

Review Article

Exfoliation Corrosion and Pitting Corrosion and Their Role in Fatigue Predictive Modeling: State-of-the-Art Review

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Intergranular attack (IG) and exfoliation corrosion (EC) 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 which include adsorption-induced, ion migration-penetration, and chemomechanical film breakdown theories. In addition, pitting corrosion (PC) fatigue models are presented as well as a critical 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 are presented.

1. Introduction

This paper 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 <http://www.holsip.com/>). This is followed by a discussion of corrosion effects on SI (Structural Integrity) with some details 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 are 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 [1–67], (numbers in parentheses refer to the references in order of appearance).

1.1. Phases of Life and Modeling. The phases of life of a structure may be classified according to the division in the Table 1. Thus, the total life (L_T) of a structure is $L_T = L_1 + L_2 + L_3 + L_4$. Figure 1 presents a depiction of the degradation process from a holistic perspective. The regions shown in Figure 1, for example, 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 paper concentrates on the phases of life L_1 and L_2 , that is, the corrosion process or processes that results in the formation

TABLE 1: Phases of Life. See Figure 1. from Hoepner, 1972 [67], 1981 [38], 1985 [39].

- (i) 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 L₁ to some other phase.
- (ii) Microstructurally dominated crack linkup and propagation ("short" or "small" crack regime). Phase L₂.
- (iii) Crack propagation in the regime where LEFM, EPFM, or PFPM may be applied both for analysis and material characterization (the "long" crack regime). Phase L₃.
- (iv) Final instability. Phase L₄.

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

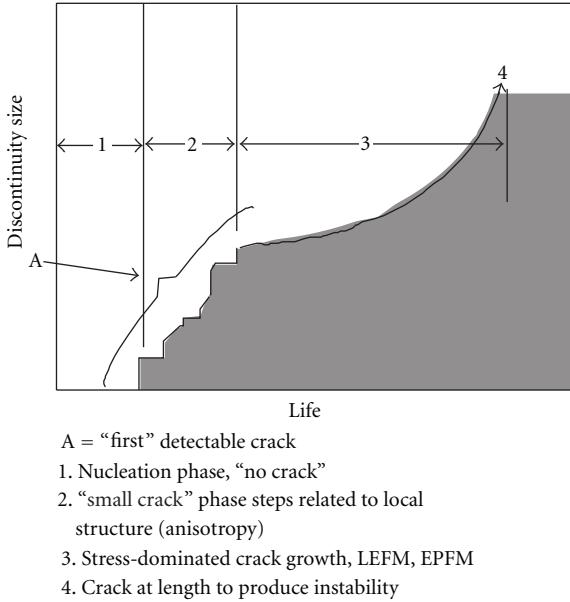


FIGURE 1: A depiction of the degradation process after Hoepner-1972 [67], 1981 [38], 1985 [39].

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 *design methods* to deal with corrosion or other time-based degradation, that is, fatigue, creep, and wear is essential and some of the elements are depicted in Figure 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 paper that follow will discuss the following major areas:

- (i) general effects of corrosion on structural integrity;
- (ii) intergranular attack and exfoliation corrosion (EC) in aircraft structural aluminum alloys;
- (iii) 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.

Nucleation	“small crack” growth	Stress-dominated crack growth	Failure (fracture)
Material failure mechanism with appropriate stress/strain life data	Crack prop. threshold related to structure (micro)	Fracture mechanics • Similitude • Boundary cond. LEFM ? EPFM	K_{Ic} etc. C.O.D.
Nucleated discontinuity (not inherent) type, size, location	Structure-dominated crack growth	Data base** Appropriate stress intensity factor	Tensile/compressive buckling
Presence of malignant D^* , H^*	Mechanisms, rate	Initial D^* , H^* size, location, type	
Possibility of extraneous effects • Corrosion • Fretting • Creep • Mechanical damage	Onset of stress-dominated crack growth Effects of • R ratio • Stress state • Environment • Spectrum -waveform	Effects of • R ratio • Stress state • Environment • Spectrum -waveform t chem T	

FIGURE 2: Methods for each life phase after Hoeppner-1972 [67], 1981 [38], 1985 [39].

