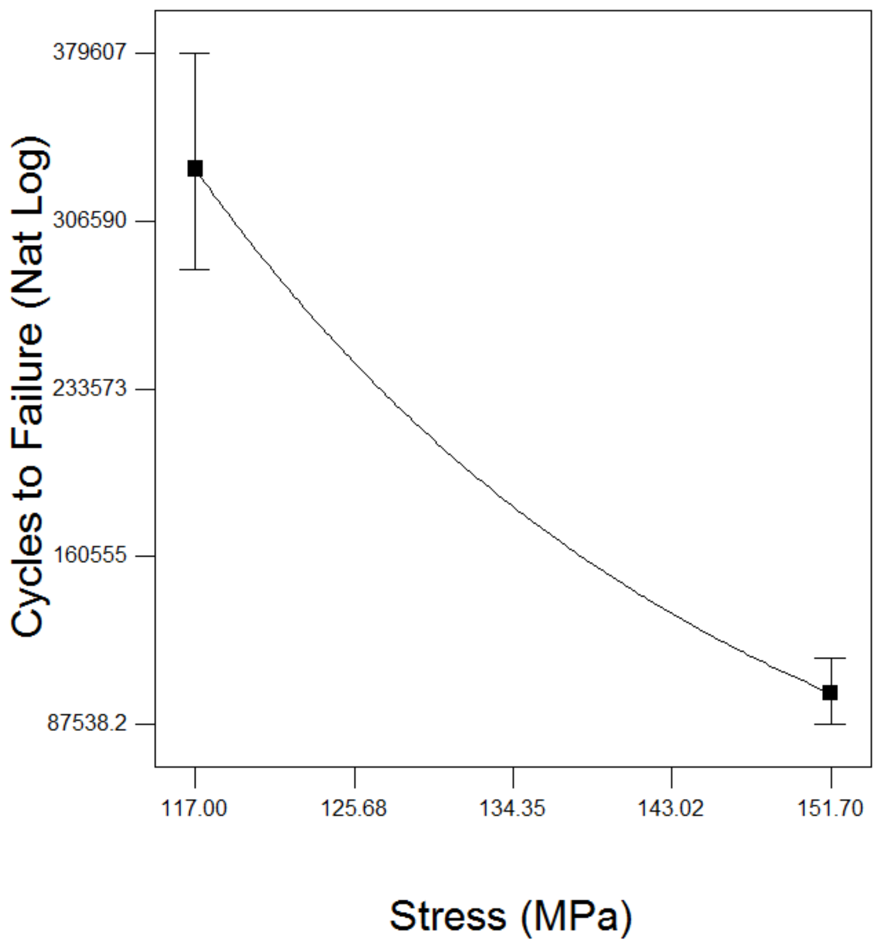


Fig. 5.6: Nf vs. Stress for Natural Log Transformation

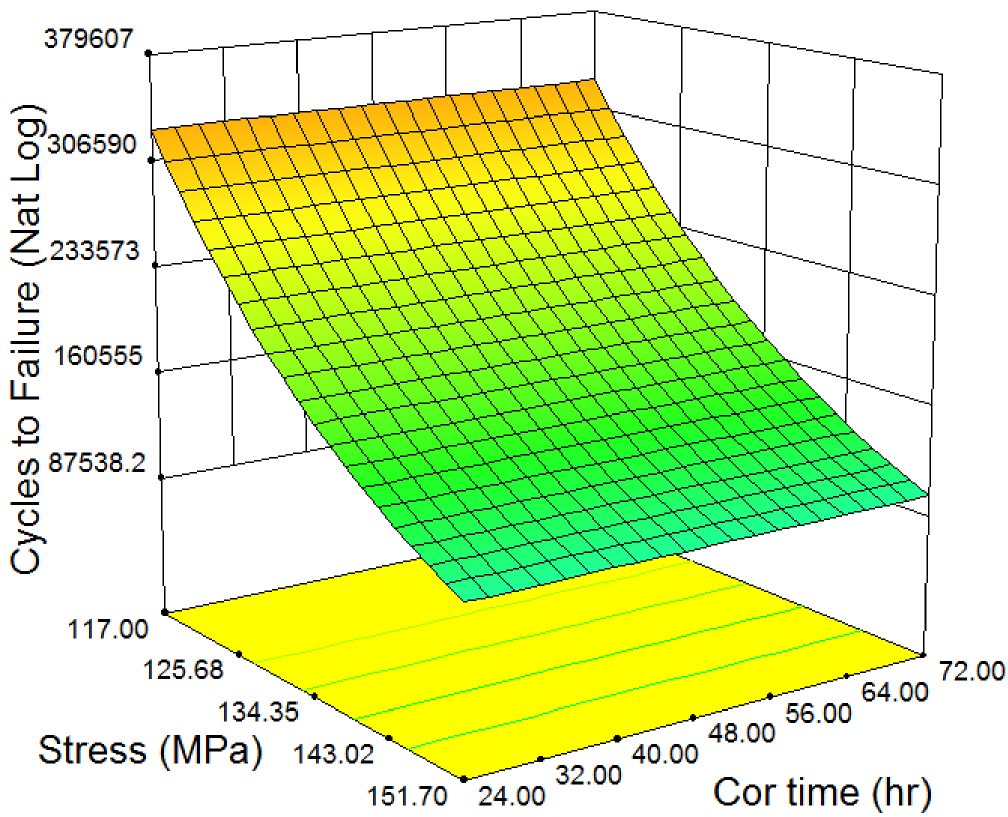


Fig. 5.7: Surface Plot for Natural Log Transformation.

Power Transformation with Lambda = 1/3 (stress only)

A similar analysis with a power transformation with lambda of 1/3, with stress as only variable was performed. ANOVA indicates that the model is statistical significant with a p-value of 0.01%. Results are shown in Table 5.5.

