**Title and Subtitle**

CORROSION AND FATIGUE OF ALUMINUM ALLOYS: CHEMISTRY, MICRO-MECHANICS AND RELIABILITY

**Author(s)**

Robert P. Wei

**Funding Numbers**

Grant F49620-93-1-0426

AFOSR-TR-91-0434

**Perfoming Organization Name(s) and Address(es)**

Lehigh University
Department of Mechanical Engineering and Mechanics
19 Memorial Drive West
Bethlehem, PA 18015

**Sponsoring/Monitoring Agency Name(s) and Address(es)**

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Aerospace Sciences/NA
Building 410
Bolling Air Force Base, DC 20332-6448

**Supplementary Notes**

AFOSR/NA Program Manager - Dr. Walter F. Jones

**DISTRIBUTION/AVAILABILITY STATEMENT**

Approved for public release; distribution unlimited.

**ABSTRACT (Maximum 200 words)**

Lehigh University undertook a multidisciplinary program of research to develop a basic mechanistic understanding of localized corrosion and corrosion fatigue crack nucleation and growth in aluminum alloys used in aircraft construction, and to begin to formulate mechanistically based probability models for reliability assessments based on this understanding. The objectives of the program are: (1) the development of basic understanding of the processes of localized corrosion and corrosion fatigue crack nucleation and growth in high strength aluminum alloys used in airframe construction, (2) the formulation of kinetic models for these elemental processes, and (3) the integration of these models into probabilistic models that can provide guidance in formulating methodologies for service life prediction. The effort included a study of the feasibility for incorporating the mechanistically based probability models into appropriate fatigue analysis codes (such as MODJRO). This final technical report summarizes research completed under this grant and reflects contributions from the companion program sponsored by the Aging Airplanes Program of the Federal Aviation Administration (FAA) under Grant No. 92-G-0006.

**Subject Terms**

This document is available to the public through the National Technical Information Service (NTIS), Springfield, Virginia 22161, 2024-T3 and 7075-T651 alloys

**Security Classification of Report**

UNCLASSIFIED

**Security Classification of This Page**

UNCLASSIFIED

**Security Classification of Abstract**

UNCLASSIFIED

**LIMITATION OF ABSTRACT**

UL
TO: AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
Aerospace Sciences/NA
Building 410
Bolling Air Force Base, DC 20332-6448
ATTN: DR. WALTER F. JONES, PROGRAM MANAGER

FROM: DR. ROBERT P. WEI, PRINCIPAL INVESTIGATOR
Department of Mechanical Engineering & Mechanics
327 Sinclair Laboratory
LEHIGH UNIVERSITY
7 Asa Drive
Bethlehem, PA 18015

REFERENCE: AFOSR Grant No. F49620-93-1-0426
"Corrosion and Fatigue of Aluminum Alloys: Chemistry, Micro-
mechanics and Reliability"

SUBJECT: FINAL TECHNICAL REPORT FOR PERIOD 1 JULY 1993
TO 31 MARCH 1997

DATE: 12 May 1997
SUMMARY

Lehigh University undertook a 3-year, multidisciplinary program of research, under AFOSR Grant No. F49620-93-1-0426, to develop a basic mechanistic understanding of the material degradation processes of localized corrosion and corrosion fatigue crack nucleation and growth in aluminum alloys used in aircraft construction, and to begin to formulate mechanistically based probability models for reliability assessments based on this understanding. This grant was a part of the AFOSR University Research Initiation Program, and was extended for a fourth year under AFOSR Grant No. F49620-96-1-0245. Research was initiated on 1 July 1993, with the experimental efforts focused on the 7000 series aluminum alloys, and is enhanced by an ongoing program on corrosion and fatigue of 2000 series aluminum alloys sponsored by the Aging Airplanes Program of the Federal Aviation Administration (FAA) under Grant No. 92-G-0006. The objectives of the program are: (1) the development of basic understanding of the processes of localized corrosion and corrosion fatigue crack nucleation and growth in high strength aluminum alloys used in airframe construction, (2) the formulation of kinetic models for these elemental processes, and (3) the integration of these models into probabilistic models that can provide guidance in formulating methodologies for service life prediction. As an addition to the program, requested by the Flight Dynamics Directorate of AF Wright Laboratory, the feasibility for incorporating the mechanistically based probability models into appropriate fatigue analysis codes (such as, MODGRO and AFGROW) was examined. This final technical report summarizes research completed under Grant F49620-93-1-0426 over the period 1 July 1993 to 31 March 1997, and reflects contributions from the companion FAA sponsored program. Reprints and preprints of technical publications that resulted from these efforts are provided as a separate submission to the AFOSR Program Manager, and are available upon request to the Principal Investigator at Lehigh University.
1.0 Background and Objectives

Performance, reliability, maintainability, and life cycle cost of aircraft and other aerospace systems depend to a large extent on those factors that affect the durability of airframe and propulsion system components. Durability is governed principally by material degradation through localized corrosion and corrosion fatigue crack nucleation and growth. Accordingly, to support the maintenance of existing aerospace structures (such as those of C/KC-135, C-141, C-5A, F-15, F-16 and T-38) and the development of Air Force structures of the 21st century, a methodology is needed for making stochastically tight estimates of structural life for conditions that are beyond the range of typical supporting data. Such a methodology would improve upon those employed currently in design, which are deterministically or statistically based and are only suitable for making interpolations within the bounds of existing data. The development of this methodology requires a quantitative understanding, characterization and modeling of the elemental processes of damage, and the integration of the various models into a suitable probabilistic framework for service life prediction.