- (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, 25–27, 31–36].
- (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, and/or 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 et al. [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. [27] 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 [27] 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” [27]. 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 US 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 [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 paper 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 appear to be sporadic and limited in number [27].

Walter Schütz addressed this issue further in the Plantema lecture at ICAF [25]. 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" [26]. 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.

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, 25–27]. Another issue that is clear is that deficiencies in the analysis of failures and the databases exist [27, 28].

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 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 [36]*).

Another quote from a different reference sheds further light on this issue [33, 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:

- (i) the chemical environment likely to be encountered on the structure of interest at the location of interest,
- (ii) the material from which the component is manufactured,
- (iii) the orientation of the critical forces (loads) applied externally and internally with respect to the critical directions in the material,
- (iv) the susceptibility of the material to occurrence of a given type of corrosion,
- (v) the temperature of exposure of the component,
- (vi) the type of forces applied (i.e., sustained force or cyclic force-constant amplitude loading or variable amplitude loading),
- (vii) 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),
- (viii) the rates of corrosion attack,

TABLE 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 "Pork chop" fitting	Fatigue, corrosion pitting	Pressurization leaks	—	1995	LMAS
C-141	FS998 main frame	Corrosion pitting, stress corrosion cracking	Found crack during inspection	—	1991	LMAS

- (ix) the potential influence of the effects of corrosion on fatigue crack nucleation and propagation,
- (x) the impact of any related corrosion degradation to residual strength,
- (xi) the potential for widespread corrosion damage to occur (WCD),
- (xii) 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 paper 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.

2. Corrosion in Aircraft Structural Aluminum Alloys

2.1. 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, namely, 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:

- (i) production of localized stress concentrations that act as crack nucleation sites,
- (ii) change of the structurally significant item (SSI),
- (iii) 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, and others. Moreover, aircraft are exposed to wide ranges of environment depending upon their route and geographical location, namely, tropical, marine, industrial, and rural [38, 51].

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 US Air Force aging aircraft as shown in Table 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].

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

TABLE 3: Corrosion and fatigue issues in the US Air Force aging aircraft.

Type of aircraft	Issues
1 C/KC 135 (Tanker aircraft)	<i>Corrosion</i> 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, <i>Stress Corrosion Cracking (SCC)</i> of large 7075-T6 aluminum forging (fuselage station 620, 820, and 960), <i>corrosion</i> and <i>SCC</i> 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)	<i>Widespread Fatigue Damage (WFD)</i> in the fuel drain holes in the lower surfaces of the wings, <i>corrosion</i> and <i>SCC</i> in the upper surface of the center wing, fatigue cracking and <i>SCC</i> around the wind shield, <i>fatigue cracking</i> in the stiffeners in the aft pressure door, <i>SCC</i> in the fuselage main frames, and <i>corrosion</i> in the empennage.
3 C-5 (Airlifter)	<i>SCC</i> 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)	<i>Cracking</i> in the bulkhead at body station 694, <i>fatigue cracking</i> in flap tracks and in the thrust brace lug of the forward engine support bulkhead, <i>cracking</i> in the side skin of the pressure cabin, aft body skins, and upper surface of the wing.
5 F-15 (Fighter aircraft)	<i>Low-cycle fatigue cracking</i> in the upper wing surface runouts, upper wing spar cap seal grooves, front wing spar conduit hole, upper in-board longeron splice plate holes, <i>corrosion</i> 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)	<i>Cracking</i> 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 box beam, and the ventral fin.
7 A-10 (Attack aircraft)	<i>Fatigue cracking</i> 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. <i>Exfoliation corrosion</i> 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. <i>Pitting corrosion</i> 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. <i>SCC</i> in the wing attach bushing flange, and the main landing gear attach bolts.
8 E-3A (Airborne Warning and Control System)	<i>Fatigue and corrosion</i> in the 7178-T6 rudder skins and spoiler actuator clevis. <i>Exfoliation corrosion</i> in the 7178-T6 upper wing skin, leading edge slats, main landing gear door, fillet flap, fuselage stringer 23, and magnesium parts. <i>Delamination</i> and disbonds in the windows, floor panels, and nose radome core. <i>Wear</i> in the antenna pedestal turntable bearings.
9 E-8 (Joint Surveillance and Attack Radar System)	“Small” <i>fatigue cracks</i> in fastener holes in the 7075-T6 aluminum stringers, in the 2024-T3 aluminum skins.
10 T-38 (Air training command aircraft)	<i>Fatigue cracking</i> 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. <i>SCC</i> in the fuselage cockpit upper and lower longerons, fuselage forgings. <i>Honeycomb corrosion</i> in the horizontal stabilizer (due to water intrusion), and the landing gear strut door.