The p-values for the model and the stress variable are less than 0.01%, therefore both the model and maximum stress are statistical significant. There is only 0.01% chance that this model is due to noise. In addition, the R^2 for the model is statistical significant with a value of 0.85. The following correlation is given by this model

$$Nf^{\frac{1}{3}} = \alpha - \beta \cdot (\sigma) \tag{9}$$

where alpha and beta are constants dependent on material and environmental parameters. Figs. 5.8 and 5.9 are graphical representation of the above equation. The first graph represents cycles to failure as a function of maximum stress. The second graph is a surface plot for the model.

Table 5.5: ANOVA Power Transformations Lambda 1/3 (stress only)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F		
Block	221.9	4	55.5			R-Squared	0.85
Model	2272.0	1	2272.0	81.1	< 0.0001	Std. Dev.	5.29
B-stress	2272.0	1	2272.0	81.1	< 0.0001	Mean	55.8
Residual	392.1	14	28.0			C.V. %	9.49
Cor Total	2885.9	19					
Transform:	Power	Lambda:1/3					

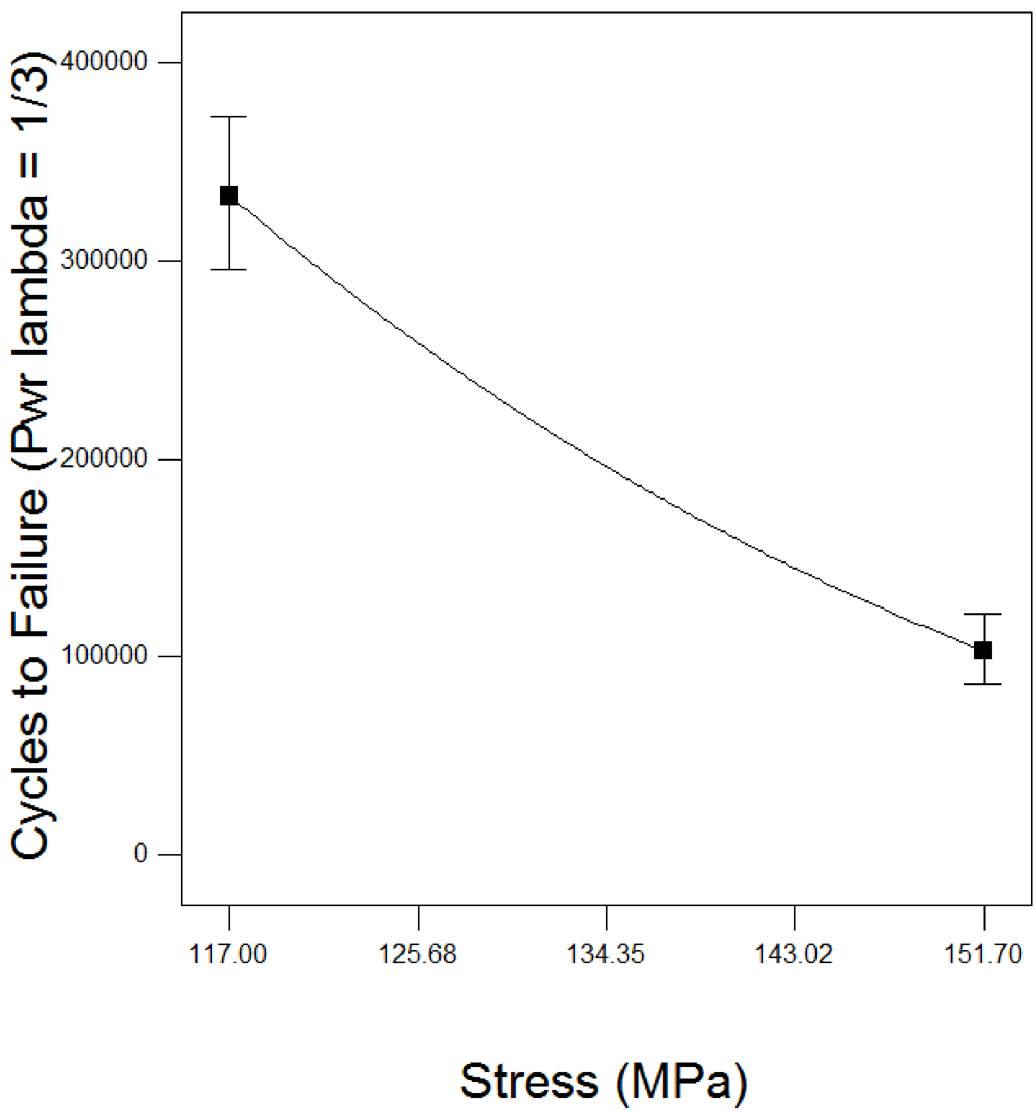


Fig. 5.8: Nf vs. Stress for Power Transformation

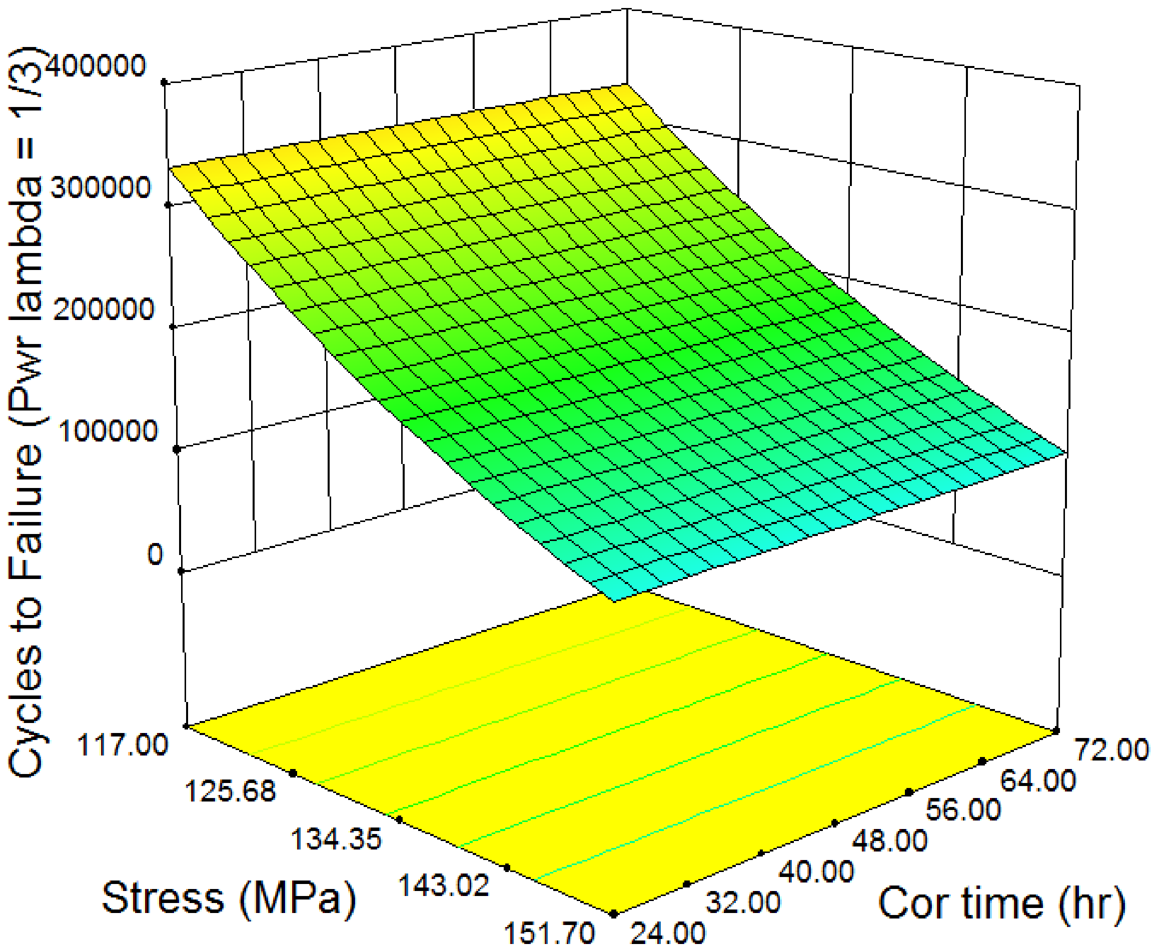


Fig. 5.9: Surface Plot for Power Transformation

.

Weibull Analysis