Lehigh University proposed and undertook a 3-year, multidisciplinary program of research, under AFOSR Grant No. F49620-93-1-0426, to develop a basic mechanistic understanding of the material degradation processes of localized corrosion and corrosion fatigue crack nucleation and growth in aluminum alloys used in aircraft construction, and to begin to formulate mechanistically based probability models for reliability assessments based on this understanding. This grant was a part of the AFOSR University Research Initiation Program, and was extended for a fourth year under AFOSR Grant No. F49620-96-1-0245. Research was initiated on 1 July 1993, with the experimental efforts focused on the 7000 series aluminum alloys, and is enhanced by an ongoing program on corrosion and fatigue of 2000 series aluminum alloys sponsored by the Aging Airplanes Program of the Federal Aviation Administration (FAA) under Grant No. 92-G-0006.

The objectives of the program are: (1) the development of basic understanding of the processes of localized corrosion and corrosion fatigue crack nucleation and growth in high strength aluminum alloys used in airframe construction, (2) the formulation of kinetic models for these elemental processes, and (3) the integration of these models into probabilistic models that can provide guidance in formulating methodologies for service life prediction. As an addition to the program, requested by the Flight Dynamics Directorate of AF Wright Laboratory, the feasibility for incorporating the mechanistically probability models into appropriate fatigue analysis codes (such as, MODGRO and AFGROW) was examined.

The development of damage is illustrated schematically in Fig. 1, and is shown in a flow diagram in Fig. 2. The early stage is dominated by corrosion, in the form of pitting or exfoliation, and the later stage by corrosion fatigue crack growth. Within the context of these mechanisms, an upper bound of damage is to be defined in terms of structural reliability and damage tolerance considerations for mandating repairs. The research was focused, therefore, on the quantitative understanding and characterization, and kinetic modeling, of the following elemental processes:
Onset of localized corrosion damage (particularly, mechanisms and kinetics of pit nucleation and growth, and exfoliation).
- Transition from pitting to fatigue crack growth.
- Early stages of corrosion fatigue crack growth (short-crack regime).
- Corrosion fatigue crack growth.

Formulation of a predictive model must include the probabilistic contributions from material properties and key variables on the rate of corrosion (particularly, pit nucleation and growth) and corrosion fatigue crack growth, and on the transition from corrosion to cracking.

The principal issues addressed are as follows:

- Identification and verification of key internal and external variables that control each of the aforementioned unit processes for corrosion and corrosion fatigue cracking and determination of the stochastic nature of each process.
- Quantification of the probability distribution function (including time variance) of each of the key variables.
- Development of a quantitative understanding of the rate controlling step and mechanism for each damage process, and formulation of a mechanistic (deterministic) model for each that describes the functional dependence on the key variables.
- Integration of mechanistic models and probability distribution functions, and formulation of mechanistically based probability models for life prediction and reliability assessment.

Research completed under Grant F94620-93-1-0426 is briefly summarized. Reprints and preprints of publications that have resulted from this program are available upon request (one set has been provided to the AFOSR Program Manager).

2.0 Summary of Research

Efforts under this grant, and the companion FAA sponsored program, included (i) investigations of pitting corrosion and corrosion fatigue in the 2024-T3 and 7075-T651 (bare) alloys, principally at room temperature; (ii) formulation of statistical models for particle and pit distribution and pit growth; and (iii) development of a mechanistically based probability approach for predicting (pitting) corrosion and corrosion fatigue life. In addition, preliminary work was carried out to examine the feasibility for incorporating information developed under these programs into the structural integrity/damage tolerance analysis codes of the Air Force Wright Laboratory. Research findings in the various areas of research are briefly summarized, and publications and presentations, as well as graduate degrees that resulted from these AFOSR and FAA sponsored programs are listed in Sections 3.0 and 4.0.
2.1 Pitting Corrosion

Studies of localized corrosion were focused upon pitting corrosion as a precursor to corrosion fatigue cracking in the 2024-T3 and 7075-T651 (bare) alloys, and were carried out principally at room temperature in 0.5M NaCl solutions. Initial results showed that localized corrosion (pitting) resulted from galvanic coupling of the matrix with micro-constituent particles in the alloys. Pitting was found to depend strongly on temperature and solution pH. The pitting rate increased with increasing temperature (corresponding to an activation energy of about 40 kJ/mol), and was higher at more basic pH levels. The process appeared to be very complex and involved 3-D interactions with the micro-constituent particles. Corrosion sensitivity appeared to be orientation dependent; being more severe in the thickness orientation (the orientation that is more representative of the surface of a rivet or fastener hole) because of local segregation of the micro-constituent particles.