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.

2.2. 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 and 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 resulting in the release of nitrate ions from a 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 MgZn₂ 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."

2.3. 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 byproduct of corrosion process) into the lattice space 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 and 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” [7]. The quest for realistic corrosion fatigue environment led Swartz et al. [51] 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 [52], 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 [53]. 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.”

2.4. 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 buildup in a joint [54]. Also, evidence shows 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” [54]. As reported by Komorowski et al. [54], 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 [55]. 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 [55]. 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 [55].

2.5. 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, that is, 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” [56]. 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 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 paper.

3. Pitting Corrosion

3.1. Overview. Pitting is classified as a localized attack that results in rapid penetration and removal of metal at “small” discrete areas [68]. 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, and 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 [69].

In passivated metals or alloys that are exposed to solutions containing aggressive anions, primarily chloride,

TABLE 4: Pit nucleation theories.

Proposed by	Theory
Evans [57] (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 [58] (1967), Hoar and Wood [59] (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.
Bohni and Uhlig [60] and Kolotyrkin and Ya [61] (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 [62–64] (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.
Lin et al. [65] (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.

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 [70]. The pit morphology depends on the metallurgy of the alloy and chemistry of the environment and the loading conditions. As observed first by McAdam and Gell in 1928 [71], these pits may cause local increase in stress concentration and cracks may nucleate from them [71].

According to Foley [72], 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.

3.2. Formation of Passive Films and Their Growth. The following discussion on the oxide film formation and its growth is extracted from [73].

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” [74].

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 [75]. It was later confirmed that the weight gain was due to formation of an oxide film [76]. 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 [77]. 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 [77]. 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 $\text{Al}_2(\text{OH})_6$ [76]. This was later determined to be incorrect [78].

3.3. 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): ($\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$),
- (2) bayerite: ($\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$),
- (3) boehmite: ($\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{AlO} \cdot \text{OH}$),
- (4) diasporite: ($\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$),
- (5) gamma alumina: ($\gamma\text{-Al}_2\text{O}_3$),
- (6) corundum: ($\alpha\text{-Al}_2\text{O}_3$),
- (7) combinations of aluminum oxides with inhibitors, for example, ($2\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$).

Gibbsite and diasporite 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 [79].

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) [78]. More recently, researchers have found small regions of crystallized γ -alumina within the amorphous layers created during anodizing [80].

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 [78].

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; 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 [78].

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 control 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, and dichromates or chromates can be added to create pores of a different structure [59].

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 [81]. 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 [78]. 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 [75].

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 [82].

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 [78]. 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 [83].

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 [84]. 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 [78].

3.4. Pitting Potential and Induction Time. According to Szklarska [69], the susceptibility of a metal or alloy to pitting can be estimated by determination of one of the following criteria:

- (i) characteristic pitting potential,
- (ii) critical temperature of pitting,
- (iii) number of pits per unit area or weight loss,
- (iv) 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, that is, 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 [69]. 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 [72]. 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 [85]. 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, that is, $1/\tau = Ae^{-E_a/RT}$; the activation energy needed for pit nucleation can be obtained from an Arrhenius plot of $\log(1/\tau)$ versus 1/temperature [72]. As well, Hoar [58] has proposed a relationship $1/\tau = K(\text{Me})^m(X^-)^n$ 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 that they grow. The following subsection presents a discussion of pit growth.