The Weibull distribution has great advantage in reliability since it may represent many life distributions. The Weibull probability density function in terms of time is

$$f(t) = \frac{\beta}{\eta^{\beta}} \cdot t^{\beta-1} \cdot \exp\left[-\left(\frac{t}{\eta}\right)^{\beta}\right] \tag{10}$$

where β is the shape parameter and η is the scale parameter or characteristic life.

Fitting the cycles to failure to the previous function yields the following graph (Fig. 5.10). It is evident that corrosion time may not have a significant difference between 24 or 72 hours in the life of the specimens.

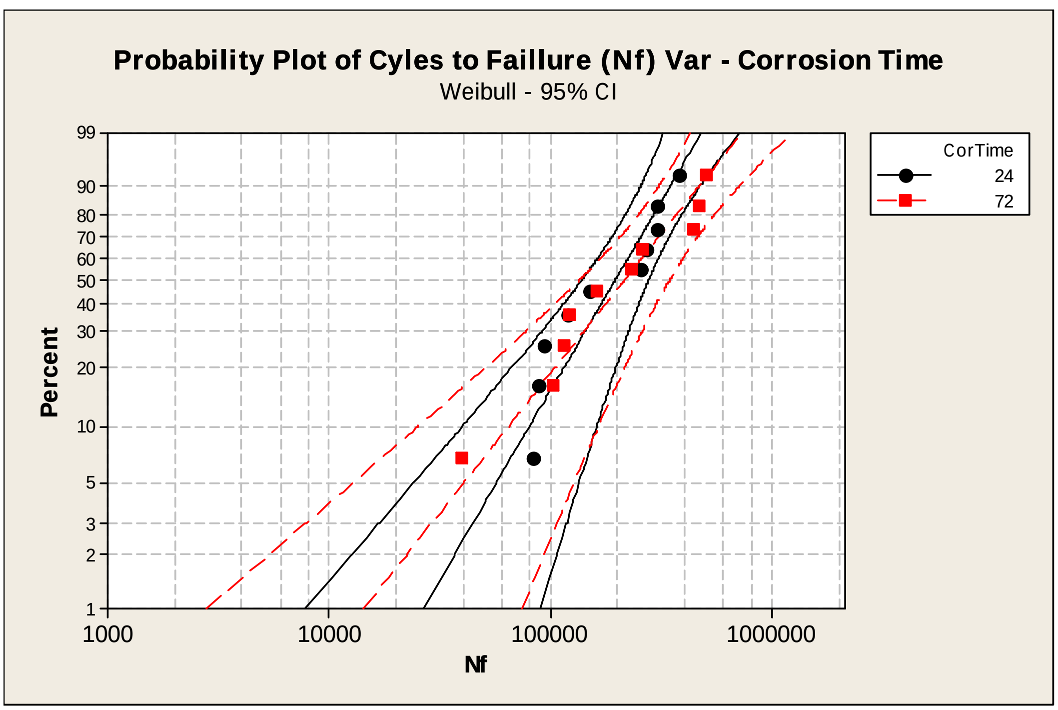


Fig 5.10: Weibull Probability Plot of Cycles to Failure with Corrosion Time Variable.

The same analysis was done with stress as the main variable and a significant difference was obtained for stress values of 117 and 152 MPa. For example, for 117 MPa, 90% of the life of the specimens is reached at 466,551 cycles and for 152 MPa the same level is reached at 148,406 cycles. A representation with 95% confidence interval is shown in the following graph (Fig. 5.11). It is evident that the effect of stress has a significant difference as compared with corrosion time in the previous figure.