To better understand micro-constituent-induced localized (pitting) corrosion, more detailed studies of pitting were carried out on the transverse sections of these alloys at room temperature, by in situ monitoring and by post-corrosion examinations using optical and scanning electron microscopy. A replication technique was developed to facilitate examinations of the morphology of corrosion pits in three dimensions, and measurements of pitting kinetics. Identification of the micro-constituent particles and observations of particle-induced galvanic corrosion were carried out by transmission electron microscopy (TEM), along with measurements of galvanic current between pure aluminum and model compounds that are representative of the composition of certain micro-constituent particles. Results from these studies are briefly summarized.

Constituent Particles -- Two types of constituent particles were identified initially by energy dispersive x-ray spectroscopy (EDS) in the scanning electron microscope (SEM): Type A particles that are anodic and Type C particles that are cathodic with respect to the matrix. In the 2024-T3 alloy, Type A particles are those that contain Al, Cu and Mg, and Type C, those with Al, Cu, Fe and Mn. Types A and C particles in 7075-T651 alloy, on the other hand, contain Al, Cu, Mg and Zn, and Al, Cu, Fe, Cr, Mn and Zn, respectively. The density of these particles (with projected surface area greater than 1 μm²) was about 3,000 particles/mm² in the 2024-T3 alloy, versus about 1,500 particles/mm² in the newer 7075-T651 alloy. The distributions in particle sizes for the two alloys are similar. Elemental maps showed that nearly 75% of the micro-constituent particles in the 2024-T3 alloy are Type A, whereas Type C constituted over 80% of the particles in the 7075-T651 alloy. More detailed characterizations by analytical electron microscopy (AEM) and X-ray microprobe analysis showed Type A particles in the 2024-T3 alloy to be principally CuAl₂ and CuMgAl₂. They tended to be small and were nearly equiaxed. Type C particles, on the other hand, were identified with complex intermetallics of the type (Fe,Mn)₅Si(CuAl)₂₉, and appear to be modified forms of Fe₂SiAl₈ or Mn₃SiAl₁₀. They tended to be larger, often elongated and aligned along the rolling direction. In the 7075-T651 alloy, Type C particles were identified as orthorhombic Fe₄CuAl₁₅ that contain small amounts of chromium, manganese and zinc. The remaining particles in this alloy are principally amorphous SiO₂, which are inert. The compositions of these particles are consistent with the results of X-ray microprobe analyses.
**Pitting Corrosion** -- Pitting in these alloys, in 0.5M NaCl solutions, showed that localized corrosion (pitting) was associated with *micro-constituent particles*. A distinction was drawn between *anodic* (Type A) and *cathodic* (Type C) particles; with anodic particles tending to dissolve themselves, while cathodic particles promoting dissolution of the adjacent matrix. The pitting process is very complex and involves 3-D interactions with constituent particles. Two modes of pitting corrosion were clearly identified: namely, (i) *general* pitting over the specimen surface, and (ii) *severe* localized pitting at selected sites. General pitting occurs almost immediately upon specimen immersion, and led to the formation of small, shallow pits over the entire specimen surface. Each pit was clearly identified with a constituent particle on the specimen surface, with particle or matrix dissolution determined by the nature (anodic or cathodic) of the particle. Severe localized pitting at selected sites was attributed to the interactions of the matrix with a *cluster or clusters* of constituent particles. The particle clusters form local galvanic cells to sustain continued matrix dissolution, and resulted in the larger and deeper pits.

Figure 3 shows scanning electron micrographs (SEM micrographs) of the cross section of pits formed from such clusters of constituent particles, along with an inset of the pits at the specimen surface. The larger of the two pits is approximately 500 μm long and 70 μm wide at the surface, and approximately 300 μm deep at this section; the overall shape reflects the planar distribution of constituent particles in this alloy. A comparison of the deeper severe pit in Fig. 3 with the SEM microfractograph of a fatigue crack origin (a corrosion pit represented by the dark region at the center of the microfractograph) in Fig. 4 shows that their overall features are nearly identical. The associated surface features of the fatigue origin (not shown) are also identical to those shown in the inset in Fig. 3. Similar comparisons clearly identify severe localized pits as nuclei for corrosion fatigue cracking.

The 3-dimensional nature of the severe pits is captured by the comparison of the corroded LS (longitudinal-thickness) surface of a 1.6-mm-thick 2024-T3 aluminum alloy sheet, after 500 h exposure to 0.5M NaCl solution, with the corresponding epoxy replica in Fig. 5. Each severe pit seen on the corroded surface is clearly associated with one on the replica (designated from 1 to 17 in Figs 5a and 5b). Many detailed features of the corroded surface may be seen on the surface of the replica; compare, for example, the lightly corroded (cathodically protected) region surrounding each pit and the many small pits on the surface (Figs 5a and 5b). The severe pits tend to be concentrated (>50%) along the mid-thickness region of the sheet, and are narrow and long, and substantially larger than the surface opening. For example, the surface length and width of pit 4 are 230 and 80 μm, respectively, as compared to an overall length and width of over 430 by 130 μm shown by the replica. The height (depth of penetration) of the pits ranged from about 100 to over 300 μm. The replicas show substantial corrosion attack beneath the specimen surface, and potential link up of several pits into a single large pit of a complex shape (see, for example, pits 5, 6 and 7). They confirm that surface measurements alone would underestimate the extent and kinetics of pitting attack.