3.5. Pit Growth Rate and Pit Morphology. Godard [86] 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 and Foley [87] 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 $\log(i - i_p)$ versus $\log(t - t_i)$ will give the slope b . Dallek predominantly observed pits of hemispherical shape. However, Nguyen and Foley [88] 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 [89] 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 [73] 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, namely, 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, Ma [90] 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. [91] 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.

3.6. 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.

3.6.1. 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. [60, 92, 93], Hoar [58], Hoar and Jacob [94], and Kolotyrkin [95] have suggested mechanisms related to the ion-adsorption concepts (see Table 5). Many of the mechanisms proposed in the literature consider this as a necessary step in the pit nucleation process. Uhlig [60, 92, 93] and Kolotyrkin [95] 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 “chemisorption.” 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, that is, 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 [95], 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 [58] and Hoar and Jacob [94] 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. [96] 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 [97], 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 [63, 64] (see Table 3). 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 [98], 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 [99] 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.

3.6.2. Ion-Migration and Penetration Models. A few models (see Table 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 [58] explained 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 films 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

TABLE 5: Adsorption-induced mechanisms.

	Proposed by	Summary	Description	Limitations
1	Uhlig et al. [92] 1950–69, Kolotyrkin 1961 [95], Hoar 1967 [58]	(i) Proposed concepts based on either competitive adsorption or surface complex ion formation.	(i) 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. (ii) 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.
2	Sato 1982 [63, 64]	(i) Proposed a theoretical concept based on the potential dependent transpassive dissolution which depends on the electronic properties of the passive film. (ii) The electrochemical stability of a passive film depends strongly on the “electron energy band structure” in the film.	(i) 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. (ii) 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. (iii) Proposed that the local thinning of the oxide film as a mechanism of pit “initiation”. (iv) 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.

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 and that the time to breakdown the film increases with the thickness of the film [94]. It was further hypothesized that Cl^- ions first fill anion vacancies on the surface of the passive film and then migrate 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 [97].

Later, Chao et al. [100] 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 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, Chao et al. expressed a criterion for pit “initiation” as stated below.

$$(J_{\text{ca}} - J_m) \times (t - \tau) = \xi, \quad (1)$$

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 Lin et al. [65] have proposed a “point defect” model for anodic films to calculate J_{ca} for “thin” films on the order of 10–40 Å. 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 4.

3.6.3. Mechanical Film Breakdown Theories—Chemomechanical Breakdown Theories. Pit nucleation

TABLE 6: Ion-migration and penetration models.

	Proposed by	Summary	Description	Limitations
1	Hoar et al. 1967 [58, 59]	(i) 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.	(i) Favored sites for ion migration are suggested to be high-energy regions like grain boundaries and impurities where thinner passive films are produced. (ii) 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.	(i) Did not explain the observation that pits often form from mechanical breaks in the oxide film or from scratches.
2	Lin et al. [65] 1981	(i) Presented a theoretical model to explain the chemical breakdown of passive film.	(i) 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.	(i) Surface discontinuities such as grain boundaries and so forth were not considered in developing the model. (ii) No direct observation of void formation was made. (iii) As the measured induction times usually show a large scatter, definite quantitative agreement is difficult to obtain.

models proposed so far based on the concepts of the “chemicomechanical” breakdown of films have not included the effect of externally applied stresses (see Table 7). Sato [63, 64] 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:

$$p = p_o + \left[\frac{(\delta(\delta - 1)\xi^2)}{8\pi} \right] - \frac{\gamma}{L}, \quad (2)$$

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, 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 [98]. 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 [101].

Hoar and Jacob [94] 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 nonmetallic inclusions; second-phase precipitates, pores or voids, grain or phase boundaries, and other mechanical damages [69]. 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

TABLE 7: Chemicomechanical breakdown theories.

	Proposed by	Summary	Description	Limitations
1	Sato 1971 [62]	(i) Proposed a breakdown mechanism for anodic films from thermodynamic considerations.	(i) Showed that thin films always contain film pressure due to "electrostriction." (ii) Hypothesized that both the surface tension of the film and the film thickness have a significant effect on film pressure. (iii) Proposed that adsorption of chloride ions, depending on their concentration, greatly reduces surface tension.	Experimental proof is not found.
2	Sato 1982 [63, 64]	(i) Derived an equation for the work required to form a cylindrical breakthrough pore in the passive film.	(i) 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.