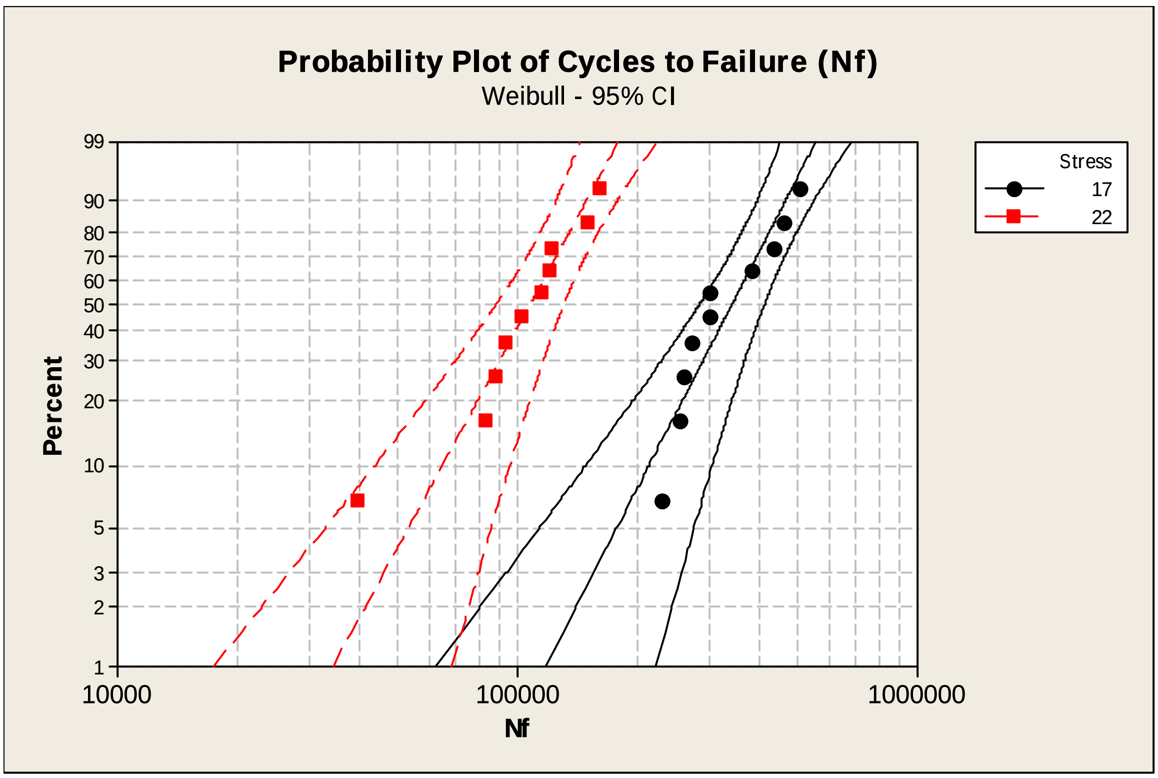


Fig. 5.11: Weibull Probability Plot with of Cycles to Failure with Stress as Variable

Fractography

Specimen CA7B

Experimentation was performed under corrosion fatigue conditions as presented earlier. The corrosive environment was an acidified (pH ~ 3) 3.5 % NaCl solution. The maximum stress for specimen CA7 was 117 MPa with R = +1, and frequency of 10 Hz. The pre-corrosion time was 24 hours.

Fracture occurred after 303,607 cycles due to a crack that formed/nucleated from a pit. Other failure modes may be seen in the micrograph of Fig. 5.12, including, subsurface pitting, tunneling and subsurface cracking.

