

Review

Mechanisms of fatigue crack initiation in metals: role of aqueous environments

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Fatigue crack initiation in engineering materials has been the subject of considerable research. Most of these investigations focused on gaseous environment effects, and extensive review articles have appeared in recent times discussing the role of gaseous environments on crack initiation. Because of experimental difficulties, the effect of aqueous environments on mechanisms of fatigue crack initiation has received little attention, despite their unquestionable importance from an engineering standpoint. In this review, several of the fatigue crack initiation models are examined in detail and their anomalies discussed. The physics and micro-mechanisms of crack initiation during cyclic deformation in aqueous environments which are highly corrosive in nature are examined. The characteristics of the crack initiation process in aqueous environments are critically reviewed in the light of the specific role of several concurrent factors involving the nature of the aqueous medium, corrosion interactions, alloy chemistry, processing treatments, intrinsic microstructural effects and test variables.

1. Introduction

The progressive failure of a material by the incipient growth of flaws under cyclically varying stresses is termed fatigue and has over the years accounted for a vast majority of in-service failures in structures and components in aerospace engineering (airframe structures), in civil engineering (off-shore platforms, buildings and bridges), and in mechanical engineering (boilers, propellers, shafts, rotors and turbines). Such failures can be the consequence of either pure mechanical loading, aggressive environments (corrosion-fatigue) or elevated temperatures (creep-fatigue). The fatigue failure process can be categorized into the following discrete, yet related, phenomena involving: (i) cyclic plastic deformation prior to crack initiation, (ii) initiation of one or more microcracks, (iii) coalescence of microcracks to form one or more macroscopic cracks, (iv) subsequent propagation of the macrocracks, and (v) final catastrophic failure [1]. The first three stages involving cyclic deformation, microcrack initiation and growth can be embodied into a single classification of macrocrack initiation. The total fatigue life of a structural alloy referred to in the engineering context as the number of cycles to failure, N_f , can be regarded as comprising the number of cycles required to initiate a microcrack, N_i , and the number of cycles required to propagate it, N_p , to final failure. Once the fatigue crack is initiated, the sub-critical crack grows to a certain length, the stress intensity factor at the crack tip reaches a critical value, and finally, the fracture becomes unstable terminating the life of a structure.

The distinction between fatigue crack initiation and

crack propagation can be critical in designing for enhanced fatigue resistance while using data from laboratory-sized specimens to predict the lifetime of complex components in field service. Conventional approaches to designing against fatigue involve the use of $S-N$ (stress against number of cycles) curves, representing the total fatigue life resulting from a given stress or strain amplitude, suitably adjusted to take into account effects of mean stress (Goodman diagram), effective stress concentration at notches, variable amplitude loading (Palmgren-Miner cumulative damage law), multiaxial stresses and environmental effects. This approach based on total fatigue life represents designing against fatigue crack initiation, because at and near the fatigue limit, especially in smooth specimens, most of the lifetime (up to 90%) is spent in the formation of an engineering size crack [2]. Thus, for either "fail-safe" or "safe-life" design philosophies, comprehensive knowledge of the behaviour of materials in hostile, seemingly innocuous and benign environments is essential to predict the useful life of a structure before catastrophic failure.

For a number of years, research on the practical importance of fatigue failure was directed towards assessing different materials with the aim of providing data for designers. These studies failed to separate the fatigue process into the separate categories of crack initiation and crack propagation. Crack initiation is the formation process of microcracks having less than detectable length, say 10^{-3} mm to 2.5×10^{-2} mm. The propagation stage is the growth process of the detectable crack until complete failure.

It has long been recognized that the fatigue resist-

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ance of metals is markedly affected by reactions with the environment which affect crack initiation and/or crack propagation. The joint action of cyclic stresses and an aggressive environment is commonly termed corrosion fatigue. Hostile aqueous or aggressive gaseous or, in some cases, liquid metal environments cause degradation in the fatigue life of structural metallic materials while undergoing cyclic loading through interactions of the chemical and mechanical processes at surfaces including crack tips. Thus, it is apparent that consideration of corrosion fatigue characteristics associated with the intended service environment is an important factor in evaluating and selecting materials to resist fatigue cracking.

The complicated response of a material subjected to cyclic loading in the presence of an environment has been an area of considerable research effort in a wide variety of metals and alloy systems. Impetus for increased activity in this field was the need for improved operational and structural reliability of components exposed to aggressive environments. However, because of experimental difficulties the effect of environment on mechanisms of fatigue crack initiation has been somewhat ignored by researchers. An understanding of the phenomenon of crack initiation in aqueous environments has a wide range of applications in the design of engineering components exposed to aggressive solutions. Examples of such components include parts of marine vehicles, boilers, water cooled and liquid metal cooled nuclear reactors, pressure vessels, heat-transfer systems, bridges and deep-diving submersibles. In spite of the considerable practical significance, only a few studies have attempted to comprehensively examine processes associated with crack initiation. An inherent problem here in the analysis is the distinction between crack nucleation and early crack growth.

In this paper, several of the fatigue crack initiation models are critically examined and their anomalies discussed from results available in the literature. In particular, the role of aqueous environments which are corrosive in nature, in influencing the micro-mechanisms for the formation of potential fatigue crack initiation sites during cyclic deformation are considered. The crack initiation process is discussed in terms of several concurrent factors involving alloy chemistry, mechanical, metallurgical and chemical parameters. Results obtained in the past decade are emphasized, although some significant work from earlier years is also included to provide continuity.