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 [102].

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.

3.7. 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 [103–106] were proposed since 1971 (see Table 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 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 [107]. This observation was made when fatigue was 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 [108]. 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 [109]. 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 [66, 106, 110].

4. 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

TABLE 8: Pitting corrosion fatigue models background-references [112, 113, 122–217].

Proposed by	Summary	Description	Advantages/limitations
1 Hoeppner [67] (1972 - current)	(i) Proposed a model to determine critical pit depth to nucleate a Mode I crack under pitting corrosion fatigue conditions. (ii) 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.	(i) 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. (ii) The stress intensity relation for surface discontinuity (half penny-shaped crack) was used to simulate hemispherical pit. i.e. $K = 1.1\sigma \sqrt{\pi(a/Q)},$ where, σ is the applied stress, a is the pit length, and Q is the function of $a/2c$, S_{ty} . (iii) Using the threshold determined empirically, critical pit depth was found from the stress intensity relation mentioned above. (iv) Then, the time to attain the pit depth for the corresponding threshold value was found using $t = (d/c)^3$, where, t is the time, d is the pit depth, and c is a material/environment parameter.	(i) This model provides a reasonable estimate for hemispherical geometry of the pits. (ii) This model is useful to estimate the total corrosion fatigue life with knowledge of the kinetics of pitting corrosion and fatigue crack growth. (iii) This model did not attempt to propose mechanisms of crack nucleation from corrosion pits. (iv) Quantitative studies of pitting corrosion fatigue behavior of materials can be made using this model. (v) This model is valid only for the conditions in which LEFM concepts are applicable. (vi) Material dependent.
2 Lindley et al. [104]	(i) Similar to Hoeppner's model, a method for determining the threshold at which fatigue cracks would grow from the pits was proposed.	(i) Pits were considered as semielliptical-shaped sharp cracks (ii) 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. $\Delta K_{th} = \frac{\Delta\sigma\sqrt{(\pi a)[1.13 - 0.07(a/c)^{1/2}]}}{[1 + 1.47(a/c)^{1.64}]^{1/2}},$ where, $\Delta\sigma$ is the stress range, a is the minor axis, and c is the major axis of a semi-elliptical crack. (iii) From the observed pit geometry that is, for a/c ratio, threshold stress intensity can be calculated. (iv) For the corresponding a/c ratio, critical pit depth can be estimated.	(i) The proposed stress intensity relation can be used in tension-tension loading situations where stress intensity for pits and cracks is similar. (ii) Critical pit depths for cracked specimens can be estimated using the existing threshold stress intensity values. (iii) This model is valid only for the conditions in which LEFM concepts are applicable. (iv) Material dependent.
3 Kawai and Kasai [105]	(i) Proposed a model based on estimation of allowable stresses under corrosion fatigue conditions with emphasis on pitting. (ii) 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.	(i) Considered corrosion pit as an elliptical crack. (ii) Based on experimental data generated on stainless steel, new allowable stresses based on allowable stress intensity threshold were proposed. i.e. $\Delta\sigma_{all} = \Delta K_{all}/F\sqrt{\pi h_{max}},$ where ΔK_{all} can be determined from a da/dN versus ΔK plot for a material, h_{max} is the maximum pit depth, and F is a geometric factor.	(i) Using this model, allowable stress in relation to corrosion fatigue threshold as a function of time can be estimated. (ii) Material dependent. (iii) This model is valid only for the conditions in which LEFM concepts are applicable.

TABLE 8: Continued.

Proposed by	Summary	Description	Advantages/limitations
4 Kondo [111]	(i) 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.	(i) Pit diameter was measured intermittently during corrosion fatigue tests. (ii) From test results, corrosion pit growth law was expressed as $2c\alpha C_p t^{1/3}$, 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. (iii) 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. (iv) The pit growth rate dc/dN was developed using ΔK relation as given below $dc/dN = (1/3)C_p^3 f^{-1} \alpha^2 \pi^2 Q^{-2} (2.24\sigma_a)^4 \Delta K^{-4}$ dc/dN was determined using experimental parameter C_p . (v) Finally, the critical pit size $2C_{cr}$ was calculated from the stress intensity factor relation. i.e., $2C_{cr} = (2Q/\pi\alpha)(\Delta K_p/2.24\sigma_a)^2$.	(i) The aspect ratio was assumed as constant. (ii) Material and environment dependent.