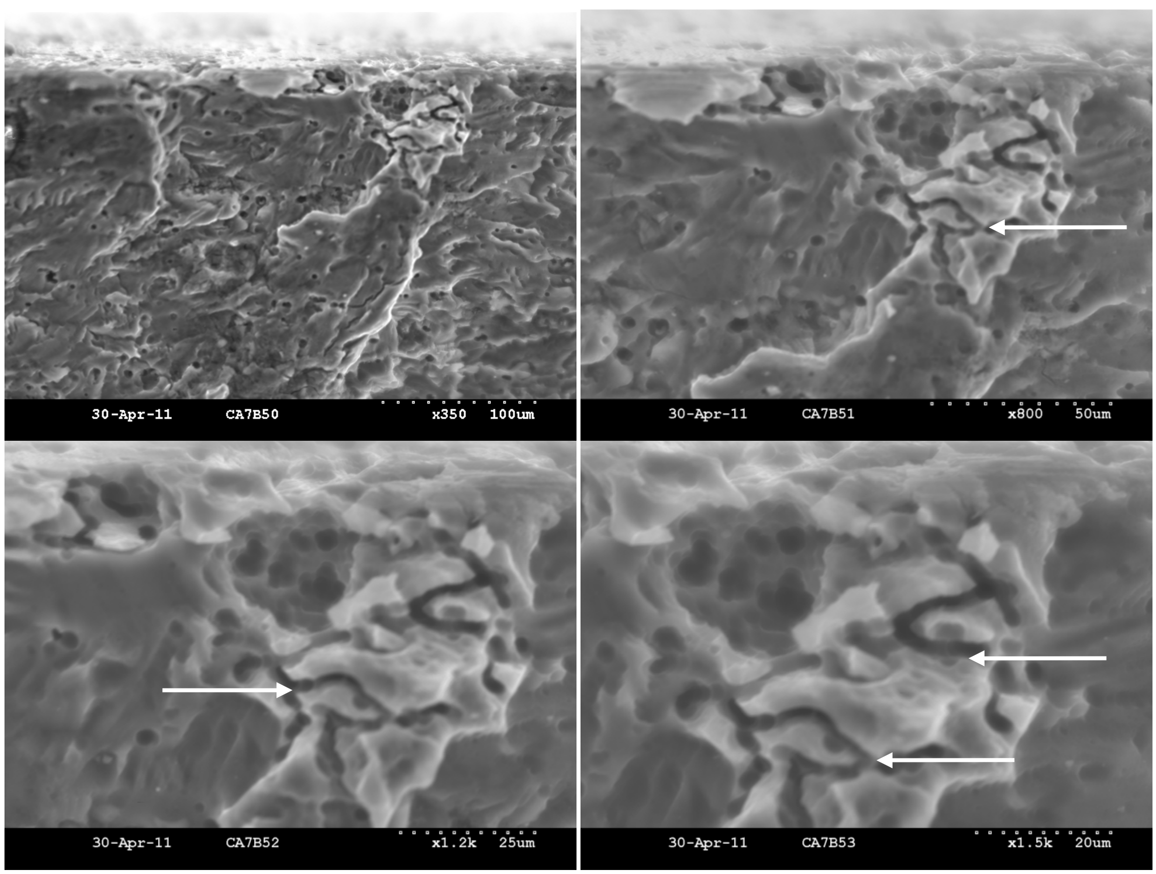


Fig. 5.12: SEM Micrograph for Specimens CA7B. Arrows indicate subsurface cracks.

Specimen CA18T

Conditions for this specimen were maximum stress of 117 MPa and it was pre-exposed to the acidified saline solution for 24 hours. The specimen failed by fracture after 271,018 cycles. SEM micrographs are shown in Fig. 5.13. It shows a pit in the surface from which cracks formed and propagated to fracture. In addition, subsurface damage is shown by tunneling, subsurface pitting and subsurface cracking.

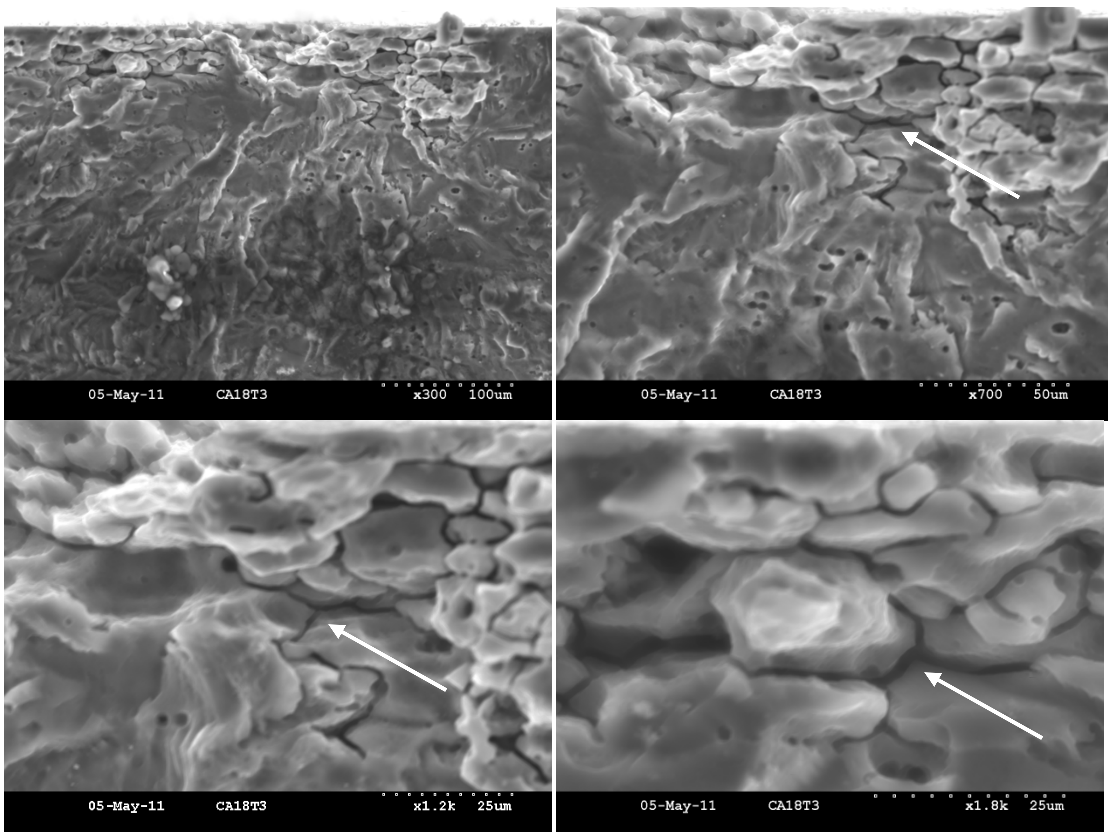


Fig.5.13: SEM Micrographs for Specimen CA18T.
Arrows indicate subsurface cracks adjacent to a pit

Specimen CA20T

Conditions for specimen CA20 were maximum stress 117 MPa and it was pre-exposed to the acidified saline solution for 72 hrs. The specimen failed by fracture after 464,665 cycles. SEM micrographs are shown in Fig. 5.14. Multiple cracks generated from surface pits, and such cracks propagated until failure by fracture was reached. In addition, tunneling, and subsurface pitting and cracking are shown.

