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Corrosion-fatigue: A review of damage tolerance models.

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Abstract

The synergistic combination of mechanical fatigue stresses and environmental agents acting together can be more detrimental than that of the summation of the contributions of each mechanism acting separately. Major attempts to understand the contribution of the different agents (microstructure, chemical composition of environment, temperature, loading conditions, etc.) have been reported in the literature. Nevertheless, current knowledge is insufficient to address life estimation with a sound physical basis from the initiation of localized corrosion (such as pitting) to the estimation of crack propagation. Major simplifications and assumptions have been required in the development of life prediction methodologies. This paper reviews recent effort made by the different interested parties, both in academia and industry, in the development of corrosion fatigue lifetime prediction procedures. The paper mainly focuses on methodologies proposed in the literature for O&G, nuclear, energy generation and aerospace applications, dealing with pitting corrosion-fatigue (CF) damage in aluminium alloys, carbon and stainless steels. The transition of a pit into a small crack and its growth is influenced by interaction of the pit stress/strain concentration and the local environmental conditions, making the modelling of this stages of the utmost complexity. A major trend in the models reviewed in this paper is to simplify the analysis by assuming the pit (a volumetric defect) as a sharp crack, decouple the CF problem and account for the mechanical and environmental contributions separately. These procedures heavily rely on fitting experimental data and exhibit low generality in terms of application to varying system conditions. There is a clear opportunity in this field to develop mechanistically based methodologies, considering the inherent dependence of the damage mechanism on the interaction of environmental, metallurgical and mechanical features, allowing more realistic lifetime estimates and defect tolerance arguments, where pit-to-crack transition and small crack initiation stages pose a significant challenge.

Key words: Corrosion fatigue, Pitting corrosion, Pit-to-crack transition, Damage tolerance, Life assessment methods.

Acronyms

ASME American Society of Mechanical Engineers
API American Petroleum Institute
BP British Petroleum
BS British Standards
BWR Boiling Water Reactor
CF Corrosion fatigue
DNV Det Norske Veritas
FCGR Fatigue crack growth rate
FCI Fatigue crack initiation
FCP Fatigue crack propagation
FFS Fitness for service
HA Hydrogen assisted
HRR Hutchinson, Rice and Rosengren stress fields
LC Long crack
LEFM Linear Elastic Fracture Mechanics
SCF Stress concentration factor
SC small crack
SEM Scanning electron microscope
SIF Stress intensity factor
S-N Stress vs. number of cycles

1 Introduction

Under service conditions, metals and alloys can be exposed to aggressive environments which leave them susceptible to different forms of corrosion. Localised corrosion is associated with relatively high rates of metal penetration at discrete sites and is perhaps the most dangerous type of corrosion in combination with mechanical load, either cyclic or monotonic. The synergistic nature of corrosion and fatigue is one of the main reasons for the premature failure of engineering structures and components causing failure at early stages of life and at stress levels far below the in-air nominal fatigue strength of structural materials. This decrease in life and resistance is likely to be attributed to the premature initiation of fatigue cracks at pit-induced stress concentrations.

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The detrimental effect of pitting corrosion-fatigue has been widely reported, covering numerous industries. For instance, in the Oil and Gas (O&G) industry, low alloy steels are common choices for offshore flowlines and risers in sour service applications. These alloys are susceptible to experiencing pitting corrosion together with fatigue loading arising from large thermal transients and bending of the pipes due to wave motion and the presence of aggressive species such as CO_2, H_2S and seawater environments.

Likewise, in the nuclear industry, exposure to water has been shown to have a deleterious effect on the fatigue strength of the most commonly used low alloy carbon and stainless steels. Recent results [1–3] have shown that exposure to water at temperatures above ca. 150^oC for carbon and low alloy steels and ca. 180^oC for stainless steels can reduce the cycles to failure (through-wall cracking) or fatigue life by up to a factor of 10 in the low and intermediate cyclic life regimes. Cyclic crack growth rates have been found to be 10 to 50 times faster in elevated temperature water than in air. The most common corrosion fatigue mechanisms usually occur in low alloy steel pipes in boiling water reactors (BWR). These failures have been attributed to low cycle corrosion fatigue [4–7].

In addition, one of the main causes of failures in aging aircraft is due to corrosion damage and fatigue of its aluminium alloy components. Pits have been frequently identified as the source of cracks on operating aircraft [8–11]. Events related to CF mechanisms have been widely reported since the 60's and procedures to characterize [12–17] the severity were developed in order to reduce corrosion maintenance costs. As a result, the aerospace industry has been one of the principal contributors to the development of corrosion and corrosion-fatigue procedures.

Similarly, the profitability of the wind energy industry relies heavily on design costs and a requirement for low level maintenance intervention [18]. Variable amplitude cyclic loads due to fluctuations in wind speed velocity or wave motion, commonly known as 'stochastic' loads, coupled with chloride containing environments threatens the structural capacity of wind turbine structures. Therefore, avoiding corrosion-fatigue is a real challenge in this industry, which seeks to be sustainable by operating as close as possible to the true design capacity.

Quantification of pitting and its critical role in crack nucleation is therefore of great relevance in the assessment of the deleterious impact on a component's fatigue performance[19]. Although LEFM based models have shown acceptable accuracy when incorporating this phenomenon for engineering applications, these models are not fully rigorous in capturing the physics of the damage process. Since it was recognised that pitting CF was a failure mechanism itself with unique features and fatigue life prediction models were incapable of incorporating such characteristics, efforts have focused to quantify the effect of different parameters such as strain rate [20,21], hold time [22], temperature [23–26], corrosion potential[27–29], mean stress [30,31], strain amplitude [32–34], cyclic history, and flow velocity effects [35,36,30] on the fatigue life, $S-N$, and cyclic crack growth rate, da/dN, behaviour of a whole range of materials now believed to be susceptible to this phenomenon. As a result, various pitting CF models have been proposed in the literature. In this context, either total life or damage tolerance approaches are of the utmost importance in order to ensure the structural integrity and residual life of machines, components and structures that operate in corrosive environments with reduced conservatism compared to the currently applied methods in common structural integrity assessment procedures [37–40], which considers corrosion in terms of local thinning area only.

This review considers the approaches which have been applied in allowing for some of the above-mentioned considerations when lifing components under CF conditions. The main intention of this paper is to review the literature on the different models and methodologies. This work recognises some of the work cited in the reviews conducted by Akid [41] and by Hoeppner and Arriscorreta [42], although the latter was focused on aircraft materials and environments only, but importantly updates this by including models proposed in recent years (2009-present) including details of work cited in a recent internal industry report on corrosion fatigue models conducted by Lishchuk and Akid [43] and by Larrosa and Ainsworth [44]. The range of applicability of the approaches reviewed in terms of mechanical, environmental and material-related parameters, and their accuracy for life prediction is discussed. A summary is given on current phenomenological approaches of corrosion fatigue based on pit and crack growth with emphasis on the damage process on fatigue life. These models usually characterize corrosion fatigue by separately assessing the different regimes. It is important to mention that major models, their advantages and limitations are discussed and the review is relevant up to its time of publication.

2 Corrosion-Fatigue regimes

Due to the very complex nature of the corrosion-fatigue process, corrosion-fatigue damage evolution is generally divided into different stages or regimes [45,46], see Fig. 1, as follows:

- Surface film breakdown
- Pit growth
- Pit-crack transition
- Cracking: Small and long crack growth

Small cracks should be distinguished from short cracks. While the former are small in all dimensions (length, width and opening), the latter are small only in two dimensions (length and opening) [47], i.e. through-thickness short cracks in fracture mechanics specimens. Experimental evidence supports this taxonomy due to the different observed behaviour of small and short cracks under the influence of corrosive environments. Recent work at NPL (UK) [19,48,49] has shown that growth rates of short cracks are enhanced by the effect of the environment and that such enhanced growth was not observed for small cracks. This enhancement was attributed to the electrochemical crack size effect. These researchers introduced the concept of a solution-conductivity dependent electrochemical crack size effect, an extension of Gangloff's chemical crack size effect [50]. In the literature, for non-aggressive environments, it is often observed that the term 'small cracks' has been used interchangeably with 'short cracks'.

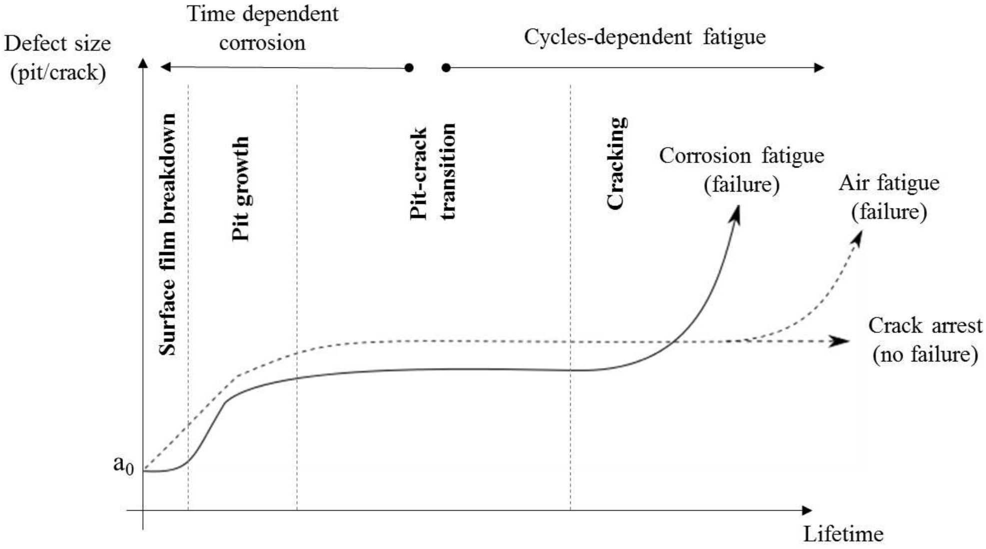


Fig. 1. Pitting corrosion-fatigue stages. Figure adapted from [45].

It is recognised that dissolution-based damage occurs in several different forms, for example exfoliation corrosion, intergranular corrosion, crevice and galvanic corrosion. The review does not specifically address these damage processes for the following reasons; in the case of exfoliation corrosion, damage tends to be widespread and lateral across the surface and does not necessarily induce isolated pit-like features that lead to stress-raisers and sites for crack initiation, see example given in Section 5. Furthermore the combination of fatigue and corrosion is almost exclusively manifest as transgranular cracking from stress raisers (notably pits) and that intergranular corrosion may be a precursor to crack initiation, but the subsequent fatigue-induced damage mechanism tends to revert to transgranular cracking. The role of crevice and galvanic corrosion is one of selective dissolution which under certain circumstances may lead to the formation of preferential site(s) for crack initiation and, in this respect, might be considered to respond in a manner akin to that of localised corrosion. The susceptibility of a metal to pitting corrosion, as well as the rate at which pitting occurs, depend upon the presence and integrity of any surface film, be it natural oxide in the case of aluminium or stainless steel or scale in the case of carbon steel in CO_2/H_2S environments. The breakdown of this film causes a separation of anodic and cathodic sites, leading to localisation of the anodic dissolution reaction, as seen in the form of pitting. In terms of the CF process, the resistance to surface film break-down might be considered a 'primary threshold'. Whilst there remains debate among researchers regarding the mechanisms of pit nucleation, local adsorption of aggressive anions on the surface of the metal is commonly accepted to be an initial step in pit nucleation and has been reported in early investigations [51–57]. As highlighted above, pitting is often associated with breaks in surface films, and also with microstructural discontinuities in an alloy, such as inclusions or constituent intermetallic particles. Physical aspects in the material such as pores, voids and mechanical damage which cause disruption to the filmed surface [58–60] are also pit-inducing features. Such locations may eventually become pit nucleation sites if conditions such as solution chemistry, local electrochemical potential difference across the surface, chemical nature of the base material and local stress state are favourable to cause permanent separation of anode and cathode sites [46,61].Further, it has been observed that the number of corrosion pits initiated on the specimen surface in stainless steels was controlled by repeated stress, with more corrosion pits initiated at higher stress amplitudes [62].This shows that fatigue can accelerate pit formation.