SEM micrographs of the replica of pit 2, in plan and side views, are shown at a higher magnifications in Fig. 6. Figure 6 shows the typically complex form of a severe corrosion pit. The appearance of the replica is consistent with the postulated role of constituent particles in promoting
pitting corrosion in the high-strength aluminum alloys. The individual rounded features are believed to correspond to galvanic corrosion of the matrix by the cathodic micro-constituent particles in the alloy, and the overall planar appearance is attributed to the planar array of these particles in the rolled sheet. The open space seen in Fig. 6b suggests the role corrosion played around a particle (or a cluster of particles) at the surface in allowing the electrolyte to penetrate into the alloy and effect substantial corrosion beneath the surface. The 3-dimensional nature of these pits is best seen through the use of stereo imaging techniques (not shown here). The shape of the replica for pit 2 might be likened to that of one-half of a pecan or walnut, with the center representing the small pit opening at the surface and the rest the cavernous pit below the surface.

To provide unambiguous confirmation for the role of constituent particles in promoting pitting, a series of experiments were carried out with the aid of transmission electron microscopy (TEM) on the 2024-T3 and 7075-T651 aluminum alloys. The constituent particles were first identified and the TEM (thin foil) samples were then repeatedly immersed in 0.5M NaCl solution and re-examined for galvanic corrosion attack. Figure 7 shows a pair of TEM micrographs to illustrate the typical galvanic corrosion of the matrix that results from the coupling with a cathodic constituent particle in the 7075-T651 alloy. The larger semi-circular region in Fig. 7a represents oxides that had been left behind by the corrosion. The smaller semi-circular depression represents the original position of the particle in the thin foil which had fallen out during corrosion. The relative positions of the particle and the corroded region are shown in Fig. 7b, with the particle photographically superimposed back into its original position. The size of the corroded region (about 5X the particle size) attests to the "throwing power" of the particle.

For the 2024-T3 alloy, CuMgAl2 and CuAl2 are anodic with respect to the matrix; CuAl2, however, is cathodic relative to pure aluminum. The (Fe,Mn) containing particles are cathodic to the alloy and pure aluminum. The TEM studies showed matrix dissolution around the (Fe,Mn) containing particles as a result of galvanic coupling between the particle and the matrix. Extensive matrix dissolution was also observed around the nominally anodic CuAl2 particles as a result of plating of Cu back onto the particles during corrosion, Fig. 8. Although the CuMgAl2 particles dissolved rapidly as a result of galvanic coupling to the matrix, some matrix dissolution was also noted as a result of Cu deposition, or Cu enrichment through preferential dissolution of Al and Mg from these particles, Fig. 9. The extent of dissolution around CuAl2 and the (Fe,Mn) containing particles were comparable to that around the Fe4CuAl2 particles in 7075-T651. Matrix dissolution was less around the CuMgAl2 particles. The fact that it can take place around all or most of the micro-constituent particles provides an important bridge for the development of the larger severe pits.

Dissolution current densities were estimated based on the estimated amounts of material removed by galvanic corrosion and reflected anodic or cathodic control by the particles. For the anodic (CuMgAl2) particles, the estimated current density was about 0.18 mA/cm² at room temperature. The estimated values were about 0.2 mA/cm² and 0.04 mA/cm², respectively, for CuAl2 and the (Fe,Mn) containing particles.

To better understand particle induced corrosion, the galvanic coupling between a model compound (FeAl3) and high-purity aluminum was investigated. Preliminary measurements at
room temperature in a 0.5M NaCl solution (exposed to air) show that the galvanic current density varied with the ratio of surface areas of FeAl₃ (cathode) and Al (anode), Fig. 10. When the cathodic area is small, current flow is limited by rate of reactions at the cathodic surface and is reflected by a constant cathodic current density. When the cathodic surface is large relative to the anodic surface, on the other hand, current limitation is transferred to the anode (or Al) and the process proceeded at a constant anodic current density. For the FeAl₃-Al couple, the limiting cathodic and anodic current densities were found to be about 0.038 and 0.031 mA/cm², respectively. The limiting cathodic current density for the FeAl₃-Al couple is consistent with that of the cathodic particles in the 2024-T3 and 7075-T651 alloys.

**Mechanistic Models** -- The findings confirm the original postulate for particle induced pitting in these aluminum alloys. Based on these, and the previous SEM observations, a conceptual model for corrosion induced by a single particle is proposed, Fig. 11. A conceptual model for pit growth associated with a cluster of particles is depicted in Fig. 12. The multiparticle interactions within a pit (or occluded region surrounding the pit), however, make the problem much more challenging. Because this severe localized pitting is clearly linked to corrosion fatigue crack nucleation, emphasis will be placed on the development of mechanistic understanding and modeling of this process during the remainder of the current program and in the proposed continuation of research. The quantitative, mechanistic model will need to incorporate potential distribution around the particle, and then integrated into a model for severe pitting that involves clusters of micro-constituent particles.