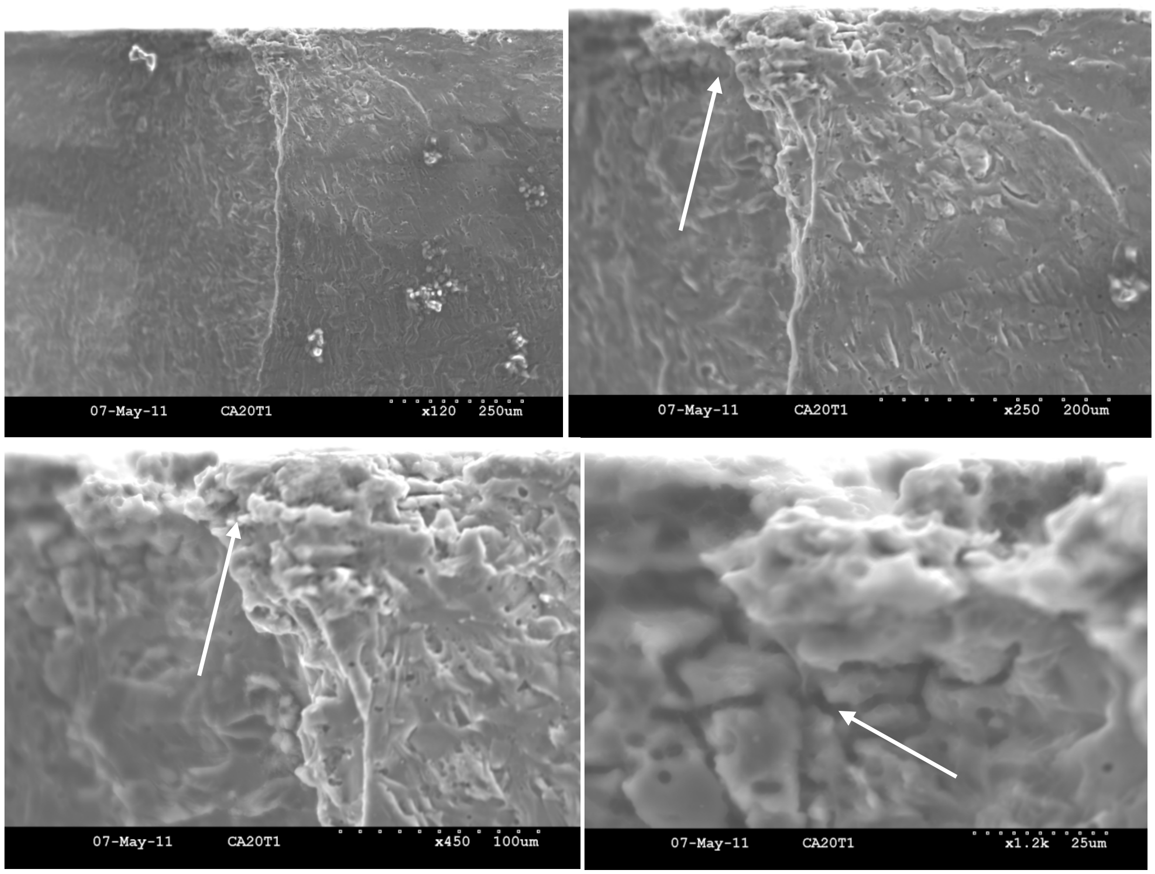


Fig. 5.14: SEM Micrographs for Specimen CA20T.
Arrows indicate location of critical pit and adjacent subsurface cracks.

Conclusions

Corrosion pits were formed/nucleated by the exposure of aluminum alloy 2024-T3 specimens to an acidified saline solution. Such pits were identified as crack origins, which continued to grow until fracture was obtained. SEM analysis revealed additional subsurface failure modes including tunneling, subsurface cracking and pitting. Such mechanisms are extremely deleterious to the integrity of structures, since these are difficult to detect by conventional non destructive methods.

Pitting is a major factor affecting the formation/nucleation of fatigue cracks. In this study the effects of corrosion time and maximum stress in the fatigue life of the specimens was evaluated. It was found that maximum stress had a greater deleterious impact to the overall fatigue life of the specimens as compared with corrosion time.

DOE was utilized to setup a testing protocol and ANOVA was implemented to develop models by stabilizing the variance using several Box-Cox transformations. Two transformations resulted in statistical significant models, natural log and power transformation with lambda of 1/3. Finally, fatigue data were fitted to several distribution functions, and the Weibull distribution fits the data with 95% confidence.

In this chapter statistical significant models have been presented for the corrosion fatigue of AA2024-T3. This manuscript was recently submitted for publication at **Corrosion-The Journal of Science and Engineering**. The next and last chapter summarizes the significant contributions of the research presented herein, and some recommendations are made.

Acknowledgements

The authors wish to acknowledge FASIDE International Inc. for their financial support and use of FASIDE facilities and the University of Utah-Material Behavior Laboratory of QIDEC (Quality and Integrity Design Engineering Center) of Mechanical Engineering for the use of their facilities. Sincere thanks are offered to Ms. Amy Hoeppner Taylor and Mr. Larry Smiltneek for their assistance related to fatigue test setup, calibration, and to fractographic examination of the specimens post fracture.

References

[1] www.cnn.com

[2] http://www.nytimes.com/2011/04/06/business/06air.html

[3] http://www.nytimes.com/2011/04/26/business/26air.html

[4] Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, 1972,

[5] D.W. Hoeppner, "Corrosion Fatigue Considerations in Materials Selections and Engineering Design", Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, 1972, pp. 3-11.

[6] W. Wallace, D. W. Hoeppner, P.V. Kandachar, "Aircraft Corrosion: Causes and Case Histories", AGARD Corrosion Handbook, Vol. 1, AGARD-AG-278-Vol. 1, 1985

[7] D.J. McAdam Jr., "Stress-Strain-Cycle relationship and corrosion-fatigue of metals", Proceedings of the ASTM, Vol. 26 (II), pp. 224-280, 1926.

[8] D.J. McAdam, Jr., "Corrosion-fatigue of non-ferrous metals", Proceedings of the ASTM, Vol. 27 (II), pp. 102-152, 1927.

[9] D.J. McAdam, Jr., "Corrosion-fatigue of metals under cyclic stress", Proceedings of the ASTM, Vol. 29, No. 2, pp. 250-313, 1929.

[10] D. Pettit, J. Ryder, W. Krupp and D.W. Hoeppner, "Investigation of the effects of stress and chemical environments on the prediction of fracture in aircraft structural materials", AFML-TR-74-183, Lockheed California Company, December 1974.

[11] G.K. Cole, G. Clark and P.K. Sharp, “The implication of corrosion with respect to aircraft structural integrity, DSTO-RR-0102, Melbourne, Victoria, Australia.

[12] D.J. Groner, “US Air Force aging aircraft corrosion: Current Awareness Bulletin, Structures Division, Wright Laboratory, Spring 1997.

[13] R.S. Piascik, R.G. Kelly, M.E. Inman, and S.A. Willard, “Fuselage Lap splice corrosion”, WL-TR-96-4094, Vol. II, ASIP, 1996.