The rate of *pit growth* is mainly dependent on material properties, local solution conditions and stress state. Pits are known to be sites of crack initiation [63], severely affecting the fatigue life of the metal or alloy. Several researchers have studied and discussed the influence of stress and strain states [45,65,64,68–75]on the electrochemical response (pit growth) and in most cases, these studies suggested that pit growth is highly influenced by the degree of plasticity in the surrounding grains. Pit growth rates begin to increase with the onset of plastic deformation and reach a plateau when plastic deformation is saturated, Fig. 2 at stresses well above yield. Conversely, below yield there is little effect on pit crack growth rate at low stress ranges, Fig. 2.

Corrosion fatigue is the process in which electrochemical and mechanical activity act simultaneously. There are cases in which these two driving forces act separately, for example when cyclic loading is applied to a corrosion defect in an inert environment. This review will not consider these cases and will only focus on the simultaneous effect of the electrochemical and mechanical driving forces. Nevertheless most stages of the corrosion fatigue process are controlled by only one driving force. Stable pit growth is usually considered a *time-dependent* phenomenon and mainly controlled by electrochemical activity. The transitional regime from the pit growth stage to crack nucleation (pit-to-crack transition) and propagation stages is critical in the corrosion-fatigue process. Hu [66] has shown that the pit size at which the transition occurs is dependent upon local solution chemistry, stress, and time, which makes the analysis and modelling of the corrosion-fatigue process complicated. Compared to pitting, cracking is predominantly a mechanical, *fatigue cycle-dependent* regime, although in the early stages of crack growth local crack tip chemistry is also a key condition to development and propagation of small fatigue cracks [67,19]. Recently, Turnbull [76] showed quantitative support for the conceptual idea that a growing pit in a static stress field induces a dynamic strain component, a key factor in stress corrosion crack initiation. This novel concept of pit growth induced dynamic plastic strain must now be considered as a possible factor determining the transition from a pit to a stress corrosion crack and provides a more substantive explanation for the localisation of stress corrosion cracks at the mouth of the pit rather than that based solely on local electrode potential or pit chemistry. Although corrosion fatigue should not be confused with stress corrosion cracking, this concept introduced by Turnbull could be considered as a possible pit to crack transition factor to elucidate the corrosion fatigue mechanism. To fully understand the pit-to-crack transition process it is necessary to identify what processes or parameters other than the stress/strain fields due to the geometry of the pit can affect the pitting process, like local chemistry and embrittlement due to the absorption of hydrogen.

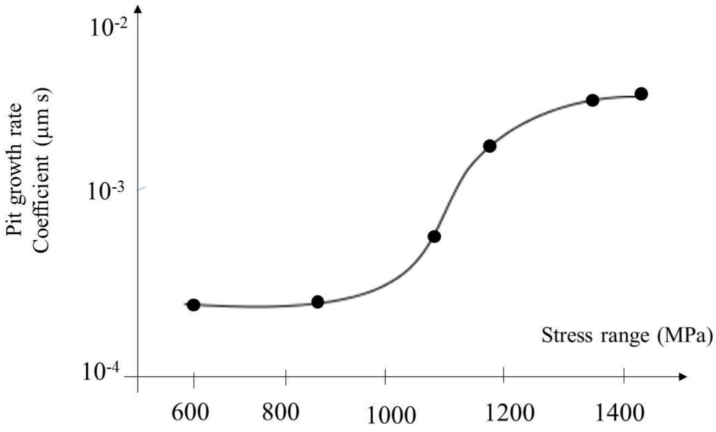
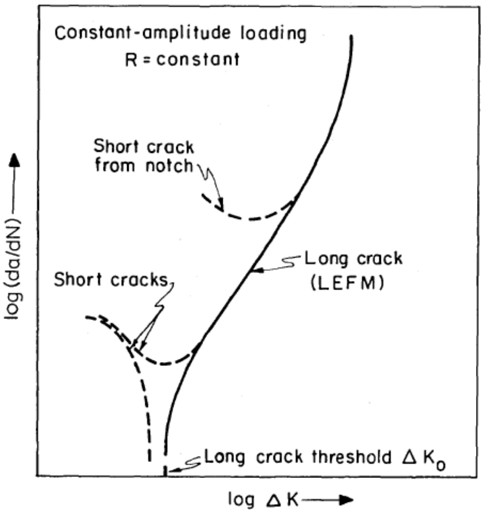


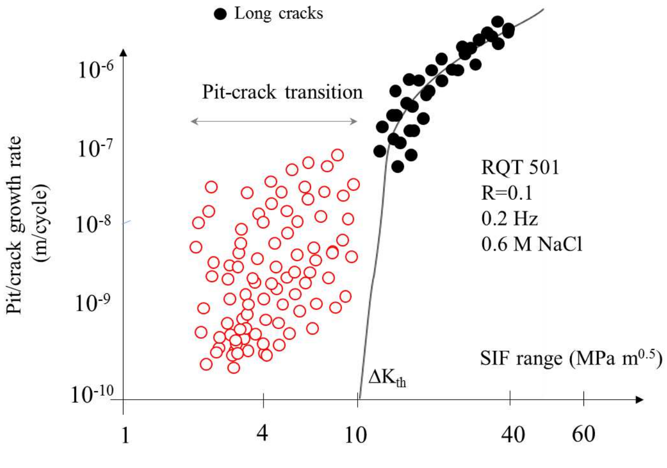
Fig. 2. Pit growth rate in artificial seawater as a function of stress range for a Q2N steel (0.12 %C), σ_y=790 MPa, 3-point bending, R=0.01,f=0,1Hz. Figure adapted from [65].

In the fatigue crack growth process in an inert environment, two main stages can be distinguished according to experimental observations: namely, *small/short* and *long crack growth.* Pioneering scientists [77–81] found that in the early stages of growth, the crack, of a few grains in length, experiences a higher mean growth rate than the rate predicted from specimens containing a long crack. Using different materials this observation was also corroborated by other authors such as Lankford [82], Brown et al.[83] or Taira [84] and Tanaka et al. [85]. As a consequence, the well-known relationship between crack growth per cycle, da/dN, and the stress intensity factor range, ΔK, obtained for long-cracks gives rise to non-conservative predictions in the assessment of the fatigue life of components containing small cracks [17,86–90], Fig. 3(a).

In addition, when pits are re-characterised as cracks for assessment purposes, some observations suggest that the pit-to-crack transition appears to be independent of ΔK, Fig. 3(b). However, this does not represent the actual behaviour of the crack emanating from a three-dimensional pit. Therefore, tests addressing the initiation of small cracks from corrosion pits are of interest in order to correlate small crack behaviour and long crack thresholds [41].



(a) Representation of small and long cracks growth in air [80].



(b) Representation of small and long crack growth in artificial seawater. Figure adapted from [45]

Fig. 3. small crack, pit-to-crack transition and long crack behaviour. Note that in [45,80] ‘short cracks’ refers to ‘small crack’ behaviour, as defined above.

3 Corrosion-Fatigue models

As the behaviour of a component may be completely different in an aggressive environment in comparison to that in air, models with the capacity to predict environmental-assisted fatigue crack growth (FCGR) and material behaviour under cyclic load (S-N curves) are of real interest for maintenance and structural integrity applications.

From the damage tolerance point of view, that is when the life of pits/cracks detected in service up to a critical size is to be assessed, modelling procedures of interest for corrosion fatigue assessment fall in the following two categories:

- Pitting corrosion fatigue models (Pit to crack transition models).
- small and long crack growth.

The review by Lishchuk and Akid [43] mainly focussed on small and long crack growth models.

Historically, corrosion fatigue models isolate and quantitatively characterize each of the regimes mentioned above. The current paper reviews methodologies in which the transition of a single corrosion pit to a single large crack is considered by deterministic models. However, the most important probabilistic models and their contribution are also highlighted.

Deterministic models attempt to represent the underlying mechanisms. While estimating the parameters of these models is usually the focus of statistical modelling. The complexity of the processes involved in corrosion fatigue mechanisms makes the development of mechanistic models a difficult task due to the number of parameters involved in the electrochemical and mechanical coupled mechanisms. In addition, as these mechanisms are material, loading and environment dependent, these models will only be applicable to specific cases and are therefore of low generality. This is the main reason why most of the deterministic models are of a phenomenological basis, i.e. based on empirical relationships.

Conversely, because corrosion fatigue is a function of many variables, many of an uncertain nature, several researchers argue that probabilistic models are more appropriate to describe the behaviour. Probabilistic models have been shown to be elegant tools to model mechanisms that are not fully understood. In the O&G industry, probabilistic approaches to pipeline life prediction have been widely reported in the literature [91–102].

Under laboratory conditions, generally, the time for crack nucleation from a pit may dominate the corrosion fatigue life, that is, until there is a transition to a crack, the pit growth process may occupy the most significant portion of the life [103]. Therefore, the evaluation of the pit growth and the pit-to-crack transition are extremely important steps for accurately assessing the corrosion fatigue damage process. In addition, pit morphology is a critical factor to model and study pit growth. However, in plant applications, loading conditions are rarely constant and loading, temperature or environmental transients may accelerate any of the stages of corrosion-fatigue life, eliminating the pit growth stage, for example. The models presented here are discussed below largely in the context of constant loading conditions. Where plant history is well known, the models may be applied to gain an indication of the importance of the detailed history. However, at the design stage, such information is rarely available and simplified cumulative damage models are generally applied, such as Miner's law in fatigue, to assess the impact of different operational loadings.

Several studies are based on the characterisation of the pit morphology and the critical conditions for crack propagation [104–110]. The pit geometry and dimensions are a function of the potential due to electrochemical activity in the pit [111,112]. Therefore, understanding the mechanisms behind the evolution of the pit size and shape are key determinant factors to correctly characterize the pit topology and the severity of the stress and strain fields around the pit and of utmost importance in characterizing the eventual transition to a crack [113–116]. The ability of the next generation of corrosion fatigue damage tolerance procedures to incorporate these aspects of the physics of the pitting process will allow more accurate designs and assessments of structural components.

In the following sections, both classical methodologies and the most recent approaches for assessing pit growth, the transition from a pit to a crack and crack propagation are presented. Particular attention is paid to the engineering applications proposed in the last 10 years. Classical methodologies are described initially with less detail as they have been reviewed elsewhere [41,43,117,118]. The main characteristics of the models are highlighted and the expressions for the parameters involved for fatigue life prognosis are summarized in Table 1.

3.1 Damage tolerance models

Since the fatigue limit is indicative of a non-propagating crack, several researchers have considered a pit as an effective fatigue crack and subsequently applied linear elastic fracture mechanics (LEFM) to evaluate the stress concentration effect of the pit. Several models, discussed below, rely on this concept to assess the pit-to-crack transition in terms of a threshold stress intensity factor range (ΔK_{th}). Basically, three-dimensional corrosion pits are treated as effective two-dimensional cracks, so the transition of pits to fatigue cracks can be described in terms of LEFM, allowing prediction of the fatigue crack nucleation life using simple analytical expressions. The main drawback of this assumption is that it is neglecting a significant part of life: the pit growth life until stabilisation, crack initiation and - both small and long crack- propagation life; it is only accounting for a long-crack growth life from an arbitrary crack size.

The model by Hoeppner [119] was the first approach proposed to estimate the time or number of cycles for a pit to reach the critical depth to nucleate a Mode I crack under pitting corrosion fatigue conditions. In this model, usually called the "critical pit size model", a corrosion fatigue crack is considered to have nucleated at a pit when the pit grows to a critical size where the local mechanical condition is adequate for the onset of crack growth, and the critical condition, in this context, is usually defined in terms of the threshold stress intensity factor range (ΔK_{th}) for corrosion fatigue conditions. The weakness of this model relies on the use of the long crack threshold (ΔK_{th}), which has been vastly established to not be applicable to small cracks. The prevailing conditions around the pit during and after initiation of small cracks, notably, strain localisation induced plasticity, causes a breakdown of LEFM conditions hence, the appropriateness of using LEFM for addressing crack initiation and growth is at least questionable.

Lindley [120] proposed a similar model to that of Hoeppner, a method for determining the threshold at which fatigue cracks would grow from pits. For an elliptical crack in an infinite plate, Lindley used Irwin's stress intensity factor solution to define an expression to estimate threshold stress intensity values related to fatigue crack nucleation at corrosion pits.

The model developed by Kawai and Kasai [121] is based on experimental data generated on stainless steel under corrosion fatigue conditions and was used to obtain an allowable stress based on an allowable stress intensity factor threshold. The model considers the corrosion pit as an elliptical crack.