### 2.2 Transition from Pitting to Fatigue Crack Growth

Studies of the 2024-T3 and 7075-T651 alloys showed that fatigue failure, by-and-large, resulted from a single nucleation site. Hence, a dominant flaw model for corrosion and corrosion fatigue would appear appropriate. The pit-to-crack transition size (or crack nucleation size), however, was found to depend on the cyclic-load frequency; being larger at lower frequencies. This frequency dependence reflected competition between pitting corrosion and fatigue. Corrosion fatigue crack nucleation, therefore, must be understood in terms of the competition between pitting and fatigue crack growth, and is characterized by the transition to fatigue crack growth from a growing pit. Two criteria for this transition have been proposed and validated. They are: (i) the cyclic stress intensity range (ΔK) for an equivalent crack must exceed the fatigue crack growth threshold ΔKₘₙ, and (ii) the time-based fatigue crack growth rate must exceed the pit growth rate; i.e.,

\[ ΔK \geq ΔKₘₙ \quad \text{and} \quad \left( \frac{dc}{dt} \right)_{\text{crack}} \geq \left( \frac{dc}{dt} \right)_{\text{pit}} \]

The use of ‘c’ in the growth rate criterion gives recognition to the fact that the aspect ratios of most of the pits (or equivalent cracks) would lead to a higher ΔK at the surface.

To provide a graphical view of these criteria, a corrosion/fatigue map is proposed which delineates the transition ΔK (ΔKₘₙ) in relation to the cyclic load frequency f, with the applied
cyclic stress range as a parameter. The map is constructed by assuming a constant volumetric rate law for pit growth and a power-law for fatigue crack growth, with an exponent n, and is shown schematically in Fig. 13. The transition $\Delta K_{tr}$ is given by one of the following relationships, which divides the $\Delta K$ versus $1/f$ space into two regions in which either fatigue crack growth or pit growth predominates:

$$\Delta K_{tr} = \Delta K_{th}$$

$$\Delta K_{tr} = \left[ \frac{\pi (1.12 k_i \Delta \sigma)^4 C_p \beta^2_{tr} \Phi_{tr}^4}{2 C_F} \right]^{\frac{1}{n+4}} \left( \frac{1}{f} \right)^{\frac{1}{n+4}}$$

where, $k_i$ is the stress concentration factor of the hole; $\Delta \sigma$ is the applied cyclic stress range; $C_p$ and $C_F$ are the pit and fatigue crack growth rate coefficients, respectively; and $\beta_{tr}$ and $\Phi_{tr}$ are the aspect ratio and shape factor (elliptical integral) for the equivalent semi-elliptical crack at transition. The first of these relationships simply reflects exceedance of the fatigue crack growth threshold ($\Delta K_{th}$). The second, on the other hand, reflects a higher value of $\Delta K_{tr}$ required by rate competition. Data on pit-to-crack growth transition for the 2024-T3 alloy are shown in Fig. 14 to illustrate the efficacy of this representation.

Nucleation of fatigue crack growth from pre-corroded (i.e., pre-pitted) specimens provides additional insight for the transition criteria. A series of experiments was performed by Harmsworth to study the influence of pre-corrosion on the lives of a 2024-T4 aluminum alloy in rotating bending fatigue. The reported data include the pre-corrosion times, pit depths and subsequent fatigue lives at a constant stress amplitude $\Delta \sigma$ of 179 MPa. These data may be used to examine the correlation between the experimentally observed fatigue lives and crack growth lives predicted on the basis of the initial pit depths and appropriate growth law.

The pit is assumed to be hemispherical in shape and to be equivalent to a semi-circular surface crack of the same radius. For these estimates, an axial-load approximation is used. Crack growth is assumed to follow a power-law of the form, with explicit recognition for a semi-circular surface crack:

$$\frac{da}{dN} = C_F \Delta K^n = C_F \left( 2.2 \Delta \sigma \sqrt{\frac{a}{\pi}} \right)^n$$

where $C_F$ is crack growth rate coefficient and n is the power-law exponent. Because the initial pits are very small, the final crack size at fracture can be neglected, and the predicted fatigue (crack growth) life is given simply by:

---

\[ N_{pred} = \frac{2\pi^{n/2}}{2\pi^{n/2}} C_f \Delta \sigma \sigma^{(n-2)/2} \]

where \( a_o \) is the radius of the initial pit. Using \( n = 3.5 \) (estimated from data on the 2024-T3 alloy), a one-to-one correlation between the predicted and actual lives is obtained for \( C_f = 1.3 \times 10^{11} \) (m/cyc)(MPa\( \sqrt{m} \))\(^{-3.5} \); a value that is reasonably consistent with available data (Fig. 15). The key message from this correlation is that fatigue cracks appear to grow immediately once the nucleation criteria are satisfied, which provides support for the proposed transition (nucleation) criteria. Nucleation time, if present at all, may be reasonably neglected.