2. Fatigue crack initiation

When a material is cycled at a stress higher than the endurance limit (stress required for 10^7 cycles to failure), a crack will be nucleated and this eventually grows and results in catastrophic failure. Over the years, research in the general area of metal fatigue and cyclic deformation has led to several hypotheses for fatigue crack initiation [3–19]. Most investigators generally agree that the fatigue cracks initiated at or near singularities on or just below the surfaces of metals. Such singularities may be inclusions, embrittled grain boundaries, sharp scratches, pits or slip bands

[20]. However, subsurface nucleation has also been observed in metals having a strong adherent surface oxide which retards crack initiation at the external surface [21–25]. The subsurface crack nucleation can be traced to “singularities” within the metal, namely, the voids and regions of high internal stress. In addition to these special cases, Wood *et al.* [24] presented strong evidence to show that bona fide subsurface mechanisms exist for fatigue crack initiation. Wood [22], in his detailed documentation, proposed that the cracks begin at point centres within the metal, termed “pores”. At high strain amplitudes, the pores developed along subgrain boundaries while at lower strain amplitudes, the pores were observed to form within slip zones. Final failure occurred by tearing of sufficiently perforated material. The suggestion by Wood that internal voids and pores were produced during fatigue cycling was found not to be without merit following extensive investigation of fatigued metals by transmission electron microscopy [11, 26]. On the other hand, Grosskrueztz [15, 27] and Alden [4] presented evidence to show that when surface initiation was suppressed, failure initiated beneath the layer along subgrain boundaries. The final appearance of such a failed sample resembled a perforated sheet. Subsurface nucleation has also been observed in several other metals that had a strong adherent metal surface oxide which retarded crack initiation at the external surface [27].

A substantial amount of evidence has been both documented and presented to support the formation of a unique surface topography as a necessary consequence of cyclic stressing. This is attributed to strain localization caused by the concentration of slip into bands. The formation of intense slip bands which are the ones with greatest localized strain and the greatest shear stress [28], results in slip steps on the surface, intrusions, extrusions, hills, valleys, and ridges or grooves all of which can facilitate the initiation of small fatigue cracks. The slip bands which penetrate several micrometres into a surface and persist even after electropolishing has removed the outer surface topography have been termed persistent slip bands (PSBs). The term PSB was introduced in 1956 by Thompson *et al.* [29]. These researchers observed slip bands on the polished surfaces of copper and nickel after various amounts of stress cycling. The dislocation arrangement within the PSB is either a well-defined ladder or cell structure. The PSBs are formed not only from the newly generated dislocations but also by transfer of matrix dislocations into the PSB structure. According to Basinski *et al.* [19], the transfer can occur rapidly over a few cycles because the matrix dislocation structure is on the boundary of stability. Most of the PSBs were easily removed by polishing and electropolishing. However, the slip bands reformed in the same places when the sample was retested. The PSBs eventually developed into fatigue cracks. The width of the PSB was observed to increase as the stacking fault energy of the material increased [28]. In evaluating the formation of slip bands, Sharp [30], in his independent study, observed that the fine narrow slip bands resulted from an

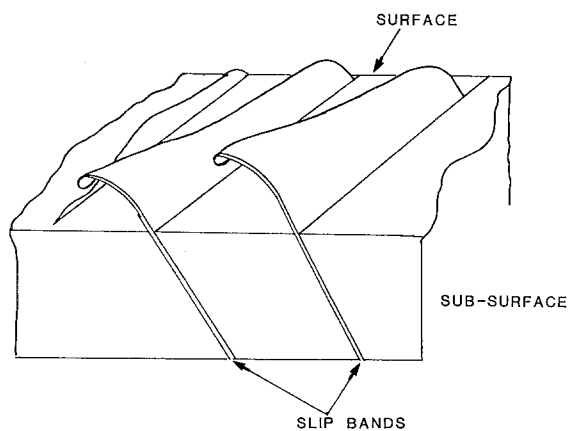


Figure 1 Schematic illustration of slip band extrusions during cyclic straining.

increasing difficulty in dislocation motion out of slip planes; in his experiments they were from exposure either to radiation or to lower temperatures.

The slip bands produced during tension–tension or tension–compression cyclic loading resulted in the formation of extrusion–intrusion pairs. The extrusions and intrusions produce surface roughness which is the direct cause of crack initiation. The formation of extrusion–intrusion pairs was first recognized by Forsyth and Stubbington [31–33] in a binary aluminium–4.5% copper alloy. When this alloy was cycled, fine slip bands formed and thin ribbons of metal were extruded from the surface (Fig. 1). In subsequent studies, both Cottrell and Hull [34] and Wood and Segall [35] observed intrusions equivalent to a crack of a few micrometres depth and associated with extrusions (Fig. 2). These early studies identified plastic strain as an essential prerequisite for fatigue, with localization of strain on the finest scale within a PSB and irreversible slip in the fine slip lines as factors responsible for promoting crack initiation [18, 19, 36].

The occurrence of extrusions has been observed by several other researchers. They were found to occur at: (a) very high stresses [9], (b) temperatures as low as that of helium [37], (c) annealing twin boundaries in association with cracks [38], and (d) grain boundaries [39]. The different mechanisms for the formation of extrusions have been comprehensively reviewed in a paper by Laird and Duquette [28]. As most mechanisms for the formation of extrusions resulted in the

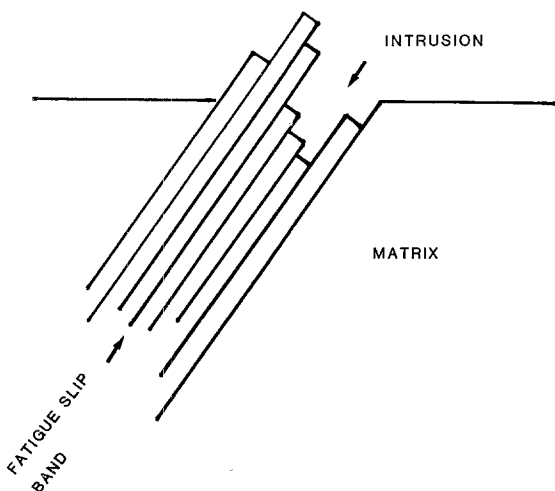


Figure 2 Schematic illustration of single slip system model of intrusion formation.

formation of intrusions, they can be regarded as a crack nucleation mechanism. However, during cyclic deformation PSBs are far more important for the nucleation of fatigue cracks than extrusion–intrusion pairs which themselves depend on PSB formation. Alternatively, it can be said that the PSBs form independent of any environmental effects, and the role of the environment is only to accelerate the process by which PSB leads to fatigue crack initiation through extrusion–intrusion formation. This can occur by one or more of the following processes:

1. Preferential dissolution at PSBs because the PSB is anodic to the matrix,
2. Film rupture by the emerging PSB causing, as a result, exposure of fresh metal and possible galvanic reactions, and
3. Localized dissolution resulting in marked local changes in dislocation arrangement, thereby affecting the extrusion–intrusion development within the PSB.