[14] T.B. Mills, “The combined effects of prior corrosion and aggressive chemical environments on fatigue crack growth behavior in aluminum alloy 7075-T651”, Ph.D. Dissertation, University of Utah, 1997.

[15] T.B. Mills, “The effects of exfoliation corrosion on the fatigue response of 7075-T651 aluminum plate”, M.S. Thesis, University of Utah, 1994.

[16] J.P. Chubb, T.A. Morad, B.S. Hockenhull, and J.W. Bristow, “The effect of exfoliation corrosion on the fatigue behavior of structural aluminum alloys”, in Structural Integrity of Aging Airplanes, pp. 87-97, 1991.

[17] D.D. Swartz, M. Miller, and D.W. Hoeppner, “Chemical environments in commercial transport aircraft and their effect on corrosion fatigue propagation”, in Estimation, Enhancement and control of aircraft fatigue performance, Vol. I, J.M. Grandage and G.S. Jost, Eds. The proceedings of the 14th Symposium of the International Committee on Aeronautical Fatigue, Melbourne, Victoria, Australia, pp. 353-364, 3-5 May 1995.

[18] J. Kamer, and D.W. Hoeppner, “Effects of cyclic immersion in 3.5% NaCl solution on fatigue crack propagation rates in aluminum 2024-T351”, Proceedings of the 1995 USAF Structural Integrity Program Conference, WL-TR-96-4093, Vol. II, pp. 1089-1112, 1995.

[19] T.B. Mills, D.J. Magda, S.E. Kinyon, and D.W Hoeppner, “Fatigue crack growth and residual strength analyses of service corroded 2024-T3 aluminum fuselage panels”, Report of Oklahoma City Air Logistics Center and Boeing Defense and Space Group, University of Utah, 1995.

[20] J.P. Komorowski, N.C. Bellinger, and R.W. Gould, “The role of corrosion pillowing in NDI and in the structural integrity of fuselage joints”, in Fatigue in New and Aging Aircraft, Proceedings of the 19th Symposium of ICAF, 1997.

[21] N.C. Bellinger, J.P. Komorowski, and R.W. Gould, “Damage tolerance implications of corrosion pillowing on fuselage lap joints”, Journal of Aircraft, Vol. 35, No. 3, pp. 487-491, May-June 1998.

[22] N.C. Bellinger, J.P. Komorowski, "Corrosion pillowing stresses in fuselage lap joints", AIAA Journal, Vol. 35, No. 3, 1997.

[23] D.W. Hoeppner, D.S. Mann, and J. Weekes, "Fracture mechanics based modeling of corrosion fatigue process", in Corrosion Fatigue: Proceedings of the 52nd meeting of the AGARD Structures and Materials Panel held in Turkey, 5-10 April 1981.

[24] D.J. McAdam, and G.W. Gell, "Pitting and its effect on the fatigue limit of steels corroded under various conditions", Journal of the Proceedings of the American Society for Testing Materials, Vol. 41, pp. 696-732, 1928.

[25] M. Goto, and H. Nisitani, "Crack initiation and propagation behavior of a heat treated carbon steel in corrosion fatigue", Fatigue Fracture Engineering Material Structure, Vol. 15, No. 4, pp. 353-363, 1992.

[26] M. Muller, "Theoretical considerations on corrosion fatigue crack initiation", Metallurgical Transactions, Vol. 13A, pp. 649-655, 1982.

[27] D.J. McAdam, G.W. Gell, Pitting and its effect on the fatigue limit of steels corroded under various conditions. Journal of the proceedings of the American Society for Testing Materials, Vol. 41, pp 696-732, 1928.

[28] D.W. Hoeppner, Corrosion fatigue considerations in materials selections and engineering design. Corrosion Fatigue: Chemistry, Mechanics, and Microstructure, NACE, pp.3-11, 1972.

[29] D.W Hoeppner, "A review of corrosion fatigue and corrosion/fatigue considerations in aircraft structural design", Proceedings of the 22nd ICAF Symposium, Lucerne, Switzerland, EMAS UK, 2003.

[30] S. Swift, "Rusty Diamond", Proceedings of the 24th International Committee on Aeronautical Fatigue (ICAF) Symposium, Naples, Italy, May 2007.

[31] K. Jones and D.W. Hoeppner. "Pit-to-crack transition in pre-corroded 7075-T6 aluminum alloy under cyclic loading." Corrosion Science 47 (2005) 2185-98.

[32] W. Schütz, "Corrosion fatigue – the forgotten factor in assessing durability", Proceedings of the 18th ICAF Symposium, Melbourne, Australia, EMAS, UK, 2005.

[33] R.P. Wei, G. Harlow, D. Muench, "Corrosion/Corrosion fatigue and material prognosis", Proceedings of the 23rd ICAF Symposium, Hamburg, Germany

[34] M.K. Cavanaugh, R.G. Buchheit, N. Birbilis. "Modeling the environmental dependence of pit growth using neural network approaches". Corrosion Science 52 (2010) 3070-77.

[35] N. Birbilis, R.G. Buchheit, "Electrochemical characteristics of intermetallic phases in aluminum alloys." Journal of Electrochemical Society 152 (4) B140-B151 (2005).

[36] G.S. Chen, K.C. Wan, M. Gao, R.P. Wei, T.H. Flournoy, "Transition from pitting to fatigue crack growth-modeling of corrosion fatigue crack nucleation in a 2024-T3 aluminum alloy." Material Science and Engineering A219 (1996) 126-132.