The earliest substantive approach to predicting the pit-to-crack transition and the associated critical flaw depth was developed by Kondo [104] for corrosion fatigue cracks. In this model, usually called the "competition model", the growth law of a corrosion pit is formulated using fracture mechanics, and the occurrence of corrosion fatigue crack nucleation is defined by a critical pitting condition, $(\Delta K)_p$, at which the crack growth rate exceeds the pit growth rate.

Experimental results by Chen et al.. [122,123] showed that the pit size and stress intensity factor at crack nucleation were frequency-dependent, with stress intensity factor increasing with decreasing frequency. The phenomena were interpreted by the transition from pit growth to fatigue crack growth based on concepts of fatigue crack growth threshold [119] and a competitive pitting/cracking rate [104]. Criteria for the transition from pitting to fatigue cracking were proposed as (1) the equivalent stress intensity factor range required for a corrosion pit to reach the threshold stress intensity factor range (ΔK_{th}) for fatigue crack growth, and (2) the time-based corrosion fatigue crack growth rate required to exceed the pit growth rate.

small crack growth theory has been neglected in the models mentioned above. Fatigue cracks may initiate from pits, even when they are small enough to result in crack stress intensity factor values less than that predicted by macroscopic LEFM crack growth threshold analysis. The fracture mechanics model developed by Rokhlin and co-workers [124] includes fatigue small crack (Stage 1) and long crack (Stage 2) propagation based on two different stress intensity factors. Crack growth during Stage 1 is modelled as corner crack growth at the edges of a through-thickness hole in a plate. This assumption was supported on the basis that fatigue cracks initiate at the edges of the pit with the highest stress concentration to form two corner cracks and that the stress concentration factor at the edges does not change significantly from that of the through-thickness hole. In Stage 2, since the crack tip is away from the pit and the stress concentration is reduced at the base of the pit, the effect of the pit on the crack growth rate can be neglected. Thus the pit with a crack can be approximated by a surface-breaking crack on a flawless flat surface. Good agreement with experimental data, with respect to describing fatigue crack initiation and growth from pits was obtained, allowing the relationship between reduction of fatigue life and artificial pit size to be predicted. Besides the questionable use of LEFM to model small crack behaviour, the corner crack model (Stage 1) proposed in this work assumes that the crack growth is independent of the stress concentration associated with the pit regardless of the pit depth. The validity of this assumption will depend on the size scale and morphology of the corrosion damage [125] and will tend to become less accurate as the aspect ratio decreases.

Wang et al. [9] described pit growth by means of Kondo's expression ($c = A(N/f)^{1/3}$, please see Table 1 for the definition of the parameters) and followed the approach of Harlow and Wei [126] to evaluate the constant ($A = A^{HW}$) in which the pit growth is taken to be solely dictated by corrosion parameters (see Table 1 for details). The pit is assumed to be of hemispherical shape and as a result the pit size at which the crack is initiated is given by fracture mechanics expressions. Fatigue crack initiation and propagation life prediction is performed by means of linear damage summation, comprising the number of cycles for a crack to initiate from a pit (pit nucleation due to fatigue and growth due to environment) and the cycles needed to propagate the crack to failure. The number of cycles to fatigue crack initiation is obtained by means of the fatigue crack initiation model proposed by Mura and Nakasone [127]. Based upon the concept of a change in Gibbs free energy, from a state of dislocation dipole accumulation along a persistent slip band to a state of crack initiation along the band, this theory predicts a critical number of loading cycles when the Gibbs free energy change reaches a maximum value. The number of cycles at which this happens is defined as the crack initiation cycle number. Several other approaches have been proposed to account for the effects of the environment-microstructure interaction on the deformation and fracture behaviour of metallic alloys by means of coupled corrosion-deformation formulations at different length scales, both considering time and considering time and spatial-dependent behaviour and are included in a recent review by Pineau [128].Although the approaches described in the review by Pineau et al. allow consideration of the sensitivity of the microstructures to aggressive agents and the effect of the intrinsic material heterogeneities (chemical composition, slip planes, precipitates, grain boundaries, strain incompatibilities,etc) in the fatigue crack initiation mechanism, the use of the outputs of these approaches for the assessment of engineering components and structures is components and structures is still a subject of discussion [129]. In addition, involved in the analysis and the complex calibration of the models makes the use of these approaches restricted to research activities only at the present time. These approaches are not These approaches are not treated in this review.

Ishihara et al. [130] proposed a pit growth model in which the pit depth is proportional to a function of the stress amplitude σ_a, the loading (frequency and time) and the number of load cycles. For assessing pit-to-crack transition, Ishihara used the LEFM approach proposed by Murakami and Endo [131] , which uses the $\sqrt{area}$-parameter (the square root of the projection area of a small flaw perpendicular to the loading direction) to evaluate the driving force for cavities/pit. This approach assumes that the fatigue strength of metallic materials containing defects depend on the non-propagating behaviour of small cracks.

Based on previous research [124,132–135], showing the sensitivity of fatigue behaviour to pit depth, the distribution of maximum pit depth was studied. This researchers proposed a modified corrosion pit growth law from that proposed earlier by Kondo, defined in Table 1, including the effects of stress amplitude and load frequency. The proposed model gives good results when the effect of the stress amplitude is considered in the corrosion pit growth law, but produces non-conservative estimates when it is neglected. Experimental results from this work showed that most of the fatigue life at very low-stress range values is occupied in pit growth period and, therefore, accurate descriptions of the corrosion pit growth law are necessary to evaluate corrosion fatigue life.

In what follows, we describe in detail several models that attempt to predict corrosion fatigue lifetime, wherein pitting is a dominant component of the damage process.

Table 1. Classical corrosion fatigue models.

Author	Summary	Model	Parameters
Hoeppner (1979) [119]	Model to determine critical pit depth to nucleate a Mode I crack under pitting corrosion fatigue conditions. Cycles to develop a critical pit size that will form a Mode I fatigue crack.	$K = 1.1\sigma\sqrt{\pi\frac{a_p}{W}}$ if $\Delta K = \Delta K_{th} \rightarrow a_p = a_p^{cr}$. Pit as half penny-shaped crack of aspect ratio $a_p/2c_p$ $t = (d/c)^3$ ΔK_{th} determined empirically	a_p^{cr} →critical pit length σ →applied stress Q → function of pit shape d → pit depth t → time c → constant f(material,environment)
Lindley (1982) [120]	Method for determining the threshold at which fatigue cracks would grow from pits	$\Delta K_{th} = \frac{\Delta\sigma\sqrt{\pi a[1.13-0.07(a/c)^{1/2}]}}{[1+1.47(a/c)^{1.65}]^{1/2}}$ Pits considered as semi-elliptical cracks of aspect ratio a/c	a → minor axis c → major axis $\Delta\sigma$ →surface stress range at the fatigue limit.
Kawai & Kasai (1985) [121]	Based on experimental data generated on stainless steel, new allowable stresses based on allowable ΔK_{th}	$\Delta\sigma_{all} = \Delta K_{all}/(F\sqrt{\pi h_{max}})$ ΔK_{all} can be determined from a da/dN versus ΔK plot for a material	h_{max} → maximum pit depth F → geometric factor
Kondo (1989) [104]	Critical pit condition using SIF relation as well as a pit growth rate relation. Aspect ratio assumed constant. (Low-alloy steels in deionized water)	$(\Delta K)_p = 2.24\sigma_a\sqrt{\pi c\alpha/Q}$ Corrosion pit law expressed as $2c \propto At^{1/3}$ where $c = A(N/f)^{1/3}$ Pit growth rate expressed as $dc/dN = (1/3)A^3 f^{-1}\alpha^2\pi^2 Q^{-2}(2.24\sigma_a)^4\Delta K^{-4}$ $2c_{cr} = (2Q/\pi\alpha)[(\Delta K)_p/(2.24\sigma_a)]^2$ $Q = 1 + 1.464\alpha^{1.65}$	σ_a →stress amplitude Q → geometric factor c, a → pit radius, depth A → experimental constant N → number of fatigue cycles f → cyclic frequency α → aspect ratio a/c

Table 2. Classical corrosion fatigue models. Continued

Author	Summary	Model	Parameters
Chen et al. **(1996)** [123]	Two criteria model: b)ΔK_{th} criterion b) Rate competition criterion Pit: semi-elliptic surface crack (2024-T3 Aluminium alloy)	$\Delta K \geq \Delta K_{th}$ $\left(\frac{dc}{dN}\right)_{crack} \geq \left(\frac{dc}{dN}\right)_{pit}$ where$\left(\frac{dc}{dN}\right)_{pit} = \frac{C_P}{2\pi}\beta^2 c^{-2}$, $\left(\frac{dc}{dN}\right)_{crack} = C_F(k_t\Delta\sigma)^n\Phi^{-n}c^{n/2}f$ $\Delta K_{tr} = 1.12k_t\Delta\sigma\sqrt{\pi c_{tr}}/\Phi = \Delta K_{th}$	$C_P, C_F, n \rightarrow$ constants $\beta \rightarrow$ aspect ratio c/a $c, a \rightarrow$ pit radius, depth $f \rightarrow$ cyclic frequency $\Phi \rightarrow$ shape factor $k_t \rightarrow$ SCF
Rokhlin **et al.(1999)** [124]	Fracture mechanics model for FCI and FCP (2024-T3 Aluminium alloy)	$N = \int_{a_{th}}^{d} \frac{da}{C_1[\Delta K_1(a)]^{m_1}}$ $+ \int_{d}^{h} \frac{da}{C_2[\Delta K_2(a)]^{m_2}}$ $\Delta K_1 = \Delta\sigma\sqrt{\frac{\pi a}{Q}}F_c f_b f_c$ $\Delta K_2 = \Delta\sigma\sqrt{\frac{\pi a}{Q}}F_s f_c$	$h \rightarrow$ specimen thickness $a_{th} \rightarrow$ crack size at ΔK_{th} $d \rightarrow$ pit depth $\Delta K_1, \Delta K_2 \rightarrow$ Stage 1,2 SIF $Q, F_c, f_b, F_s \rightarrow$ geometry factors $f_c \rightarrow$ crack closure factors $C_1, m_1, C_2, m_2 \rightarrow$ experimental constants
Wang et al. **(2001)** [9]	CF process composed of 2 stages: 1) initiation (pit nucleation and growth) 2)SC and LC propagation. Pit: semi-circular surface crack Linear damage summation model (Aluminum alloys)	$\Delta K = \beta k_t \Delta\sigma\sqrt{\pi a}$ $a_i = \pi\left(\frac{\Delta K_{th}}{2.2k_t\Delta\sigma}\right)^2$ $N = N_i + N_p$ $N_p = \frac{a_i^{(1-n/2)} - a_{SC}^{(1-n/2)}}{C\Delta\sigma^n\beta_1^n k_t^n \pi^{n/2}(n/2-1)}$ $+ \frac{a_{Sc}^{(1-n/2)} - a_f^{(1-n/2)}}{C\Delta\sigma^n\beta_2^n k_t^n \pi^{n/2}(n/2-1)}$ $1/N_i = 1/N_i^{fat} + 1/N_i^{cor}$ $N_i^{fat} = AW_s/(\Delta\tau - 2\tau_f)^2$ $N_i^{cor} = A^{HW}/(a_i^3 - a_0^3)$ $\beta_1 = 1$, through crack, $\beta_2 = \frac{2.2}{\pi}$ semicirc $A^{HW} = \left(\frac{3MI_p}{2\pi n^e F\rho}\right)^{1/3}$	$k_t, \Delta\sigma \rightarrow$ SCF, stress amplitude $a_0, a_i \rightarrow$ initial/critical pit size $N_i, N_p \rightarrow$ FCI and FCP cycles $W_s \rightarrow$fracture energy $N_i^{fat}, N_i^{cor} \rightarrow$ fatigue/corrosion components $A^{HW} \rightarrow$ constant from [126] $A \rightarrow$ Mura et al. constant [127] $\Delta\tau \rightarrow$ shear stress amplitude $\tau_f \rightarrow$ friction stress $C, n \rightarrow$ material properties

3.2 Sriraman and Pidaparti (2009) [136]

Sriraman and Pidaparti [136] proposed a simple deterministic model for life prediction that (according to their point of view) considers the synergy between pitting and fatigue. They were interested in estimating the life of an aircraft aluminium alloy under conditions where a corrosive environment and cyclic stressing were both present. The model was developed to take into account the accelerated fatigue damage produced in a corrosive environment and the modification of the fatigue curve.