A number of models for fatigue crack initiation have been proposed and can be generally classified into: (a) single slip system models, (b) models for slip on alternating parallel slip planes, and (c) models based on two intersecting slip lines. Models from each of the above categories are described and their relevance discussed in the following section.

3. Models for fatigue crack initiation

Several of the models proposed for the formation of fatigue cracks [34, 40–44], during the early years suffered from at least one of the following disadvantages.

1. Only a few dislocations were assumed to be present and these were assumed to run along specific paths and in a specific sequence. Obviously in practice, use of polycrystalline materials prevents such simplistic assumptions.
2. The prescribed dislocation movements produced work hardening which monotonically increased, so that the mechanism would eventually stop before a macroscopic crack could form.
3. There is no physical asymmetry or irreversibility in the model which could produce the irreversible growth of a crack, in spite of reversible dislocation motion and of symmetrical tensile and compressive stresses.

Limitations associated with the above models disappeared when considering the fact that slip is much coarser during cyclic deformation than in unidirectional tests, i.e. when dislocation movement is distributed very inhomogeneously. Coarse slip is almost always due to an instability.

Neumann [45] proposed a model for crack nucleation based on the formation of coarse slip steps caused by the build-up of excess dislocations of one sign along an active slip band during cyclic plastic straining. In his investigations, Neumann observed that when one slip plane had an excess of dislocations of one sign, a neighbouring slip plane would have an excess of dislocations of the opposite sign resulting in an interaction energy between the two slip planes. The extrusion–intrusion pairs formed by avalanche from these neighbouring slip bands contained the excess dislocations of the opposite sign. Fig. 3 illustrates how

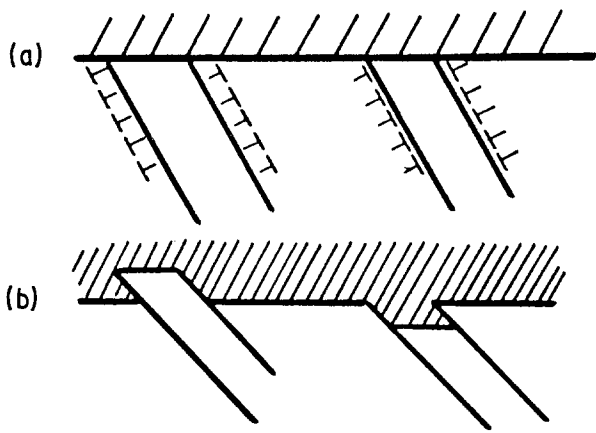


Figure 3 Schematic illustration of dislocation pile-ups during cyclic straining resulting in extrusion-intrusion formation [45].

such an avalanche gives rise to an extrusion and an intrusion. The intrusion once formed acts as a stress raiser and concentrates slip at the notch root.

On the basis of extensive observations of slip and surface topography in single crystals, Neumann [45] also proposed a model for the nucleation of cracks by coarse slip on alternating slip planes. This model does not require extrusions as depicted in Fig. 4. During tension, alternate slip on two intersecting slip systems is essential for the mechanism to operate. Slip on the first system is activated during tension and then assumed to stop because of work hardening following which the second slip system becomes active. During compression, the excess dislocations on the slip planes are assumed to run out resulting in the initiation

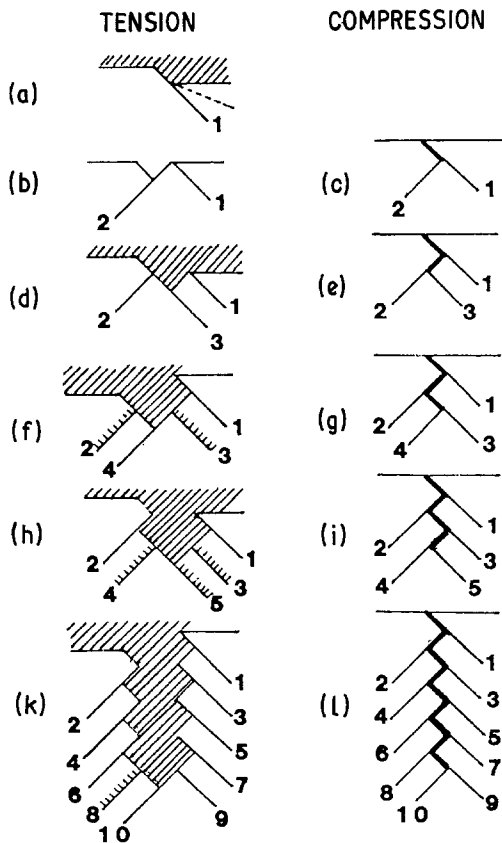


Figure 4 Model for the formation of a crack by coarse slip. The sequence of events is (a) to (l). In the figures on the right the apparent stress is either zero or compressive. As the dislocations (l) run out, a crack is created because motion along both planes occurs simultaneously [45].