2.3 Short-Crack Growth

Studies of the transition from pitting to corrosion fatigue crack growth (or crack nucleation) suggested that the pit size at transition is in the range of 40 to 200 \( \mu m \) (or 0.04 to 0.2 mm). The extent of fatigue crack growth of interest (for example, in fuselage lap joints), on the other hand, is on the order of a few millimeters. As such, characterization and modeling of the early stage (or chemically short regime) of corrosion fatigue crack growth is important to the accurate and reliable assessment of service lives of aircraft structures.

Experiments were performed to study the fatigue crack growth response of 1.6-mm-thick 2024-T3 (bare) alloy sheet in 0.5M NaCl solutions at room temperature, using single-edge-cracked tension (SEC(T)) specimens tested under constant stress intensity range (\( \Delta K \)) conditions at 10 Hz. The relationship between crack growth rate and crack length (0.5 to 15 mm) was determined at \( \Delta K \) of 4, 5, 6, 7, 8 and 10 MPa\( \sqrt{m} \), with \( R = 0.1 \). Three dissolved oxygen levels ([\( O_2 \]) = 0, 7 and 30 ppm) were investigated. Experiments in high-purity oxygen and water vapor were also conducted to provide for comparison.

The results showed no crack length dependence (i.e., no short-crack effect) in high-purity oxygen and water vapor, and in deaerated solution ([\( O_2 \]) = 0 ppm) (see Fig. 16 for example). The crack growth rates, however, showed a strong influence of environment and were nearly 10 times faster than those in high-purity oxygen. Chemically short-crack growth behavior was observed in some of the aqueous environments. The behavior is quite complex and depends on \( \Delta K \) and dissolved oxygen concentration (see Figs 17 and 18). The effect manifested itself in increased crack growth rates at a crack length of 0.5 mm, by as much as a factor of two at the lower \( \Delta K \) levels (see, for example, data for \( \Delta K = 5 \) MPa\( \sqrt{m} \) in Figs 17 and 18), and in a subsequent decrease to the long-crack rates at crack lengths that depended on \( \Delta K \). The short-crack effect gradually disappeared at higher \( \Delta K \) levels; the particular level depended on oxygen concentration. The same pattern is observed for 7075-T651 aluminum alloy.

Fractographic examinations showed no noticeable differences in the micromechanisms for crack growth of short and long cracks, and between water vapor and aqueous solutions. These observations are consistent with a single cracking (hydrogen embrittlement) mechanism, and showed that the effect resided with the external chemical environment. Its absence in the deaerated solution strongly indicates that the effect is associated with dissolved oxygen near the
crack tip, which altered the kinetics of electrochemical reactions and the subsequent embrittlement. A model for estimating the dissolved oxygen concentration at the crack tip was developed, based on consideration diffusive and convective transport of oxygen and other species, as well as oxygen reduction along the crack surfaces. The predicted reduction in oxygen concentration correlated reasonably well with the observed effect of crack length. The model, however, was not able to account for the disappearance of short-crack effect with increasing ΔK.

Because much of the corrosion fatigue life is expected to be spent in the short-crack regime (i.e., from a nucleating corrosion pit to several millimeters), the crack growth response can significantly influence the service lives of aircraft structures. This is task, therefore, is being continued under Grant F49620-96-1-0245.

2.4 Statistical Modeling of the Spatial Distribution of Constituent Particles

Because particle-induced pitting has been identified as the precursor for corrosion fatigue crack growth, information on the spatial distribution of constituent particles and the ability to estimate the probability for encountering a certain size or group of particles becomes important to a mechanistically based probability method for life prediction. This effort is focused, therefore, on the characterization and statistical modeling of the spatial distributions (relative locations and sizes) of these particles in the alloy, prior to and during pitting corrosion.

Extensive data analysis has confirmed that the particles tend to be clustered. On the rolling (LT) surface a more regular pattern is apparent after corrosion. A schematic representation of the spatial pattern of particles before corrosion is shown in Fig. 19. This diagram was generated by using a circular disk, with an area equal to the particle area about its centroid, to represent each of the particles observed metallographically. Since the spatial distribution of the particles is a geometrically dependent stochastic process, advanced estimation techniques using the first and second order properties of spatial point processes were also used to examine the data. Figure 20 is a plot of the second order properties, which confirms the clustering of particles and the fact that the distribution of particle-induced pits become more regular as corrosion progresses.

It is recognized that the extent and distribution of severe pit are determined by the size and distribution of particle clusters. Recognizing further that nearly all of the micro-constituent particles behave cathodically, and that they respond differently (i.e., having different galvanic current densities) during corrosion, further efforts need to be directed at characterizing and modeling precisely the spatial distribution of each type of micro-constituent particles. Particular attention will be given also to characterizing and modeling the clustering of particles in the alloy (including the number, size, shape, and chemical composition of the particles in the clusters). This effort is being continued under Grant F49620-96-1-0245.