The model is formulated assuming the material being exposed to a chloride ion-containing aqueous environment and fatigue stress involving complete load reversal, where the pitting corrosion-fatigue process is composed of the following stages: pit initiation and growth (under the influence of both cyclic stresses and the aqueous environment), nucleation of a crack from a pit of critical depth (pit-to-crack transition), propagation of a small crack, and eventual long crack propagation to signify failure.

Pits are assumed to stabilise almost instantaneously and the initiation and growth of pits are controlled both by the pitting current and the stress amplitude. When the pit attains a critical depth, exceeding the threshold level for crack initiation, and thereby nucleating a crack. The crack is instantly formed from the pit that has reached critical depth, and the crack initiation time is, in effect, the time for the pit to grow to this stage. The crack responsible for material damage is initiated only at the pit site. In other words, pitting is a prelude to crack nucleation and propagation.

It is important to mention that the emphasis here is not on simulating any actual environmental or loading condition of an aircraft structure/ component but only on estimating the life under conditions when corrosive environment and cyclic stressing coexist. The authors claim that the model can be used to predict the corrosion-fatigue life of any alloy system that exhibits pitting corrosion. In the paper [136] an aircraft aluminium alloy 2024-T3 was assessed and the results obtained showed good agreement with experimental data.

The model addresses the coupling effect of load on pith growth by means of a stress factor on pit current density, thus considering only an elastic component. Compared with the plastic strain, the effect of elastic strain has been reported to be not significant or to have no effect [137–139,108]. In addition, as it has not been validated for coupling conditions, the proposed model can used for aircraft service conditions, where experiences corrosion when it is on the ground and fatigue loading during flight, or for assessing steam turbine blades for power generation, which are exposed to similar service conditions.

Pit growth model

The model is a modification of that proposed by Wang et al. [9]. The pit depth at any time t is evaluated according to Kondo's approach and the constant factor B is expressed based on Faraday's law as expressed in [135] (see Table 1). However, the model incorporates the stress-dependent behaviour of pit growth, according to Ishihara's model:

$$a_p = \left(\frac{3M}{2\pi n F \rho}\right)^{1/3} (I_p)^{1/3} (A') (t)^{1/3} \tag{1}$$

where M is the atomic mass of the alloy, n is the valence of the atoms, F is the Faraday's constant, ρ is the density of the alloy, I_p is the pitting current and A' is taken to be 1.01^{σ_a}, where σ_a is the stress amplitude in MPa. Using this equation to obtain the expression for t and substituting $t = N/f$, the number of cycles required for a pit to reach a particular depth a_p under coupled corrosion-fatigue conditions is:

$$N = \left(\frac{2\pi n F \rho}{3M}(f a_p^3)\right)\left(\frac{1}{I_p}\right)\left(\frac{1}{1.01^{\sigma_a}}\right)^3 \tag{2}$$

Pit-to-crack transition model

The pit is considered to be of hemispherical shape and the SIF to be similar to that for a semi-circular surface flaw in an infinite plate. The SIF is calculated as $\Delta K = (2.2/\pi) k_t \Delta\sigma \sqrt{\pi a_p}$, where k_t is the SCF. The critical pit size is also obtained from the threshold requirement for crack initiation, according to linear elastic fracture mechanics [9] as:

$$a_{pc} = \pi \left(\frac{\Delta K_{th}}{2.2 k_t \Delta\sigma}\right)^2 = \pi \left(\frac{\Delta K_{th}}{4.4 k_t \sigma_a}\right)^2 \tag{3}$$

The number of cycles to crack initiation N_i is then obtained inserting the expression for a_{pc} into eq. (2):

$$N_i = \frac{2\pi n F \rho}{3M}(f)\left[\pi \left(\frac{\Delta K_{th}}{2.2 k_t \Delta\sigma}\right)^2\right]^3 \left(\frac{1}{I_p}\right)\left(\frac{1}{1.01^{\sigma_a}}\right)^3 \tag{4}$$

This equation shows several experimental features of crack initiation. A larger current induces greater pitting, thereby reducing crack initiation life. In addition, higher stress amplitudes produce lower initiation lives, given by the stress factor, i.e., the last term in eq. (4).

Crack growth model

After some modifications to the approach of Wang et al. [9] the following expression for crack propagation is used to calculate the cycles corresponding to crack growth:

$$N_p = \frac{a_{pc}^{(1-m_1/2)} - a_{tr}^{(1-m_1/2)}}{C_1(2\sigma_a\beta_1\pi^{1/2})^{m_1}(m_1/2-1)} + \frac{a_{tr}^{(1-m_2/2)} - a_f^{(1-m_2/2)}}{C_2(2\sigma_a\beta_2\pi^{1/2})^{m_2}(m_2/2-1)} \tag{5}$$

where C_1 and C_2 are the fatigue coefficients for the small and long cracks, respectively, m_1 and m_2 are the corresponding fatigue exponents, and β_1 and β_2 are the corresponding crack geometry factors defined in Table 1. The crack length corresponding to the transition length from a small to a long crack is a_{tr} , and a_f refers to the final critical crack length that would signify failure, defined as:

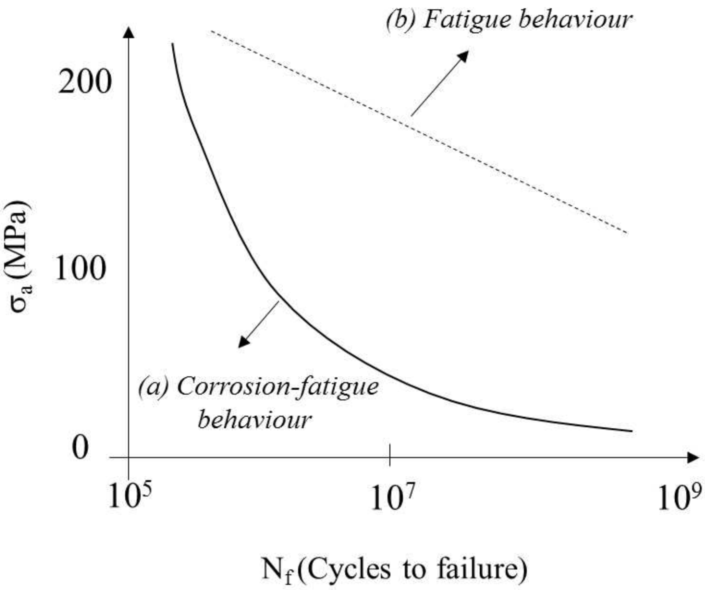
$$a_f = \frac{1}{\pi}\left(\frac{K_{IC}}{1.12\sigma_a}\right)^2 \tag{6}$$

Figure 4(a) shows the $S-N$ curve for aluminium alloy 2024-T3 under conditions for a) corrosion fatigue and b) normal fatigue.

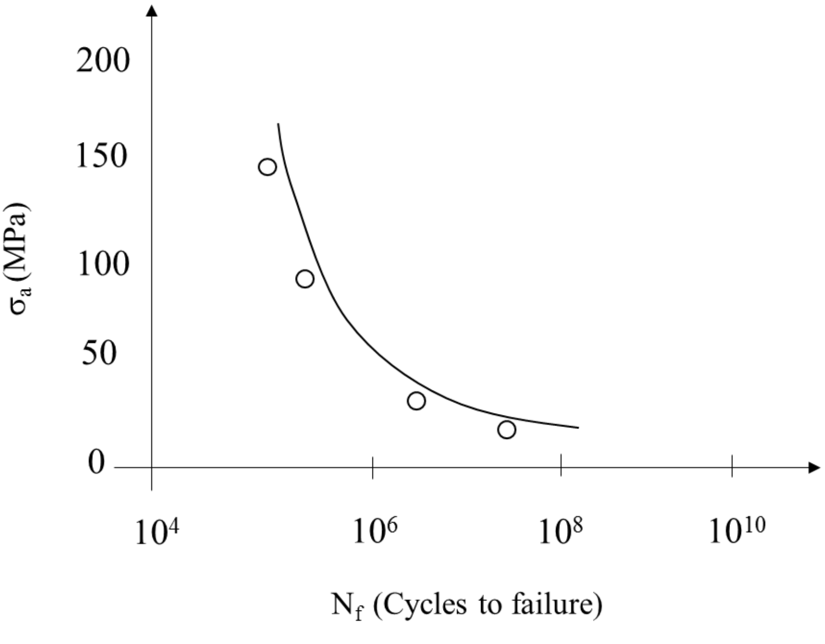
Finally, Fig. 4(b) depicts the $S-N$ curve for corrosion fatigue behaviour compared with the experimental data reported by Ishihara et al. [130].

Summary

- The model takes into account the influence of fatigue loading on pit propagation.
- The model shows good predictive capability for assessing the corrosion-fatigue life of aluminium alloy 2024-T3, although the authors suggest that any alloy system exhibiting pitting corrosion can be tested.
- Crack initiation from pit sites is faster at high stress levels and can even occur from relatively small pits.
- At lower stress levels, the crack initiation stage could contribute to a major part of the materials life. The stress factor is seen to be particularly sensitive for decreasing stress values.
- The model has not been validated under conditions of simultaneous cyclic stressing and exposure to a corrosive environment.



(a) Effect of stress amplitude on the model predictions of the fatigue life of aluminium alloy 2024-T3 under fatigue and corrosion-fatigue conditions.



(b) $S-N$ diagram for corrosion-fatigue behavior in aluminum alloy 2024-T3 as shown by Newman [140] and corrosion fatigue predictions. Solid curve: proposed model. Symbols: experimental results from Ishihara et al. [130].

Fig. 4. $S-N$ diagrams for corrosion-fatigue behaviour in 2024-T3 Aluminium Alloy by Sriraman and Pidaparti. Figures adapted from [136].

3.3 Li and Akid (2013) [141]

Li and Akid [141] conducted a study on a medium strength structural steel in an artificial seawater environment, using plain and pre-pitted specimens in air and under corrosion fatigue condition under fully reversed rotating bending, Fig. 5. Emphasis was placed on the study of corrosion pit formation and the development of cracks from pits but pit development, pit-to-crack transition and crack growth were quantified throughout the fatigue lifetime, Fig. 6, allowing a three-stage model, to predict corrosion-fatigue life, to be developed.

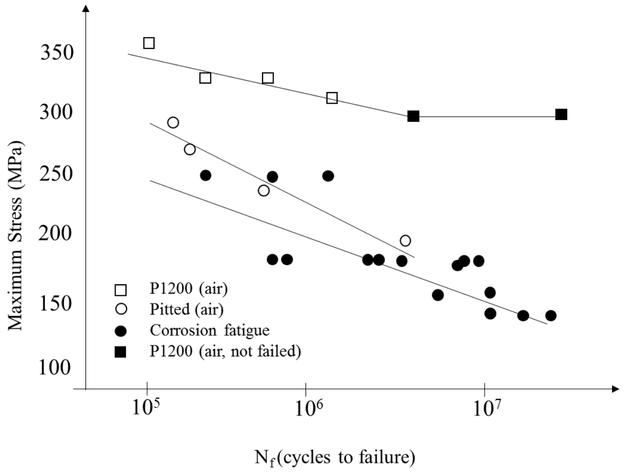


Fig. 5. $S-N$ data for a medium strength structural steel in air and artificial seawater environments. Figure adapted from [141]

Pit growth model

Two different growth models proposed by other authors [104,136,142] have been used in this work: a) an exponential growth model and b) Faraday's law. As a result the expressions for the pit growth are given by:

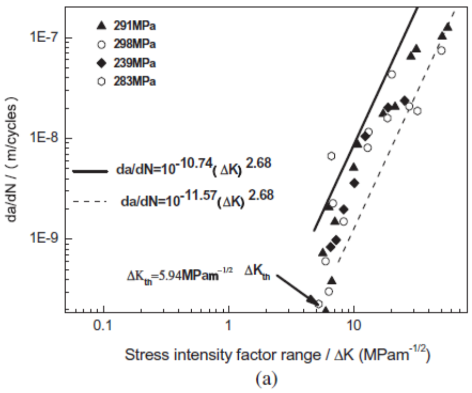
a) Exponential law:

$$a_p = A\left(\frac{N_{pit}}{N_f}\right)^B \tag{7}$$

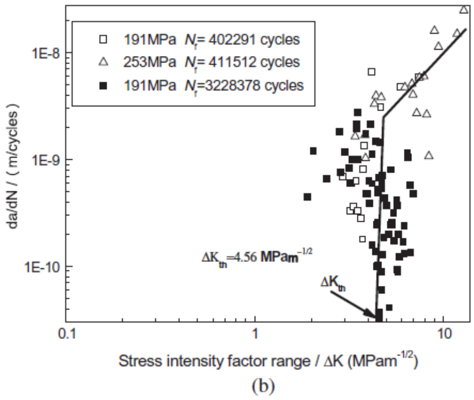
where N is the number of applied cycles, N_f is the fatigue endurance and the constants A and B (pit growth parameters) were interpolated using the data in Fig. 7(b).

b) Faraday's law:

$$a_p = \left(\frac{3M}{2\pi nF\rho}\right)^{1/3}(t)^{1/3} \tag{8}$$



(a) Crack growth rate versus SIF range: air fatigue



(b) Crack growth rate versus SIF range: corrosion fatigue

Fig. 6. Experimental data obtained by Li and Akid [141].

where all the parameters have been previously defined. The critical pit size was obtained from Fig. 7(a) and the cycles to crack initiation by substituting eq. (3), where N_f was obtained from experimental data, Fig. 5. Therefore,

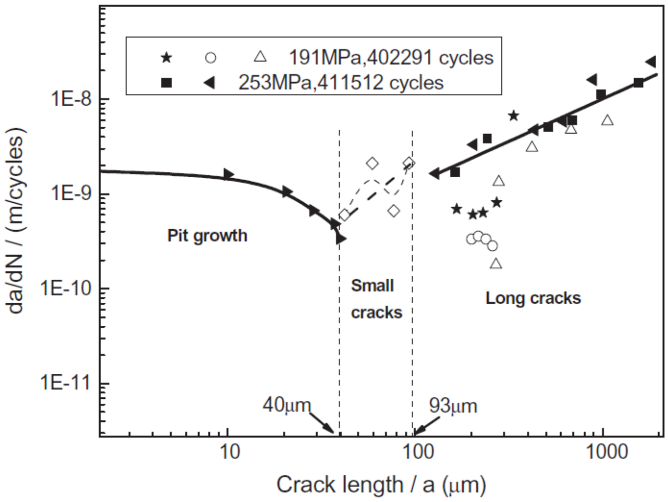
$$N_{pit} = \left(\frac{a_{pc}}{A}\right)^{1/B} \left(\frac{10^{9.19}}{e^{0.036\sigma_a}}\right) \tag{9}$$

Crack growth model: small and long crack models

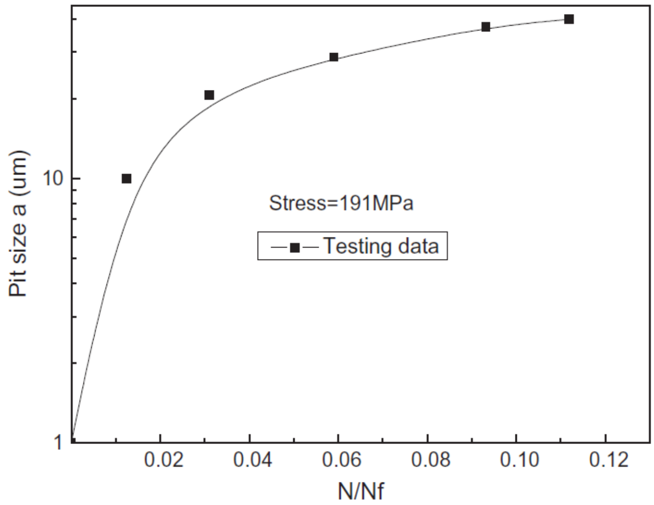
Small and long crack growth behaviour has been considered in this model, using an empirical formulation similar to the Paris law:

$$\frac{da}{dN} = \frac{da}{dN_{SC}} + \frac{da}{dN_{LC}} = C_{SC}\Delta K^{m_{sc}} + C_{LC}\Delta K^{m_{LC}} \tag{10}$$

where the constants C_{SC}, m_{SC}, C_{LC} and m_{LC} were determined by fitting



(a) Corrosion pit and crack growth rate versus crack length.



(b) Corrosion pit growth versus fraction of lifetime (N_f).

Fig. 7. Experimental behaviour of pit depth or combined pit and crack depth for a carbon steel in artificial seawater.

experimental data. The predictions of the model are in reasonable agreement with the experimental data, as shown in Fig. 8, using both pit growth models, however the exponential model seems to be more conservative.

In addition, the Kitagawa-Takahashi diagram, relating the fatigue limit and the threshold SIF, was produced for both test environments (Fig. 9) where it is indicated that the fatigue limit can be eliminated in a corrosive environment.

Summary

- A corrosion fatigue model based on pit growth, pit-to-crack transition and

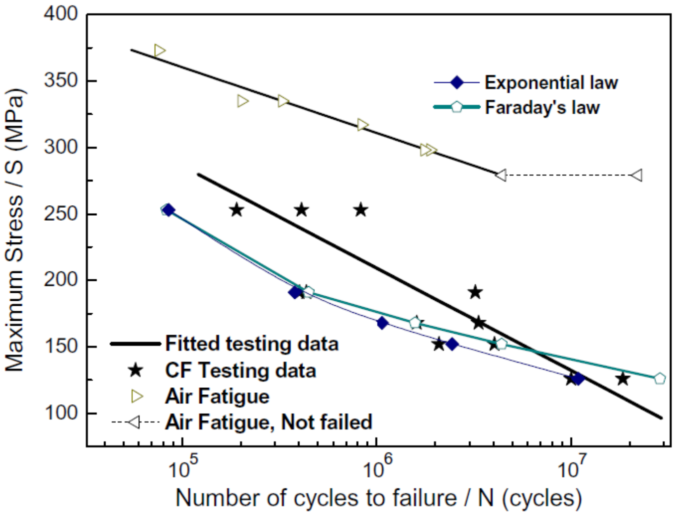


Fig. 8. Life prediction based upon the pit and crack growth model [141].

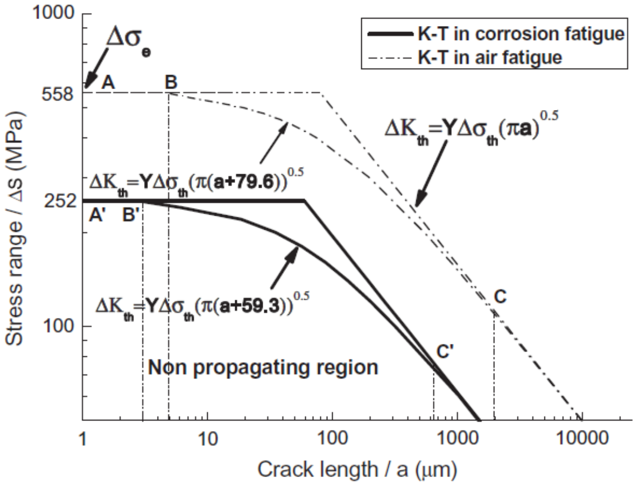


Fig. 9. Comparison of the Kitagawa-Takahashi diagrams for air and artificial sea-water environments [141].

crack growth gives predictions in good agreement with experimental data.

- $S-N$ curves and Kitagawa-Takahashi diagrams were constructed for both in-air and corrosion fatigue test conditions. Results show a much smaller non-propagating crack region for the corrosion-fatigue test, due to a reduction in the fatigue strength of the material under such conditions.
- As the electromechanical effect on fatigue life is not taken into account in the diagram, a fatigue limit may not exist under corrosion fatigue conditions.
- The model uses a linear superposition methodology to assess lifetime, which does not account for chemical and mechanical coupling.

This research involved fatigue crack growth rate measurements in the near threshold regime and fatigue life tests with pre-pitted specimens using an ultrasonic fatigue testing technique for 403/410 12% Cr martensitic steel. The work focused on pit-to-crack transition assessment and creating tools to predict critical pits in steam turbine blades.
To study the pit-to-crack transition, artificial pits were generated (Fig. 10) in the gauge length of specimens. Test environments included air and two aqueous solutions at 90 ^{o}C. Fractographic investigations with a scanning electron microscope (SEM) were carried out to identify the mechanisms of fatigue crack initiation and propagation.

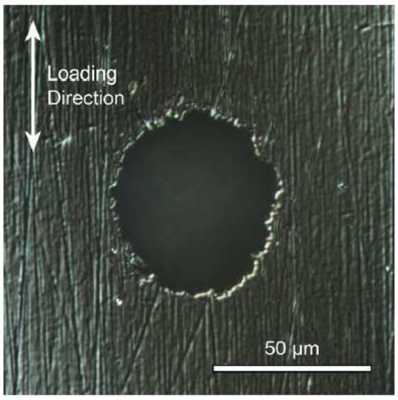


Fig. 10. Artificial pit on a fatigue specimen [146].

Pit-to-crack transition model

The pit is considered as a semi-elliptical two-dimensional crack, Fig. 11(a), where the average ratio a/c was found to be 1.91. Data obtained with pre-pitted specimens were evaluated in terms of linear elastic fracture mechanics, taking a similar approach to all the methodologies described above:

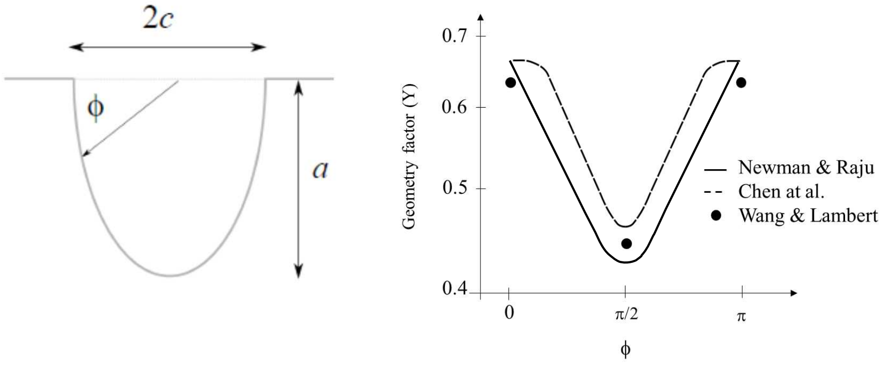
$$\Delta K = \Delta\sigma\sqrt{\pi a}Y \tag{11}$$

where Y is the geometry factor which includes the shape and boundary effects. As shown in Fig. 11(b), the geometry factor Y along the boundary of the pit (semi-elliptical crack) is a maximum at the surface which gives a maximum value of the stress intensity factor at the pit mouth and not at the base of the pit. Crack initiation has been observed at these sites, as shown in Fig. 13. These results are also in accordance with previously observed crack initiation sites by Turnbull et al. [76] in which for certain pit aspect ratios, the crack is more likely to initiate at the pit mouth, although the explanation given in that work for the initiation is the accumulation of plastic strain.

Moreover, results are correlated with threshold stress intensity factors of long cracks and fatigue limits of smooth specimens in Kitagawa-Takahashi diagrams which allows prediction of the endurance stresses of pitted components, where ΔK has been calculated using the value of the half surface width (c), instead of the pit depth (a).

Although eq. (11) gives useful description of the SIF along the pit, it does not consider the anomalous behaviour of small cracks. The authors included the El Haddad et al. expression [147] for the small crack regime, by adding the so-called intrinsic crack length c_0 to the observed length c. The data were plotted in modified Kitagawa-Takahashi diagrams where the abscissa is the normalised crack size c/c_0 and the ordinate the normalised stress intensity factor range $\Delta K/\Delta K_{th}$, where the intrinsic crack length c_0 is given by:

$$c_0 = \frac{1}{\pi}\left(\frac{\Delta K_{th} Y}{\Delta \sigma_{FL}}\right)^2 \tag{12}$$



(a) Schematic representation of pit geometry.

(b) Geometry factor along periphery for a/c ≥ 1

Fig. 11. Pit characterization. Figures adapted from [146].