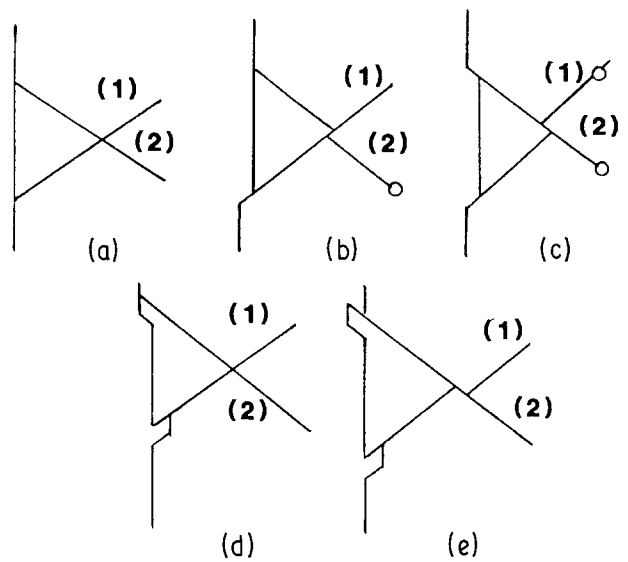


Figure 5 Operation of two intersecting slip bands in sequence resulting in the formation of intrusions and extrusions. The forward cycle is represented by (b) and (c), and the reverse cycle by (d) and (e) [34].

of a fatigue crack. No slip is assumed to take place during compression. As the process of forming a new increment of crack surface is repeated, a substantial crack nucleus develops. The advantage of this model of Neumann is that it does not require prior surface roughening. However, the presence of surface roughening increases the local stress resulting in an instability.

Cottrell and Hull [34] propounded a model for the formation of extrusion-intrusion pairs due to sequential duplex slip. In their model, during the first half cycle, one slip system, and then another slip system is imagined to operate giving two slip steps of the same sign (Fig. 5c). During the second half-cycle, the first slip system operates and is followed by the second slip system, one producing an extrusion and the other an intrusion (Fig. 5e). The main drawback of this model is that it failed to explain convincingly the formation of extrusion-intrusion pairs in the absence of cross-slip, that is, when only one family of slip planes was operating. Further, contrary to experimental observations this model suggests a fairly large separation of the extrusion-intrusion pairs.

Cyclic deformation which refers to the early stages of fatigue deformation is important to both crack initiation and crack propagation primarily because the mechanisms governing these processes are based on the characteristics of deformation [11]. The forward and reverse stressing associated with cyclic deformation results in different amounts of net slip on different planes. Consequently, a general roughening of the surface occurs [22]. Wood, in propounding this mechanism, suggested that the valleys so formed act as stress-raisers which promote additional slip to occur. Subsequently, May [46, 47] developed a purely statistical formalism to show that with continued cycling, progressively deeper valleys result due to random slip. The Wood-May mechanism is operative in isolated cases, for example, in a planar slip material cycled at low plastic strains. Several other independent investigators [48-53] have observed that the slip reversibilities in fatigue slip bands suggest that a

systematic rather than a random series of dislocation events result in the initiation of a crack.

The various models outlined so far are attractive for ductile materials which, in general, have an abundant availability of slip systems. None of the models discussed require specific slip systems nor do they require specific dislocation interactions. The models of Neumann [45], Cottrell–Hull [34] and Wood–Segall [35] are, therefore, preferable to several other models which require specific conditions to be operable.

More recently, Lin *et al.* [54] developed a theoretical expression for the initiation of fatigue cracks based on the accumulation of dislocations along slip bands. In this model, the plastic strain within the dislocation accumulated bands was calculated using Eshelby's theory of internal stresses [55, 56]. The slip bands were simulated by domains of uniform plastic strain. During cyclic fatigue, the tension and compression portions of the cycle were modelled to take place in domains of slightly different size giving rise to irreversibility. In order to account for the irreversibility, the researchers considered the slip bands to be elliptical domains, with the domain size for tension being slightly different from that for compression. Using continuous dislocation theory, the accumulation of dislocation dipoles at the boundary between the slip domain and the matrix was calculated. Cracking was assumed to occur when the accumulated dipoles reached a critical number required to give a degree of displacement that could cause fracture. While this model may have conceptual value, it lacks experimental evidence and must, therefore, be verified before it can provide any fundamental mechanistic understanding on initiation.

The models based on repeated slip cannot, however, satisfactorily rationalize the crack initiation behaviour in brittle materials. Typically, such materials include dispersion strengthened composites, medium- and high-strength steels and materials containing a large volume fraction of brittle intermetallic phases. Another model that was proposed by Thompson and Wadsworth [3] required the condensation of vacancies which resulted in the formation of voids that nucleated a fatigue crack. The vacancies were produced by dislocation interactions during fatigue cycling. This mechanism depends essentially on diffusion and is unlikely to occur at either room or low temperatures. Thus, it cannot serve as a valid explanation for crack initiation at low/ambient temperatures. Such a mechanism may, therefore, be operable only at high temperatures where the creep phenomenon will also begin to play a synergistic role in determining the active mechanism for initiation. Other models involving the initiation of cracks at grain boundaries in pure fcc and bcc metals require polycrystalline samples [57–61] and are therefore not readily acceptable because they lack the ability to predict mechanisms of failure in single crystals.

In polycrystalline metals, the grain boundary often plays an important role in crack initiation. During deformation, the grain boundary serves as an impediment to the slip bands resulting in the build-up of high stress concentrations at the boundary and the triple

junctions. Such high stress concentrations promote early crack initiation during fatigue [62]. The mechanism of grain-boundary crack initiation can be considered as being purely geometrical because it occurs even in the absence of an inherent grain-boundary weakness. Initiation of fatigue cracks at grain boundaries is therefore applicable often at higher temperature, higher stresses and lower speeds. Such conditions exist when a given stress minimizes strain [3].

Cracking at twin boundaries cannot be considered as a case of grain-boundary failure, even at low operating stresses. In face centred cubic (fcc) metals, the twinning plane and slip plane are the same and it is possible that the presence of the twin boundary enhances the possibility of slip band failure [33]. The reason for this is two-fold. Firstly, the twin boundaries are good sources for dislocation [63] and, secondly, the slip processes in neighbouring crystals co-operate by helping to extrude the material [47]. Thus the multitude of deviations prevent the grain-boundary crack initiation mechanism being accepted as a generalized model for fatigue crack initiation in metals.