2.5 A Mechanistically Based Probability Approach to Life Prediction

A dominant flaw, probability model for pitting and corrosion fatigue has been developed. This model assumes pitting corrosion proceeded at a constant volumetric rate. Transition from
pit (hemispherical) to crack (semi-circular) is based on a matching of the stress intensity factor for an equivalent semi-circular crack against the fatigue crack growth threshold. A power-law model is used to represent subsequent fatigue crack growth. The models for the elemental processes are assumed to capture some of the key mechanistic features, and provide reasonable predictions of response. The overall model incorporates initial defect (or particle/cluster) size, corrosion rate, fatigue crack growth rate coefficient, and fatigue crack growth threshold (ΔKth) as random variables, and permits examinations of the contribution of each of these variable to the distribution in life. This model has been modified to account for corrosion and fatigue from an open circular hole, with the inclusion of a further transition from the semi-circular crack at an open-hole to a through-thickness crack.

It is recognized that a fatigue crack would nucleate from the largest (particle nucleated) pit that is present at the region of highest stress, statistical modeling of pit nucleation and growth has been initiated, and is focused upon the development of a simplified model of pit growth due to the clustering of particles. Pit growth begins from a surface particle in a cluster, and is governed by the composition and relative positions of particles in the cluster, and the size of the cluster. The goal is to develop an approximation for the cumulative distribution function for the time of the occurrence of a critical sized pit for use in age-dependent reliability estimations, and for the spatial distribution of pit (or corresponding crack) sizes at a given time for use in MSD analysis. This effort is being continued under Grant F49620-96-1-0245.

2.6 Interactions with Wright Laboratory

To facilitate the reduction of mechanistic understanding developed under these programs to practice, a new task was added to the AFOSR program in 1994 with funding from the Flight Dynamics Directorate at the Air Force Wright Laboratory to define work that would be needed to incorporate models developed under these program into the current Air Force structural integrity and durability analysis methodologies, with specific emphasis on MODGRO and PROF. The feasibility for incorporating a mechanistically based probability approach into the PC-based fatigue life analysis program MODGRO, to include key internal and external variables (in addition to initial crack size), was assessed. This study included examinations of the influences of temperature, material properties, the coupling of fatigue loading and thermal profiles, and load sequencing on fatigue lives under spectrum loading. A power-law model, modified into an Arrhenius form, was used to represent fatigue crack growth and the influence of temperature. For simplicity, only the growth rate coefficient and initial crack size were included as key internal random variables. Load variations were introduced through the use of the FALSTAFF spectrum as a reference, and through the generation of other flight-load spectra to examine sequencing effects. The influences of temperature and thermal-mechanical coupling were assessed by incorporating the coordinated thermal profiles (ENSTAFF) into MODGRO. The cumulative distributions (CDFS) of fatigue lives were computed using Monte Carlo simulations. A sampling of results is shown in Figs 21 and 22.

Figure 21 shows the CDF for fatigue lives at room temperature. The discrete steps in the CDF reflects the typically deterministic nature in which FALSTAFF is applied, in that the "randomly" arranged sequence of 200 flight-loads is used repeatedly in fatigue testing or analysis.
The steps in the CDF clearly corresponded to deterministic encounters with peak loads in the spectrum associated with specific flight profiles. Re-randomizing the 200-flight spectrum in FALSTAFF altered the predicted fatigue lives, but retained the deterministic character of the results. Discrete steps in the CDFS can be eliminated by randomly selecting flights (e.g., from 30×200 flights from FALSTAFF, without replenishment) to construct ‘truly’ random load spectra. The use of these random spectra, however, reduced the mean fatigue life by about 30 percent. The influence of temperature and the combined effects of variations in load and temperature are illustrated in Fig. 22. These results indicate that temperature can significantly affect fatigue life. The influences of temperature are manifested directly through its effect on crack growth rates, and indirectly through its effect on yield strength and its role in crack growth retardation (i.e., load-interaction effects).

These results demonstrate the viability and potential value of the mechanistically based probability approach for service life prediction, and indicate that understanding developed under these and similar basic research programs can be readily transferred to ongoing Air Force support activities. Further research is needed to develop improved mechanistic models for fatigue crack growth (in both the short- and long-crack regimes), and to incorporate a mechanistically based model for pitting into the fatigue analysis programs.

3.0 Presentations and Publications

Presentations and publications based on results from this program and the FAA sponsored program are given in the following subsections.

3.1 Presentations


"Transition From Pitting Corrosion to Fatigue Crack Growth in a 2024-T3 Aluminum Alloy", **G. S. Chen**, K.-C. Wan, M. Gao and R. P. Wei, TMS Materials Week '95, October 29-November 2, 1995, Cleveland, OH.
"In Situ Monitoring of Pitting Corrosion in Aluminum Alloys", Chi-Min Liao, Ming Gao and Robert P. Wei, TMS Materials Week '95, October 29-November 2, 1995, Cleveland, OH.

"Mechanical and Environmental Effect on Growth of Short-Fatigue-Cracks in a 2024-T3 Aluminum Alloy", K.-C. Wan, G. S. Chen, M. Gao and R. P. Wei, TMS Materials Week '95, October 29-November 2, 1995, Cleveland, OH.


3.2 Publications


Chi-Min Liao, Jean Marc Olive, Ming Gao and Robert P. Wei, "In Situ Monitoring of Pitting Corrosion in a 2024 Aluminum Alloy", submitted to Corrosion.