Small corrosion pits have also been assessed using this approach in [121,148,149], among others. Therefore, estimates for the threshold stress intensity factor for small cracks were obtained, as plotted in the dashed lines in Fig. 12, using the expression:

$$\Delta K_{th,pits} = \frac{\Delta K_{th}}{\sqrt{1+\frac{c}{c_0}}} \tag{13}$$

Equation (13) is used to assess the threshold SIF of cracks, initiated from pits, that lead to failure (propagating cracks); and those that although initiated will become non-propagating ($\Delta K \leq \Delta K_{th,pits}$). As observed in Fig. 12, good estimates are obtained in comparison with experimental data.

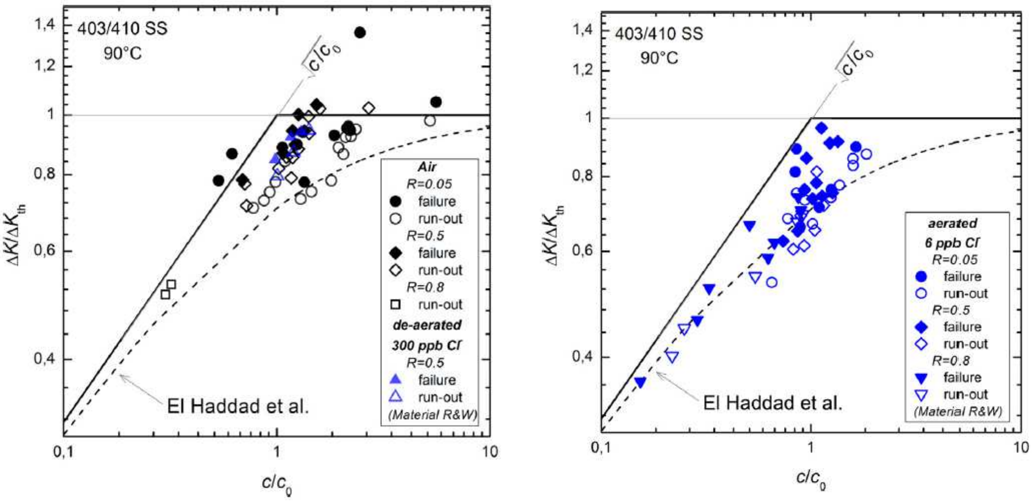


Fig. 12. Modified Kitagawa-Takahashi diagram for fatigue tests with pre-pitted specimens: a)air and de-aerated 300 ppm Cl^- solution at 90 ^{o}C b) aerated 6 ppm Cl^- solution at 90 ^{o}C. Figure from [146].

Summary

- Empirical equations were derived for the determination of ΔK_{th} and the $\Delta\sigma_{FL}$ for different stress ratios in two different environments, which allow the calculation of critical stresses for pitted components according to the local stress range.
- A decrease of ΔK_{th} with increasing loading ratio R was observed for all environments as expected. However, increasing corrosiveness of the environment did not produce a decrease in the SIF threshold value. Closure effects were considered in that work to be the main reason for this effect.
- The pit width (c) is used as the corresponding geometry parameter.
- Corrosion pits can be treated as cracks. The data for transition from a pit-to-crack have been correlated using the Kitagawa-Takahashi Diagram, which relates the endurable cyclic stress and pit width to the prediction of fatigue failure. All data for the survival and failure stress intensity were well represented by the extension of the Kitagawa Diagram by El Haddad's expression.

Using the detected value of c as a critical parameter has been recently analysed by the authors [150,151]. Note that, at the time of detection, c is smaller than at failure (c+Δc) (see Fig.13), and therefore the threshold condition for failure, which will give the endurance limit of the configuration, is not given by c at the time of detection. This is the main reason for seeking for development of an alternative approach in accordance with experimental observations. At at the time of addressing reviewers' comments, we have noticed that Schönbauer et al. [152] evaluated the pit-to-crack transition by means of the $\sqrt{area}$-parameter proposed by Murakami and Endo [131]. Experimental results (R=-1) are depicted in Fig. 14, where the fatigue strength of 17-4PH stainless steel specimens containing small artificial defects (corrosion pits included). As shown in the figure, the threshold stress intensity factor range, ΔK_{th}, exhibited a defect size dependency for $\sqrt{area} \leq 80\mu$m, and it became a constant value for a transition value $\sqrt{area} > 80\mu$m independent of R. A good predictive capability of the approach is shown.

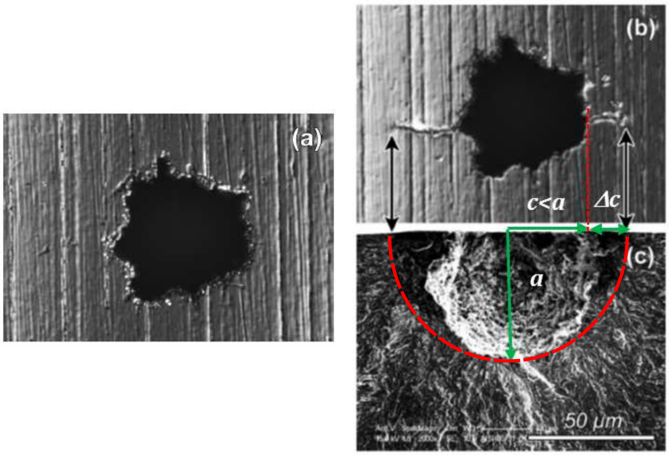


Fig. 13. a) Pit with no cracks; b) Non-propagating small cracks at the pit mouth c) Fracture surface after further loading at a higher stress range indicating shape of crack before failure. Figure adapted from [146]

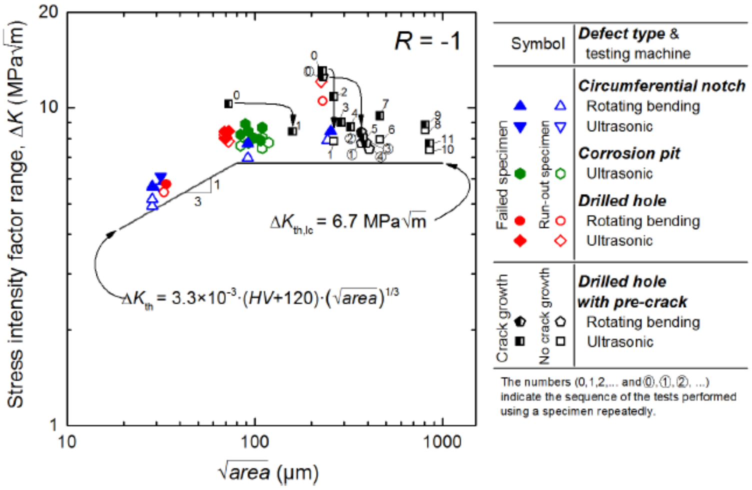


Fig. 14. SIF range, ΔK, vs. defect size, $\sqrt{area}$, at R=-1 [152].

Following on from a cellular automata (CA) modelling approach used by Akid and co-workers [164] to predict intergranular corrosion, a Cellular Automaton Finite Element Model (CAFE) model has been developed for simulating the interaction between localised corrosion and mechanical loading at the mesoscopic level. In this model the accumulation of pitting damage under stress is decoupled into a localised corrosion component, modelled using cellular automata, and a mechanical component wherein the deformation, due to localised loss of solid material is analysed with the finite element method. Synchronous execution of the two analyses and provision of a feedback loop between both, in real time, provides a good approximation of the interaction between the electrochemical (localised corrosion) and mechanical (deformation) damage processes. The model has been employed to simulate the influence of different electrochemical parameters and applied stress on the evolution of depth, aspect ratio and morphology of pits, with time. Qualitative and quantitative comparison of simulation results with experimental measurements show good agreement.

A typical CA mesh and CAFE output contour plot is shown in Fig. 15 [109], illustrating the different types of site involved in the process, Fig. 15(a), and the stress contour around a developing pit, Fig. 15(b). These include:

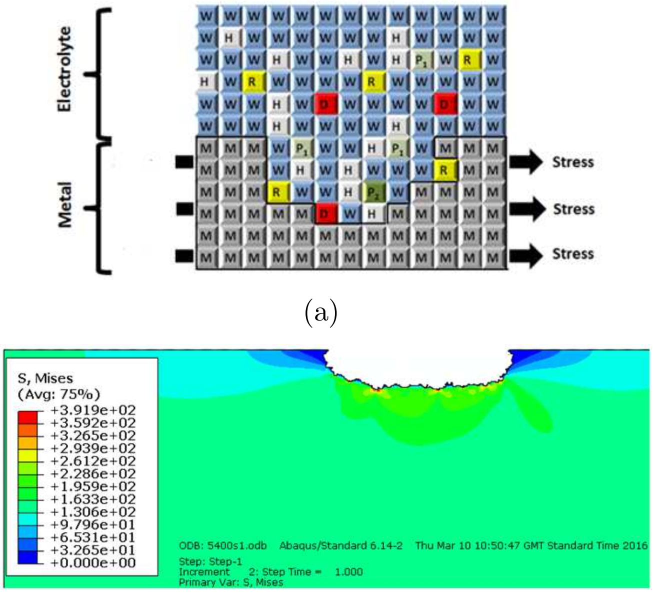
- M - metal site in solid state
- H - proton site
- D - passive film
- R - metal site
- W - water site
- P1- Iron (II) Hydroxide
- P2 - Iron (III) Hydroxide

Anodic dissolution of metals and alloys can be promoted by both elastic and plastic deformation [165,166]. This mechanical-electrochemical interaction has been modelled based on bulk thermodynamic analysis of metals [167,168]. From this model, under non-equilibrium conditions and during strain hardening, a kinetic equation relating anodic dissolution due to deformation can be determined:

$$\text{Elastic deformation} \quad \frac{I}{I_n} = \exp^{\left(\frac{\Delta P V_m}{RT}\right)} \tag{14}$$

$$\text{Plastic deformation} \quad \frac{I}{I_n} = \left(\frac{\Delta\epsilon}{\epsilon_0} + 1\right) \exp^{\left(\frac{\sigma_m V_m}{RT}\right)} \tag{15}$$

where I is the anodic current of deformation, I_n is the anodic current for no deformation, ΔP is the hydrostatic pressure, V_m is the molar volume, $\Delta\epsilon$ is



(a)

(b)

Fig. 15. (a) Typical CA mesh used to represent corrosion in an aqueous environment; (b) typical distribution of equivalent stress around a growing pit. Stress(σ_{max})=200 MPa, [A-time: 5400 s, maximum pit depth: 126 μm, aspect ratio: 0.47], [109].

the plastic strain, ϵ_0 is the onset of strain hardening, σ_m is the spherical part of the macroscopic stress tensor depending on the applied stress, R is the gas constant and T is the temperature. Typical results of this modelling approach can be found in Fig 16:

An extension of this model to 3-D is currently being developed along with a criterion for the transition from pitting to cracking

In a follow-on study, Akid, Fatoba [108] and Evans [110] conducted a series of fatigue and corrosion fatigue studies using API 5L X-65 HSLA linepipe steel. Mechanical factors, notably stress and strain fields produced by real pit geometries were evaluated by means of an experimental digital image correlation technique [108] and modelled numerically by a finite element method. Chemical effects, notably pit growth was modelled using the aforementioned CAFE approach.

During initial baseline data collection, it was observed that, in air, cracks were initiated predominantly from the pit mouth irrespective of stress level. As indicated by Turnbull [76], a mechanics-based explanation for this was obtained from FEA of artificial pits, which indicated that, whereas stress is localised towards the pit bottom, strain is localised towards the pit mouth. Conversely, when equivalent tests were conducted in an aggressive aqueous chloride environment, cracks initiated from both the mouth and bottom of pits depending on stress level. Cracks tended to initiate at the pit base at

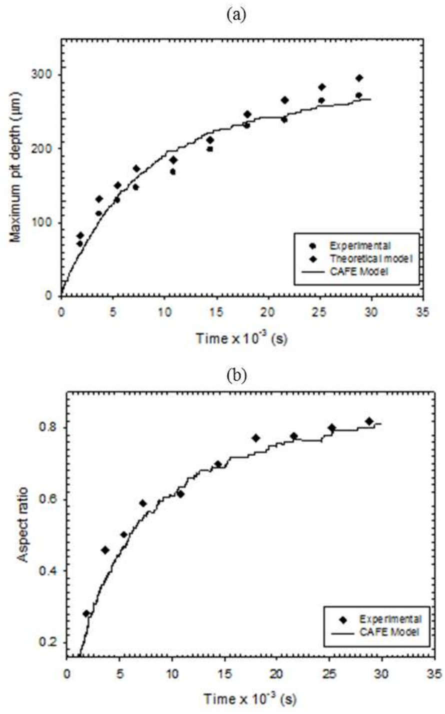


Fig. 16. Plots of (a) maximum pit depth and (b) pit aspect ratio as a function of time simulating pit growth under stagnant (without flow) conditions [109].

low stress and at the pit mouth at higher stresses, suggesting an increasingly important role of the environment at decreasing stress levels.