The above facts assimilated together suggest that a comprehensive understanding of crack initiation characteristics in a material must serve as a vital parameter for designing against fatigue in the structure. Because of the complicated nature of the initiation process in different materials and alloy systems, it is difficult to pin down the exact mechanism operative in every material. The presence of an aggressive environment adds additional complexities and is discussed in the following section.

4. Environmental effects on fatigue crack initiation

Generally, fatigue cracks are surface initiated and thus the character of the surface, chemical and diffusion processes, as well as interactions of chemical, mechanical and adsorption processes are important. Environmental interactions are, by nature, surface interactions, that is, the environment acts on the material through the surface. An active environment plays a significant role in influencing the total fatigue life of a material by either affecting the formation of persistent slip bands (PSBs) or by affecting the mechanisms by which a crack develops from a PSB. The influence of a liquid test environment on fatigue has in recent years been the subject of intense research activity. The extent of such an influence depends on a complex interplay of the mechanical (frequency, stress-ratio and loading waveform), chemical (chemistry and electrochemical potential) and metallurgical (grain size and morphology of second-phase particle) factors. Several mechanistic explanations have been put forth to explain the intrinsic effects of gaseous environments on fatigue crack initiation in metals. The various mechanisms have been comprehensively reviewed in a recent review by Sudarshan and Louthan [64].

Most investigators have paid little attention to understanding the nature of underlying interactions between the aqueous environment and the structure. Two important variables in aqueous corrosion fatigue

are alloy composition and solution chemistry. Different corrosion fatigue systems (specimen/environment) have different electrochemical reactions, therefore, a wide variety of corrosion fatigue behaviour can be expected. However, it is generally agreed among the few researchers who have studied this topic that corrosion fatigue behaviour parallels environment sensitivity, with increasing corrosion rates resulting in decreased fatigue lives as a consequence of higher fatigue crack growth rates in metallic specimens. It has also been observed that the properties of a component subjected to corrosion fatigue conditions are considerably degraded compared with the fatigue properties in a benign environment. Moreover, several researchers have found the corrosion fatigue properties of materials to be worse than the properties which would apply if the effects of cyclic loading and corrosion were separately summed [65–68]. The growing recognition of in-service corrosion fatigue failures has altered traditional design considerations and efforts are now being made to include corrosion fatigue data in design codes [69].

The initiation of fatigue cracks in smooth polished specimens may occupy as much as 90% of the total fatigue life in the absence of any environmental interaction, but corrosive reactions in an aggressive aqueous environment reduce the percentage of total fatigue life required for initiation to as low as 10% [70, 71]. Contact with an aggressive environment was found to have the same effect on fatigue life as does the incorporation of a sharp geometrical discontinuity into an otherwise smooth surface of the specimen [70]. As a result, a stress raiser develops and initiates a fatigue crack. It may be surmised that corrosive environments facilitate the formation of geometric discontinuities on the surface of the specimen. These discontinuities then become fatigue cracks during cyclic loading. However, improved corrosion fatigue resistance has been observed in some metallic specimens and was found to be inversely related to corrosion rates. The improved corrosion resistance can be ascribed to a delay in either crack initiation or early crack propagation caused by the dissolution of microcracks or stress concentrators [72].

In corrosion fatigue, the cracks can initiate at the surface either intergranularly or transgranularly. Intergranular corrosion provides initiation sites at the surface for fatigue cracks which could then grow transgranularly [72]. On the other hand, when slip intersects the surface and fresh slip steps contact the solution, the initiation could be transgranular and result in the dissolution of metal atoms [73]. Formation of cracks ensues due to localized corrosion at slip steps. Many small cracks are generated by this process and they eventually could coalesce and grow. Kitagawa *et al.* [74] have summarized the events leading to fracture due to the presence of small distributed cracks.

Sensitivity of fatigue to environment varies appreciably for different metal–environment systems and for different microstructural conditions in the same alloy. For example, Endo *et al.* [75] observed degradation in the fatigue strength of a high strength steel in an

aqueous environment to be higher when the steel was tempered below 400°C. This larger effect was attributed to an increased sensitivity to hydrogen embrittlement. Cornet and Golan [76] observed positive improvement in the fatigue behaviour of steel drill rods tested in a 2.5% NaCl solution at temperatures approaching the boiling point of water (82°C). These researchers attributed the beneficial effect to differences in pitting attack at higher temperatures, that is, the pits were observed to be more uniformly distributed and shallower. Further, the ratio of cathodic to anodic areas was found to be higher at lower temperatures [76].

Oxygen content in an aqueous environment is another important factor required for the electrochemical interaction between solution and the component, because aqueous environments contain some amounts of dissolved oxygen. A decrease in oxygen concentration of the aqueous medium at higher temperatures and a concomitant reduction in corrosion rate are factors which contribute to the improvement in fatigue resistance. Lehmann [77] in his independent study observed an actual improvement in the fatigue life of steel specimens when they were completely immersed in an NaCl solution at 96°C. This observation led him to conclude that the improvement was due to the limited solubility of oxygen at this elevated temperature. Improvements in the fatigue life of steel specimens were observed when exposed to an NaCl solution dripped through a commercial hydrogen atmosphere with enhanced improvement occurring as the purity of hydrogen was increased [78]. However, NaCl solution dropped through air proved to be extremely damaging to fatigue specimens.