[37] K. Jones, S.R. Shinde, P.N. Clark, and D.W. Hoeppner, "Effect of prior corrosion on short crack behavior in 2024-T3 aluminum alloy, Corrosion Science 50 (2008) 2588-2595.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The research reported herein had three goals: 1) study the effects of prior corrosion of an acidified saline environment and cyclic loading to high strength aluminum alloys 7075-T6 and 2024-T3; 2) determine what variable had major impact in the fatigue life of the specimens, corrosion time or maximum stress; and 3) develop statistical models to predict the life of the specimens exposed to corrosion time and stress. The magnitude of stress was chosen based on "typical" stresses that military aircrafts are exposed, including critical areas such as the fuselage bulkheads in the F-16. The null hypotheses as indicated previously include the following:

1) Aluminum alloys 7075-T6 and 2024-T3 will dissolve by pitting when pre-exposed to an acidified saline environment. Furthermore, cracks will nucleate from pits and propagate until failure by fracture is reached. This hypothesis was not rejected during experimentation.
2) Stress magnitude will have a greater deleterious impact as compared with corrosion exposure time on the fatigue life of the specimens. This hypothesis was not rejected, and the alternative option was rejected. In other words, the stress magnitude had higher detrimental impact than corrosion time in the fatigue life of the specimens.

3) Statistical models will predict with confidence the life of specimens exposed to stress and an acidified saline environment with limits defined by a DOE matrix This hypothesis was not rejected and models were developed which predicted with statistical confidence the life of the specimens.

Preliminary studies were performed in AA 7075-T6. In this study, specimens of aluminum alloy 7075-T6 were pre-exposed to an acidified saline solution. Pits nucleated by the acidified saline solution, and cracks originated from each of the pits for all specimens. Such cracks propagated until failure was reached by fracture. SEM analysis revealed additional mechanisms including subsurface pitting, subsurface cracking, tunneling and intergranular attack. Protocol for testing was based on full factorial design with two variables and two blocks. The variables studied were pre-corrosion time and stress, and the response was cycles to failure. ANOVA was used to develop models by using transformations to stabilize the variance. Three Box-Cox transformations were chosen, natural log, inverse square root, and power with lambda of 1/3. Statistical analysis revealed that these models fit the data with statistical confidence; such analysis suggests that stress has a higher detrimental impact in the fatigue life of the specimens as compared with pre-corrosion time. Statistical significant models were obtained as result of this initial study. Four manuscripts were presented for publication, one to **International Journal of Aerospace Engineering,** which has been published. Two were presented to **Corrosion, The Journal of Science and Engineering**, and another to **Corrosion Science**. One manuscript presented to **Corrosion** has been recently **accepted for publication**, while the manuscript presented to Corrosion Science was recently submitted and currently waiting for feedback.

Once the methodology was established testing was performed on AA 2024-T3, increasing the repeatability of experiments to five blocks. Corrosion pits were formed/nucleated by the exposure of aluminum alloy 2024-T3 specimens to an acidified saline solution. Such pits were identified as crack origins, which continued to grow until fracture was obtained. SEM analysis revealed additional subsurface failure modes including tunneling, subsurface cracking and pitting. Such mechanisms are extremely deleterious to the integrity of structures, since these are difficult to detect by conventional non destructive methods. Pitting is a major factor affecting the formation/nucleation of fatigue cracks. In this study the effects of corrosion time and maximum stress in the fatigue life of the specimens was evaluated. It was found that maximum stress had a greater deleterious impact to the overall fatigue life of the specimens as compared with corrosion time. ANOVA was implemented to develop models by stabilizing the variance using several Box-Cox transformations. Two transformations resulted in statistical significant models, natural log and power transformation with lambda of 1/3. Finally, fatigue data were fitted to several distribution functions, and the Weibull distribution fits the data with 95% confidence. The results from this study have been recently submitted for publication to **Corrosion - The Journal of Science and Engineering**.

Research Contribution

The following are some of the unique contributions obtained from the research reported herein:

1) A methodology for accelerated corrosion fatigue was developed for high strength aluminum alloys. Based on previous studies done by researchers at the University of Utah, modifications were done and a protocol was developed based on

electrochemical principles. In addition, in order to assure that the experiments have some degree of validity related to an operating aircraft, stress levels were used such as those exposed by fuselage bulkheads in the F-16 aircraft.

2) A statistical based methodology to assess the impact of multiple variables into the corrosion fatigue of high strength aluminum alloys was developed. Several statistical methods were used including design of experiments (DOE) to setup matrix for experimentation. Analysis of variance (ANOVA) combined with Box-Cox transformations were used to analyze the data and assess the impact of the variables into the response. Weibull distributions were also utilized to correlate the percent of life remaining in the specimens as a function of fatigue life.

3) Statistical based models were developed to predict with confidence the effects of multiple variables into the fatigue life of specimens exposed to simultaneous corrosion and fatigue. To stabilize the variance several Box-Cox transformations were examined and those that resulted in statistical valid models included inverse square root, power with lambda 1/3 and natural log.

4) Corrosion fatigue modeling is an inherently challenging undertaking, due to the many factors that are involved in this process. In addition, conventional inspection methods may be limited and inadequate for critical components since, as shown in this study, significant damage to the structures occur at the subsurface level. Development of statistical based models to predict with confidence the behavior of materials will increase our ability to predict and prevent catastrophic structural failures thereby increasing the safety of our aircraft structures.

5) Numerous studies are found in the literature which characterize qualitatively the issue of corrosion fatigue; however statistical modeling studies, such as the research presented herein are very limited.

Four manuscripts resulted from this study, one has been **published by International Journal of Aerospace Engineering**, another has been **accepted for publication by Corrosion – The Journal of Science and Engineering**, and the other two have been submitted to **Corrosion Science** and **Corrosion**, all reputable peer reviewed journals.

It is desired that the reader may find this work relevant as other subject matter experts have found it worthy of publication. Finally, the research presented herein attempts to build upon the 'shoulder of giants' in the field by presenting a unique methodology based upon statistical modeling and mechanical concepts.

Recommendations

The effects of size including area effect on corrosion, and thickness on FCG, must be studied. Evaluation with other corrosion times is desirable. One area not addressed is the effect of either prior corrosion and/or concomitant corrosion on the short crack growth region. These issues are extremely important to the overall area of model development and consideration should be given to expanding at many laboratories in the future. Application of the methodology presented herein should be expanded to other materials and environments, including alloys such as Ti-6Al - 4V.