4.0 Personnel and Degrees Granted

Faculty and Staff:

Wei, R. P., Professor, Mechanical Engineering & Mechanics. Dr. Wei served as Principal Investigator for the program and had overall responsibility for program coordination and technical direction. (He completed two 3-year terms as Chairman and returned to the faculty at the end of June, 1996)

Harlow, D. G., Professor, Mechanical Engineering & Mechanics. Dr. Harlow had responsibility for probability modeling.

Gao, M., Principal Research Scientist, Zettlemoyer Center for Surface Studies. Dr. Gao addressed the microstructural and chemical aspects of corrosion and corrosion fatigue.
Postdocs, Research Scientists and Visiting Scientists:

Chen, Gim-Syang (non-U.S. citizen), Ph.D., Research Scientist, Zetlemoyer Center for Surface Studies. Dr. Chen contributed to the microstructural and chemical aspects of pitting corrosion and crack nucleation.

Chen, Shuchun (non-U.S. citizen), Ph.D., Postdoctoral Research Associate, Zetlemoyer Center for Surface Studies. Dr. Chen contributed to the microstructural aspects of the program.


Graduate Students and Degrees (including those supported by FAA):

Degrees Granted:


Continuing Students:


Liao, Chi-Min (non-U.S. citizen), Ph.D. in Materials Science & Engineering, expected July 1998 (supported by China Steel Corp., Taiwan). Dissertation: “Particle-Induced Pitting Corrosion of Aluminum Alloys”.


Undergraduate Summer Interns:

Figure 1: Schematic representation of pitting corrosion and corrosion fatigue.

Figure 2: Flow diagram showing the overall processes for corrosion and fatigue damage.
Figure 3: SEM micrograph of the cross-section of severe corrosion pits in a 2024-T3 alloy (TS) surface along with an inset, showing the corresponding surface appearance of the pits.

Figure 4: SEM microfractograph of fatigue fracture surface of a 2024-T3 alloy showing a severe corrosion pit as the crack nucleus.
Figure 5: (a) The LS surface of a 2024-T3 aluminum alloy specimen after 500 h in 0.5M NaCl solution, and (b) the corresponding 3-D replica.

Figure 6: Replica corresponding to pit 2 in Fig. 5: (a) plan (bottom) view, and (b) elevation (side) view; relative to the original pit.
Figure 7: TEM micrograph of 7075-T651 aluminum alloy showing oxide left behind by particle-induced corrosion: (a) residual oxide, and (b) reconstructed image showing position of original particle.
Figure 8: Low and high magnification TEM micrographs showing a CuAl₂ particle and its environs in a 2024-T3 aluminum alloy (a) before and (b) after 180 min. (cumulative) immersion in 0.5M NaCl solution at room temperature. Inset in (b) is an EDS spectrum that shows Cu to be the principal component in the corrosion product film.
Figure 9: TEM micrographs showing a CuMgAl$_2$ particle and its environs in a 2024-T3 aluminum alloy (a) before and (b) after 15 min. immersion in 0.5M NaCl solution at room temperature.
Figure 10: Comparison of *anodic* and *cathodic* current densities as a function of cathode-to-anode surface area ratio for an Al (*anode*) - FeAl$_3$ (*cathode*) couple in 0.5M NaCl solution at room temperature.
Figure 11: Conceptual models of particle-matrix interactions (local corrosion) for (a) a cathodic and (b) an anodic particle.
Figure 12: Schematic diagram of a conceptual model for pitting in the transverse orientation involving matrix dissolution around clusters of cathodic (Type C) constituent particles.
Figure 13: Schematic of a proposed corrosion/fatigue map showing the relationship between stress intensity factor range and frequency with the applied cyclic stress range as a parameter.

Figure 14: The relationship between the stress intensity factor range of equivalent cracks at fatigue crack nucleation and the frequency of the applied cyclic stress.
Figure 15: A comparison between observed fatigue life and that predicted from the initial pit size using a crack growth law.

Figure 16: Effect of $\Delta K$ level on crack growth response in a deaerated 0.5M NaCl solution, with $[O_2] = 0$ ppm.
Figure 17: Effect of $\Delta K$ level on crack growth response in an aerated 0.5M NaCl solution, with $[O_2] = 7$ ppm, showing chemically affected short crack growth.

Figure 18: Effect of $\Delta K$ level on crack growth response in an aerated 0.5M NaCl solution, with $[O_2] = 30$ ppm, showing chemically affected short crack growth.
Figure 19: Locations and equivalent areas of particles in the rolling (LT) plane of a 2025-T3 aluminum alloy prior to corrosion.

Figure 20: Plot of second order properties for the distribution of particles/pits in a 2024-T3 aluminum alloy.
Figure 21: CDF for fatigue lives at 298 K with FALSTAFF spectrum showing discrete steps at points associated with repeated applications of the same spectrum.

Figure 22: CDF for fatigue lives showing the influences of temperature and temperature spectrum (ENSTAFF) under FALSTAFF spectrum loading.