Other investigators [79] in their study on the effect of dissolved oxygen on the fatigue behaviour of a 1035 low carbon steel exposed to 5% NaCl solution found that complete deaeration of the sodium chloride solution caused the reappearance of the fatigue limit observed in tests conducted in the dry air environment (Fig. 6). These studies reveal that dissolved oxygen is important for corrosion fatigue to occur. The exact nature of interaction of oxygen with the component and the aqueous environment still remains speculative. However, there are several possibilities for the manner in which oxygen influences the corrosion fatigue behaviour: (a) by acting as a catalyst to stimulate the electrochemical reaction between the metal and solution, (b) by reacting directly with either the component or solution and thus affecting the slip behaviour, (c) adsorbing on the metal surface so as to affect the adsorption process of ions in the solution, and (d) providing a medium for a reduced reaction.

Fatigue resistance of steels, aluminium and titanium alloys was found to be generally lower in salt water and natural sea water than in laboratory air environment [80, 81]. However, the influence of salt water relative to that of distilled water is not very clear. While few investigators have found no difference between the two environments, most studies found salt water to be more aggressive. Ebara *et al.* [82] observed that distilled water had no influence on the fatigue strength of stainless steels, while a 3% NaCl

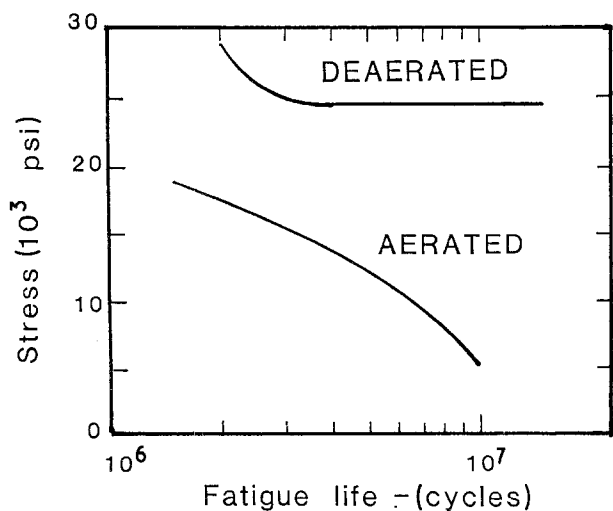


Figure 6 The effect of dissolved oxygen on the fatigue behaviour of a 1035 low carbon steel in 5% NaCl solution [79].

solution significantly lowered the fatigue strength. Furthermore, as NaCl content increased, fatigue life was found to decrease.

Mechanical parameters, namely stress level and strain range, also control the response of a material to the environment. Chu and Macco [80] observed that the overall fatigue resistance of an aluminium alloy was not appreciably affected by salt water in the low cycle regime, but it was sharply degraded in the high cycle regime. Further, high stress rates were observed to lower fatigue resistance.

Severe anodic polarization has also been observed to cause degradation in the overall fatigue resistance of several carbon steels and copper alloys [68, 83]. Examination of specimens subjected to large amounts of anodic dissolution revealed that the cracks initiated at the surface were blunted by the corrosive aqueous medium. Consequently, a local decrease in stress concentration resulted in an actual improvement in fatigue resistance. In a recent study on understanding the effect of cathodic polarization on the corrosion fatigue behaviour of a high purity, precipitation-hardened aluminium (Al-Zn-Mg-Cu) alloy in the peak-aged, maximum strength condition, a series of load-controlled fatigue tests were performed on both polycrystalline and monocrystalline samples [84]. The tests were conducted in environments of dry laboratory air and 0.5 M NaCl solution at the corrosion potential and at applied potentials cathodic to the corrosion potential. Smith and Duquette observed from the tests that the saline solution caused considerable degradation in the fatigue resistance of the alloy (Fig. 7). The decrease in fatigue life was mainly due to intergranular crack initiation and propagation under freely corroding conditions for polycrystalline samples. Applied cathodic potentials in the saline solution up to -1.3 V caused no significant changes in the fatigue behaviour from that observed under freely corroding conditions (Fig. 8). However, more active cathodic potentials resulted in a significant reduction in the fatigue resistance of the high purity aluminium alloy (Fig. 8). The observed degradation in fatigue resistance of the polycrystals was associated with increases in the degree of transgranular crack initiation and

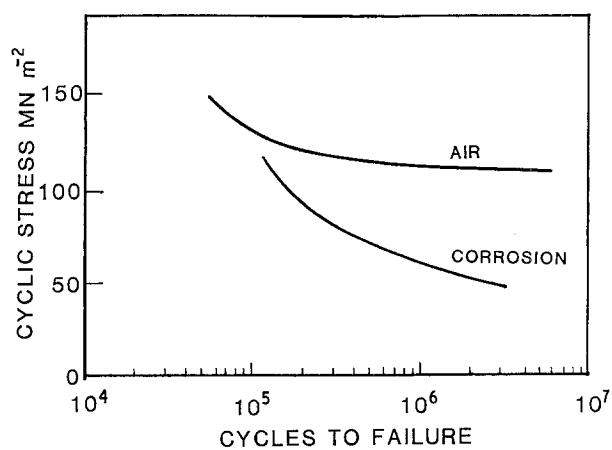


Figure 7 *S-N* fatigue behaviour of a polycrystalline Al-5Zn-2.5Mg-1.5Cu alloy, in the T6 temper, in environments of dry air and 0.5 M NaCl solution [84]. Mean stress = 207 MN m^{-2} ; 298 K.

propagation. At lower applied cyclic stresses and, consequently, longer test times, increasing amounts of intergranular cracking was observed. The relative amounts of intergranular cracking was a function of the applied stress level and, for the most active condition, lower stresses resulted in an increased amount of intergranular cracking. This suggested that stress-corrosion cracking and corrosion-fatigue processes were acting simultaneously and the competition was between hydrogen embrittlement of the process zones of transgranular fatigue cracks and hydrogen transport to grain boundaries.

Halide ions have been found to be particularly damaging to the fatigue behaviour of aluminium alloys. When the alloys were cathodically charged during cyclic stressing, the sulphate ion was found to be equally damaging, particularly at long lives and low cyclic stresses (Fig. 9). At higher cyclic stresses, the degradation in fatigue resistance in chloride-containing solutions was associated with damage of the passive film.