Crack initiation lifetimes were shorter in corrosion fatigue compared to air, suggesting that strain-enhanced dissolution of slip steps facilitates crack initiation than in air and that this effect was seen to be stress dependent. At higher stress levels, this effect (ratio of crack initiation lifetime in air to that in the aggressive environment) was lower. This was attributed to the domination of mechanically-driven crack initiation with little need for corrosion processes to contribute to crack initiation process. Burns et al. [115,17] identified four local driving forces governing fatigue crack formation and early growth: site geometry, microstructure- scale plasticity and two forms of environmental interaction. Furthermore they pointed out that their results established that a macro-elastic analysis leads to erroneously large predicted values of Ni that are likely too non-conservative for prognosis of corrosion impact on fatigue. This is in line with recent pit-crack studies [110] that suggest threshold microscopic strain values for crack initiation may be a more appropriate parameter for modeling the pit-crack transition, see below.

In acknowledgement that corrosion fatigue failure is often the result of multiple pit-initiated crack growth and crack coalescence, a series of tests were conducted to assess the role of pits in close proximity. For single and double pits in both air and an aggressive environment, crack initiation lifetime decreased with increasing pit size and stress level. FEA analysis also shows that increasing pit size and stress level resulted in increased localised plastic strain. A correlation between plastic strain and the crack initiation lifetime, using a mechanical model for crack initiation, showed that increase in magnitude of plastic strain increases susceptibility to early crack initiation and consequently shorter crack initiation lifetimes.

When two pits are in close proximity, cracks initiated at the pit mouth in the region separating the two pits. This behaviour was explained based on FEA results, which indicated that strain is localised in this region [169]. It was also observed that crack initiation lifetime for double pits generally decreased with decreasing pit-to-pit separation distance and that localised strain increased with increasing pit size and stress level and, with decreasing pit-to-pit separation distance. The dependency of crack initiation lifetime on pit-to-pit separation distance was seen at distances lower than a threshold separation distance, which increased with stress level and pit depth.

Other approaches that have been used in modelling environment-assisted fatigue include that of equivalent initial flaw size (EIFS) and equivalent stress raiser (ESR). EIFS is used to characterize initial fatigue quality of a durability critical component. It is a quantity extrapolated from experimental data simply to facilitate life prediction by using only long crack growth analysis and avoiding the difficulties of small crack growth.

Liu and Mahadevan [170] presented a new methodology to calculate the equivalent initial flaw size (EIFS) distribution. The proposed methodology is based on the Kitagawa-Takahashi diagram. Unlike the commonly used back-extrapolation method for EIFS calculation, their proposed methodology was reported to be independent of applied load level and only used fatigue limit and fatigue crack threshold stress intensity factor. Their methodology is combined with probabilistic crack growth analysis to predict the fatigue life of smooth specimens.

Rusk et al. [114] presented the ESR approach wherein they proposed the following procedure; (a) Calculate fatigue notch factor (K_{fc}) for each test plate using the appropriate probabilistic strain-life model with Neuber notch-strain relation; (b) Calculate critical notch K_t, equivalent notch root radius and fatigue notch ratio (q_c) for each test plate; (c) Fit the notch ratio model to corrosion-fatigue test results; (d) Perform ROI analysis of surface topography data for the corroded component, and extract characteristic notch dimensions; (e) Calculate notch notch K_t and equivalent notch root radius for each region of interest (ROI); (f) Calculate fatigue notch ratio (q_c) and fatigue notch factor (K_{fc}) for each ROI using notch ratio model. And (g) calculate the survival probability for the damaged component using all ROI's found. It should emphasized that the effects of corrosion electro-chemistry and diffusion processes interacting with fatigue damage progression are not included in this model, and may result in additional fatigue life reductions than those demonstrated here.

Summary

Cellular automata (CA) are discrete computational systems in which the evolution of the state of each cell in the modelling space may be determined by the current state of the cell and that of its neighbourhood cells based on local transformation rules [171]. CAs differ from partial differential equations (DE), in that space, state and time and other dynamic variables are discrete and not continuous as in DEs [172]. All the cells have access to the same set of states at any time and can assume only a finite number of states. Based on the local transformation rules, which apply to all the cells in the automaton, all cells are updated synchronously. CAs allow physical metal-environment system to be discretised into a metal/film/electrolyte cellular lattice of sites (referred to as 'cells'), where each cell in the lattice can represent a different species taking part in the corrosion process. CAs are becoming increasingly popular, especially in corrosion, due to their stochastic nature and the ability to simulate electrochemical processes at a mesoscopic scale [173–175]. Previous studies have shown that the nature of electrochemical processes, wherein the state of the species in corrosion reactions changes as a result of interaction with other species around it, makes CA a convenient tool for simulating localised corrosion [164,176]. However, to date, simulation of pitting corrosion systems involving mechanical loading have not been reported in the literature, with perhaps the exception of the work of Wang and Han, on metastable pitting [176].

4 CF characterization and life prediction methods in industry.

The O&G, Aerospace, electric power and nuclear industries, among others, experience corrosion and corrosion fatigue, on a daily basis, across a wide range of components and structures. At the time of this literature review no corrosion-fatigue procedure, which considers the mechanism as a whole, is currently applied in these industries.

Existing structural integrity assessment procedures [37–39] provide simplified guidelines on the appropriate steps to take when corrosion fatigue cracking, as well as local thinning, has been detected in service and an assessment of the implications for structural integrity has to be carried out. The burst pressure is usually determined for the remaining ligament thickness when defects (e.g., pits) are blunt; as the likelihood of failure is controlled by plastic collapse considerations. When the corrosion defect is classified as sharp the use of fracture mechanics is the most common approach to consider for sub-critical crack growth assessment. Fatigue crack growth rates in aggressive environments are available for a limited number of instances in BS 7910 (Section 8) [38], R6 (Section II.8) [40], FITNET (Section 9)[39], although there are no recommendations on how to deal with pitting corrosion. API 579 [37] includes a whole section on pitting corrosion, based on local thinning area. Sources for fatigue crack growth data for various materials and service environments are provided in paragraph 9. These procedures [37–40] are not intended to cover applications where the corroded component is subject to significant fatigue loading, or brittle fracture is likely (even under static loading).

In this section, an overview of the corrosion fatigue problem in different industrial contexts is given together with a brief description of some of the current approaches used by industry and a number of projects that are currently under development in the search to improve current methodologies for assessing the significance of corrosion fatigue in fatigue life of components.

4.1 Oil & Gas.

Corrosion fatigue is major challenge to the O&G industry [177]. In the modern O&G industry, water depth in offshore production regions is increasing and the drilling process is occurring within wells under high pressure-high temperature (HPHT) conditions. High strength and toughness, combined with corrosion resistance, are fundamental characteristics sought in alloys used for such applications. Floating production systems (FPS) have been used for the last 30 years to exploit offshore O&G wells. However, in many cases the increasing water depth makes the use of current flexible-line designs impractical, both technically and economically. Two main approaches are thought to be feasible solutions for deep and ultra-deep wells. The first involves the use of rigid carbon steel lines. However, corrosive gases in the fluids make the system even more complicated, as corrosion-fatigue can be a problematic issue for these types of steels. The second approach, aims to improve the efficiency of the flexible line technology, where fatigue is a limiting factor in the design life of flexible risers. To date fatigue design of flexible risers has been based on $S-N$ [178] data obtained by component testing in air with the addition of a 'knock-down' factor to account for corrosion. However, seawater flooding of flexible pipes due to leakage of the external sheath, is a possible scenario leading to the development of localised corrosion (pitting) and subsequent cracking and potential failure. This situation is not appropriately accounted for in design codes [179–181]. In addition, to the authors‘ knowledge, there is no current O&G standard code which includes the synergetic effect of corrosion and fatigue.

4.2 Aerospace

Damage tolerance design and maintenance practices in the aerospace industry are not structured to handle corrosion. Corrosion fatigue is considered by the acceleration of crack propagation and the use of safety factors. USA Aircraft Structural Integrity Program (ASIP) methods employ da/dN curves that are modified for ‘standard environmental effects’ [182]. It is not clear whether this method is excessively conservative, sufficiently accurate, or speculative. For decades, as a result, a more holistic structural integrity approach was sought by the industry to account for the impact of damage accumulation both from operational loads and environmental effects built into a systematic assessment framework [183]. Several research programs were aimed to improve structural integrity assessment methods to properly account for the structural effects of corrosion in critical aircraft structure [184]. The Australian Defence Science and Technology Organisation (DSTO) [185] used the concept of Equivalent Crack Size (ECS) for corrosion pitting in D6ac steel. Relationships between corrosion morphology and fatigue life of laboratory coupons were established that allowed corrosion pits to be described as cracks to provide input for durability and damage tolerance analyses. This procedure was extensively used [186,187] by DSTO to assess the effect of pitting corrosion in life assessment of primary and secondary structures. Basically, it considered that the stress concentration effect of the pit on the beta solution associated with an effective crack, causes a shift in stress intensity, an increase in crack growth rate, and a decrease in fatigue life. A Structural Integrity Prognosis System was developed within the Defence Advanced Research Projects Agency (DARPA) [188] research program in which high fidelity microstructurally-based models of the actual structural degradation processes and novel sensor systems were used to detect and quantify corrosion fatigue.

4.3 Power generation

Other industries such as power generation continue to play an important role in the advancement of knowledge and understanding of damage mechanics relevant to pressure vessels in wet environments at elevated temperatures, notably corrosion fatigue. The effective operation of steam turbine blades depends primarily on the accuracy of the prediction of corrosion/cracking damage in order to ensure plant availability and reduce maintenance costs. Low-pressure blades and disks are components that frequently operate in environments of high humidity and at elevated temperature. The need to generate robust predictive models is now even greater since the inception of two-phase on-demand operation where blades are subject to peak period high frequency running in nominally ‘dry’ conditions, followed by periods off-peak, where blades operate at low frequency in ‘wet’ environments. As recognized by Schönbauer et al. [146], no predictive methodology appears to have been developed for the remaining life estimation for turbine blades which have been exposed to corrosion fatigue (CF) damage. The EPRI research program [143], in collaboration with NPL (UK), BOKU (Austria) and STI Technologies (USA) involved testing and characterization of CF mechanisms in turbine blades made from martensitic steels and the development of a life prediction methodology. Maintaining structural integrity of reactor internal and primary coolant pressure retaining components, such as reactor pressure vessels (RPV) is one of the key responsibilities in terms of safety and plant life in the nuclear industry. Early efforts by the nuclear industry in dealing with corrosion-fatigue assessment and life prediction remain dated to late 70s and early 80s [189] and there is vast experience in dealing with corrosion and environmental assisted cracking of RPVs [26,190,191]. The International Cooperative Group on Cyclic Crack Growth Rates (ICCGR) was created in 1978 to coordinate work undertaken worldwide on fatigue crack growth in light water reactor (LWR) pressure vessel materials and environments, thus increasing the value of the data and avoiding unnecessary duplication of effort. The EDEAC [192] database was established as one of the ICCGR activities to facilitate collection of the worldwide data in a consistent format. Although the recent Fukushima Daiichi catastrophe (2011) has impacted on public and political confidence, the nuclear industry continues to make a primary contribution to the energy supply matrix [193]. There has been significant concern about enhanced fatigue crack growth rates in light water reactor (LWR) environments [194] and as result interest in a more fundamental understanding of the mechanisms behind these effects [195]. Due to the lack of recommendations, fatigue crack growth data for steels in Pressurized Water Reactors (PWR) environments are currently prescribed using crack reference data in air from the ASME Boiler and Pressure Vessel code (Section XI)[196]. The draft ASME Code Case N-809 [197] provides a Fatigue Crack Growth (FCG) law for austenitic stainless steel. The testing on which the FCG law is based is predominantly sawtooth loading applied to Compact Tension (CT) specimens in isothermal conditions and explicitly considers the effect of the environment through the additional parameters of temperature and rise time applied in conjunction with a standard Paris equation. FCG calculations using the PWR environment growth law are shown to have the potential to produce significantly enhanced growth rates over those predicted using the law for an air environment[198].