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 ($< 1 \text{ MPa} \sqrt{\text{m}}$). As well, Kondo [111] 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 (Hoeppner [now Taylor] [112]). 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, 1979, [103]) in which pitting was modeled statistically with different materials and specimen types, recently, as discussed before in this paper, there was a study demonstrating that corrosion fatigue induced “short” crack formation from pits [113]. Also, recent studies [73, 110, 112] 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 [111], further studies to characterize the formation of cracks from pits in the “short” crack regime must be evaluated as indicated by A. Hoeppner [112]. 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.

5. 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:

- (i) section change that affects the area/volume that modifies the stress,
- (ii) formation/nucleation of localized debris that may modify the stress (part of pillowowing) that modifies the stress or stress intensity;
- (iii) nucleation of intergranular corrosion that is involved in pillowowing that modifies the stress or stress intensity;

- (iv) nucleation of localized corrosion (pitting, fretting, etc.) that modifies the local stress and may ultimately nucleate cracks;
- (v) 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 University of Utah as discussed in the earlier sections of this paper. From the work of L. Grimes at Utah as well as additional efforts at the University of Utah, the use of the confocal microscope will be of great assistance in characterizing the three-dimensional (3D) 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 [114–116] has introduced excellent reference books on aspects of corrosion and also a web page (<http://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 [117] states that the USA DOD spends "22.9 billion a year fighting rust". There is little doubt that this number will become much larger and more of the structures in use in aircraft and many other applications age and it is unlikely that 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 3D 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 [118]

and Swift [119] 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 be noted

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.

Age Degradation Process (ADP). 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.

Crack-like discontinuity (CLD). 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.

Durability and Damage Tolerance Analysis (DADTA). 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 unrepairs 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.

Discontinuity Evolution Process (DEP). The specific process by which a population of discontinuities evolves.

Discontinuity Nucleation Process (DNP). 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.

Discontinuity State (DS). See IDS, EDS, and MDS below.

Discontinuity State Evolution Process (DSEP). 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.

Discontinuity State Evolution Response (DSER). Any change in state of an IDS population.

Environmentally Assisted Cracking (EAC). It may occur under sustained load from either applied load or “residual stresses” EAC_{sl} . And may also occur under either constant amplitude cyclic forces or variable amplitude cyclic forces $EAC_{fatigue}$.

Equivalent Corrosion Damage (ECD). 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.

Evolving Discontinuity State (EDS). 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).

Equivalent Initial Flaw Size (EIFS). 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.

Fatigue Crack Propagation (FCP). Extension of a crack under cyclic or repeated loads. The stages of crack propagation are divided into four phases, namely, (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.

Initial Discontinuity State (IDS). 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, and so forth.

Manufacturing processes such as machining and assembly can introduce additional discontinuities at fasteners, fillets, and so forth, that extend the tail (larger discontinuity sizes) of the IDS distribution.

Initial Material Discontinuity (IDS_{ms}). The initial population of intrinsic material discontinuities. See IDS.

Initial Manufacturing Discontinuity (IDS_{mfg}). 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 (namely, mechanical joining, thermal joining, and adhesive bonding).

Initial Geometric Discontinuity (IDS_{geo}). The initial geometric discontinuities in a product. These often are generally referred to as a “notch”.

Modified Discontinuity State (MDS). 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. Example2: 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.

Principal Structural Element (PSE)

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, subcritical crack growth, directed inspection, and inspection intervals are not dealt with for fatigue, corrosion, and related items.

Structurally Significant Location (SSL). 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 [120].*

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 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 [121].

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 that 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 [121].

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 [121].

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 Corrosion. Corrosion damage occurring between successive inspections that is *local* and can be reworked/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 rework/blendout 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 blendout approaching the allowable rework 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.

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