Several mechanistic explanations and semi-quantitative models have been proposed in an attempt to provide meaningful explanation for the degradation in fatigue resistance in aggressive environments. Because crack initiation is primarily a pure surface phenomenon, aqueous environments which react mainly with the surface of the material, certainly play an important

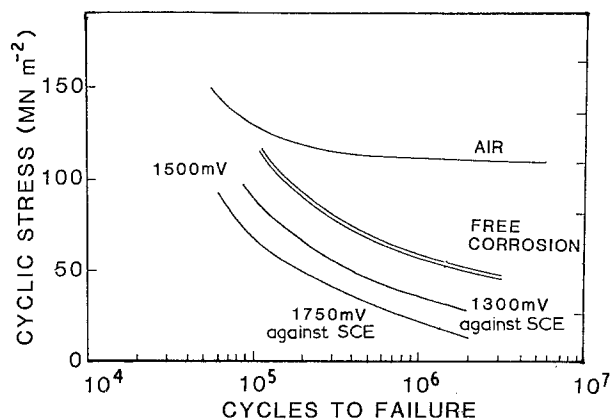


Figure 8 *S-N* fatigue behaviour of polycrystalline Al-5.5Zn-2.5Mg-1.5Cu alloy tested in 0.5 M NaCl solution as a function of applied cathodic potentials [84]. Mean stress = 207 MN m^{-2} ; 298 K.

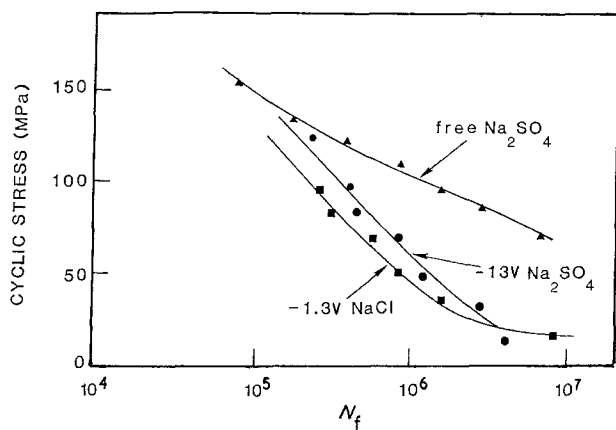


Figure 9 Effect of cathodic polarization on the fatigue behaviour of an Al-Zn-Mg-Cu (7075) alloy in environments containing NaCl and Na_2SO_4 [68]. Mean stress = 172 MPa; 30 Hz.

role in the initiation process. The mechanisms for aqueous fatigue crack initiation include:

1. Formation of corrosion pits and consequent stress concentration at the base of the pit.
2. Electrochemical attack at plastically deformed areas of the metal with the undeformed metal acting as cathode.
3. Rupture of the surface film with concomitant electrochemical attack at the ruptured sites.
4. Lowering of the surface energy of the metal due to absorption of a specific species from the environment.

All of the above mechanisms involve a synergistic interaction between mechanical, metallurgical and chemical parameters. While some of the mechanisms are governed primarily by the mechanical and metallurgical aspects, other mechanisms are influenced by the chemical aspects of the phenomenon. Each of the above four mechanisms are described and discussed in light of available experimental data.

4.1. Mechanism of pitting in corrosive environment

Early work by investigators [70, 85] on corrosion fatigue revealed that the corrosive media assists in the nucleation of fatigue cracks by the formation of pits on the metal surface. Formation of pits in both metals and alloys when exposed to aggressive aqueous environments resulted in significant degradation in fatigue resistance or life. McAdam observed that the pits induced during the corrosion fatigue process, prematurely initiated fatigue cracking [85]. In the case of materials such as high-strength steels which exhibit a well-defined fatigue limit in a laboratory air environment, the applied stress required to initiate a fatigue crack was reduced [85]. Pre-pitting followed by testing in the same corrosive environment was observed to enhance the degradation in fatigue resistance and life. Formation of pits on the surfaces of metals and alloys exposed to aggressive environments was found to result in degradation in fatigue life. However, several other independent investigations have observed the corrosion fatigue phenomenon to occur in environments where pitting did not occur. For example, Simnad and Evans [86] found low carbon steels to be highly susceptible to corrosion fatigue in acid

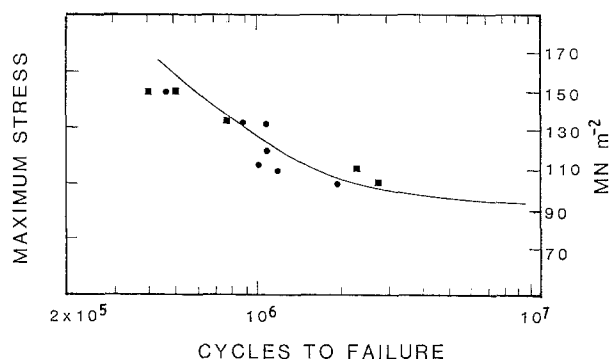


Figure 10 Schematic illustration of the variation of stress against number of cycles to failure (●) in air and (■) in 0.5 N NaCl solution [83].

solutions which did not cause pit formation to readily occur on the steel surface.