5 Discussion and concluding remarks

The present review has demonstrated the extensive research effort that continues to progress the improvement of CF life estimation. It is recognised that the synergetic mechanisms involved in the evolution of pit growth and the lack of knowledge concerning the coupling between mechanical and chemical contributions to the initiation of cracking for different materials and loading conditions makes the assessment of corrosion fatigue an extraordinarily complex problem with a significant amount of uncertainty.

At the time of this review, most of the damage tolerance methodologies, found in the literature, consider corrosion pits as equivalent cracks in order to make use of LEFM, which necessitates experimental testing to obtain the required parameters to generate Paris-law type curves. The models do not describe a methodology to assess the pit-to-crack transition mechanism, taking into account the synergetic interactions of environmental and mechanical features, each of significant impact on the mechanisms affecting the initiation and propagation of corrosion fatigue defects. Most corrosion-fatigue life prediction methods are based on linear superposition, in which the separate contributions to damage of each stage of the corrosion fatigue process are taken in isolation; the main reasons being:

- There is insufficient knowledge on the underlying mechanisms involved in the evolution of corrosion damage, particularly the pit-to-crack transition, to develop and follow a mechanistically based assessment methodology.
- Phenomenological approaches can be followed once an extensive experimental campaign is performed, as data on initial pit size, aspect ratio, and average growth rate to define the relevant Paris law fitting parameters are required.

McDowell and Dunne [199]] reviewed computationally based microstructure-sensitive fatigue models and the driving forces associated with crack initiation. The authors discussed the applicability of LEFM methodologies based on ΔK and pointed out that these are not strictly applicable as a crack driving force for fatigue within the microstructural small crack regime and early portions of the physically small crack regime due to the roles of slip localization and microstructure; where the value of ΔK is modified by shielding of the crack tip due to short and long range fields of dislocations, where the spatial arrangement of local features or 'states' in the internal structure (e.g., morphological attributes) at various constituent length scales play an influential role in determining the overall properties of the material. Material durability and utility in service are often dictated by mesoscopic heterogeneity of structure and its lack of reversibility under cycling or in extreme environments.

Each material class and response of interest is influenced by a finite, characteristic set of length and time scales associated with key controlling microstructure attributes [200] . For this reason, including cooperative damage mechanisms in a model is performed by using sets of models that are scale appropriate to the length scales and microstructure attributes deemed most influential on the target response(s) at the scale of the application, usually of high complexity and low generality.

Hochhalter and co-workers reported, in two papers [201,202] , on the development of a mechanistic and probabilistic multi-scale fatigue crack simulation methodology, where finite element models of replicated grain and particle geometry were used to compute mechanical fields near monitored cracked particles using an elastic-viscoplastic crystal plasticity model that captures the effect of the orientation of the grains near each monitored particle. Nonlocal, slip-based metrics were used to study the localization and cyclic accumulation of slip near the cracked particles providing mechanics-based insight into the actuation of the nucleation event.

They concluded that such semi-empirical models were based upon; (i) the application of cyclic accumulation rate of slip-based metrics to model which incubated cracks are likely to nucleate, however such an approach does not accurately model the number of cycles to nucleate a crack; (ii) The local maximum tangential stress acts as the driving force and should be incorporated to model accurately the number of cycles to nucleate an incubated crack. (iii) slip-based metrics provides a basis to calculate the reduction in local critical driving stress required to nucleate an incubated crack due to cyclic slip accumulation; and (iv) the nucleation direction is normal to the computed, local, maximum tangential stress direction and the observed crack path tortuosity is apparently due to the altering of the direction of maximum tangential stress due to local heterogeneous features. This is consistent with observations of stage-II cracking in peak- and over-aged alloys, where multiple-slip rather than single-slip is dominant.

Burns et al. [115] discussed the governing mechanical driving forces at microstructure-scale lengths that are intermediate between safe life and damage tolerant feature sizes, in this case a crack is considered to initiate at 1-25 μm surface features and grow to retirement within the depth range of 250-1000 μm. Applied stress and corrosion-geometry effects are modelled based on the local strain approach to fatigue prediction, with input from elastic-plastic finite element analysis (FEA) rather than more basic stress and strain parameters. The authors concluded that experimental characterization of crack formation validated the various assumptions used in fracture mechanics corrosion-modified equivalent flaw size modelling of corrosion degraded fatigue life.

Chan [203] published a review, for various alloy systems, examining the roles of microstructural features such as grain size, texture, porosity, non-metallic inclusions in the fatigue crack initiation process and the manner by which these microstructural effects affect the shape of the stress-life curves. Here he concluded that: (i) microstructure can produce internal textural stresses that can alter the stress-life relations in multiphase alloys; (ii) fatigue crack initiation at defects such as pores, inclusions, and machined marks can lead to $S - N_f$ curves with no, one, or double fatigue limits, depending on the defect (pore, inclusion, or machine mark) size distribution; coalescence of non-propagating microcracks to form a larger crack by continuous crack nucleation appears to be the predominant fatigue mechanism responsible for the occurrence of an apparent fatigue limit in a double-stage $S - N_f$ curve and competition between initiation-controlled and growth-controlled fatigue mechanisms results in large variations in fatigue life.

Wang et al. [204], adopted a slightly different approach applying three-dimensional finite element analysis using a crystal plasticity constitutive theory to understand and quantify various parametric effects on microstructurally small fatigue crack growth in a AA7075 aluminum alloy. The study concluded that simulations clearly showed that the load ratio is the most influential parameter on crack growth. The next most influential parameters are maximum load and the number of initially active slip systems. The particle modulus, misorientation angle, particle aspect ratio, and the normalized particle size showed less influence on crack growth. Another important discovery in this study revealed that the particles were more important than the grain boundaries for inducing resistance for microstructurally small fatigue crack growth. It should be recognized that this study did not consider the effects of environment and in the impact the role of anodic dissolution has on the pit-crack transition.

It is clear that one of the main issues with current corrosion fatigue assessment methodologies is that they are all based on fitted phenomenological curves. Hence there is a clear challenge to improve these methodologies through a greater understanding of the fundamental mechanisms involved, especially the conditions leading to the transition from pit growth to crack initiation (pit-to-crack transition) and subsequent growth of small cracks.

Whilst it is recognised that a linear superposition methodology does not account for chemical and mechanical coupling, this approach does appear to be the most workable lifetime assessment methodology of the approaches reviewed to date. These methods could be further developed by the improved characterisation of the different corrosion fatigue stages, focusing on the initiation of corrosion damage (pitting) and the initiation and growth of small cracks. As a result, pitting models should be coupled with fatigue approaches to account for the effect of loading and corrosion on the damage driving force. To achieve this, the driving force should also include the pit stress and strain concentration effect, which depend on the macro and micro topology of the pit and the interaction with the environmental agents. Advanced numerical approaches to account for the mechanical-environmental coupling, as described in the Cellular Automata Finite Element approach, offer a way forward in terms of the next generation of assessment methodologies.

The use of Microstructural Fracture Mechanics (MFM) techniques within finite elements [205,206] to model the growth of microcracks through the stress gradient associated with a stress concentration feature (e.g, pit/notch, contact, etc.) are becoming available and would allow enhancement of current assessment methods to make them more realistic and accurate. However, the limitations of these fundamental models are related to the ability to measure appropriate microstructure-scale material parameters.

There is a clear opportunity in this field to develop mechanistically based methodologies for assessing the onset and propagation of small cracks from corrosion defects in engineering structures, which should be validated both for new and old materials in operation. From a scientific perspective, the current uncertainties in crack formation mechanism need to be addressed in order to incorporate such modelling into a prognosis capability. To achieve this, a number of areas are worthwhile for further study. At the microstructural level, development of greater understanding of the effect of cyclic plastic deformation (slip motion) on the electrochemical behaviour at the pit surroundings is of great interest. This would allow better modelling capabilities of the growth of pits and the conditions that may lead to the initiation of small cracks. The role of the environment on reducing the material microstructure capacity of arresting cracks is capital and need to be further understood. Empirical life models that account for this dispersion do not provide insights into the physical mechanisms that lead to this scatter. Probabilistic analysis need to assist mechanistically based models in order to address the statistical nature of pitting, the behaviour of small cracks and microstructures [207,208,90].

From an engineering perspective, for conservative assessments relevant to many industries, the crack initiation phase can be neglected when severe pitting damage is observed. As stated by Burns et al.[115], it can be argued that in a surface presenting severe corrosion, the initiation stage can be considered to have occurred, and the analysis starting at the propagation stage using the appropriate existing flaw size or at the minimum detectable crack size by the standard NDT equipment. For better accuracy, the recharacterisation of the pit as an equivalent crack need to be avoided and improved methodologies considering the pit macro and micro topographic features together with the use of small crack growth models [67] are more realistic alternatives.

It should be recognised that both anodic and cathodic reactions can lead to damage. In the former case localised anodic dissolution leads to pit formation as previously described in this review. What is often not appreciated is that a sequential reaction that occurs on release of metal ions, especially Fe^{2+} and Cr^{3+}, is that of metal ion hydrolysis:

$$M^{n+} + H_20 \rightarrow M(OH)_n + H^+ \tag{16}$$

The generation of atomic hydrogen (H^+) can, in turn, lead to hydrogen embrittlement through adsorption into the metal matrix. Hence the question arises as to whether damage is an anodic dissolution driven mechanism or a hydrogen embrittlement mechanism.

Kamoutsi and co-workers [209] studied the response of AA2024-T351 under exfoliation conditions (25 ± 0.5 ^{o}C, in a solution containing 234 g NaCl, 50 g KNO_3 and 6.3 ml concentrated KNO_3 (70 wt.%) diluted to 1 L of distilled water) up to 96 hr exposure. Hydrogen uptake was measured by thermal desorption and corrosion damage by atomic force microscopy. They concluded that corrosion damage starts with pitting and proceeds to pit-to-pit interactions, intergranular attack and exfoliation. Hydrogen is produced during the corrosion process and is being trapped in distinct states in the interior of the material. Whilst the authors point out that yield strength is restored on removal of the exfoliated layer, this study does not elucidate the role of hydrogen in the corrosion fatigue process. This was partially addressed by Burns and Gangloff [210] in a fatigue study on AA7075-T651 subject to controlled pitting and EXCO-solution exposure used to produce localised corrosion damage. Tests were performed at room temperature [296 K(23 ^{O}C)] in water vapour saturated nitrogen (RH>85%), or in dry nitrogen (99.99% pure) at 223 K and 183 K (50 ^{o}C and 90 ^{o}C). The study concluded that localised corrosion prior to fatigue develops a H (or H-vacancy complex) concentration gradient about the pit surface which promotes crack formation. It should be noted that such behaviour may be consistent with high strength materials susceptible to hydrogen embrittlement, e.g. Al alloys, but may not be appropriate for lower strength materials such as carbon steel, where it is noted in corrosion fatigue tests that crack growth rates in the environment are similar to that in air at crack lengths of the order of a millimeter and above, see figure 17.

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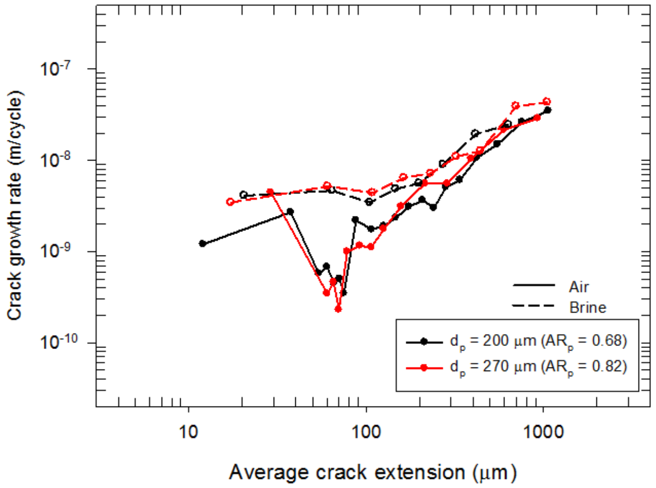

Fig. 17. Influence of initial pit size on crack growth rate in air and brine [108]. Note similarity of crack growth rates in both environments above 1mm crack extension.

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