Electrochemical reactions between the metal and the aqueous medium are determined by the polarization potential of the metal. Consequently, the crack initiation process and corrosion fatigue life are markedly influenced by the applied potential. Degradation in fatigue resistance was observed in steel specimens tested when a small anodic current was applied to the sample, whereas a cathodic current was found actually to improve the fatigue resistance [83, 87–91]. Masuda and Duquette [83] performed a series of axial load-controlled tension-tension fatigue tests at a constant frequency on high purity polycrystalline copper in environments of laboratory air and 0.5 N NaCl solution with applied anodic current. Results of their study revealed that under freely corroding conditions, aerated NaCl solutions did not appreciably affect the fatigue life of annealed copper (Fig. 10). Further, when compared to experiments conducted in laboratory air, applied anodic currents greater than $10 \mu\text{A cm}^{-2}$ caused pronounced degradation in fatigue life (Fig. 11). The researchers attributed this to slip intensification and broadening. Further, crack initiation was observed to change from predominantly transgranular in air to an intergranular mode in the aqueous solution. The fatigue damage was explained in terms of enhanced interaction between the dislocations and the environment. In an earlier study [79], Mehdizadeh *et al.* found the presence of chloride ion in a deaerated 5% sodium chloride solution to be adequate in lowering the fatigue life. Subsequently, Duquette and Uhlig [92] found that the fatigue limits of steel specimens tested in a 3% NaCl and in a sodium hydroxide solution at pH 12 to

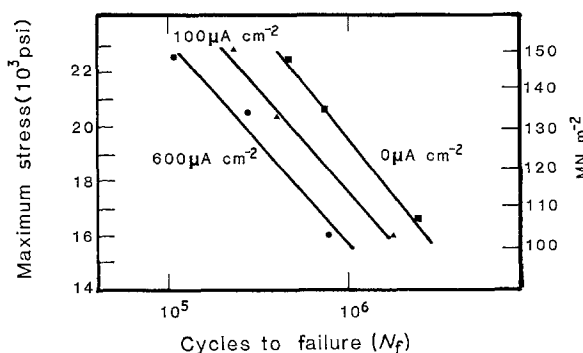


Figure 11 Effect of anodic current on fatigue life at different values of maximum stress [83].

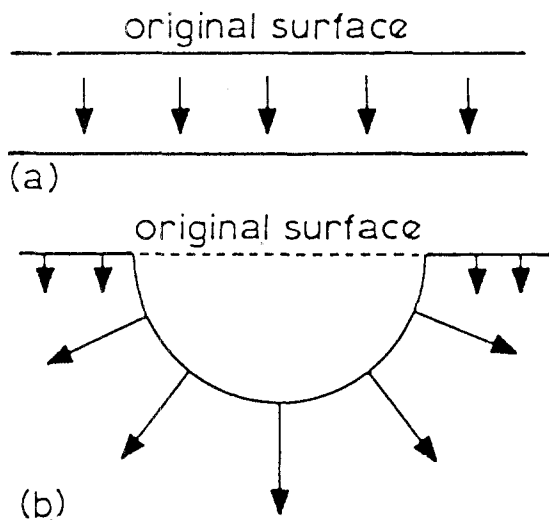


Figure 12 Schematic illustration of the hemispherical morphology of a corrosion-induced pit. (a) Dissolution during general corrosion, (b) dissolution during pitting corrosion.

be identical with those observed in laboratory air. Results of this study suggested that the stress concentration factor associated with corrosion-induced pits which are hemispherical in nature (Fig. 12) is not large. These researchers also observed that for a low carbon steel specimen exposed to deaerated 3% NaCl solution the corrosion rates were controlled by the applied anodic current (Fig. 13). This observation indicated the necessity for a critical corrosion rate to initiate corrosion fatigue failures.

Metallographic examination of low carbon steels fatigued in a neutral 3% NaCl solution revealed that the pits formed by preferential corrosion of already existing intrusions [72]. No cracks were observed to emanate from the hemispherical pits on the specimen surface and the extent of growth of initiated fatigue cracks in specimens cycled for longer periods was equivalent to the depth of the pit. This result reveals that while the corrosion pits do play an active role in crack initiation, they are not the only cause for initiating fatigue cracks [72]. Another factor which the pre-pitting mechanism failed to satisfactorily explain was the initiation of fatigue cracks in the absence of gravity effects. In normal pitting processes, gravity plays an important role in determining the shape, size and severity of the pit. Further, the pitting mechanism depends strongly on chemical contributions which

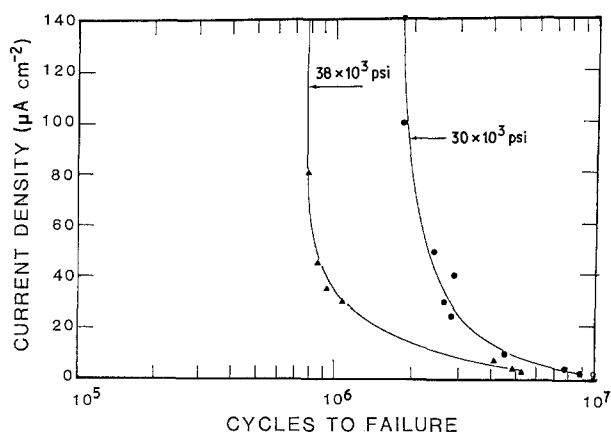


Figure 13 Effect of applied anodic currents on the fatigue behaviour of low carbon steel specimens in deaerated 3% NaCl solution [92].

may not be necessarily dominating in a corrosion fatigue process. Thus, the pre-pitting mechanism breaks down when rationalizing the synergistic interactions that are required to initiate cracks during the process of corrosion fatigue.

4.2. Mechanism of surface film rupture

Rupture of an otherwise protective layer of film on the surface of the metal was another mechanism put forth to explain crack initiation during corrosion fatigue. An important step in this mechanism is the formation of a protective oxide film on the surface (Fig. 14a). Such films are easily formed in materials which have a high affinity for oxygen, which is readily available in an aqueous environment. The formation of an oxide film involves a chemical reaction which dominates the mechanism of corrosion fatigue before mechanical parameters can participate in the initiation process. Prior to formation of the protective film, both anodic and cathodic reaction sites exist on the surface of a metal exposed to an aqueous solution. Formation of the protective oxide film shields the potential corrosive sites from the environment and, thereby, prevents corrosive attack from taking place. However, the protective film is ruptured when subjected to mechanical stressing. Rupture of the protective film causes fresh metal to be exposed which acts as an anodic or cathodic reaction site. The various stages of film rupture mechanism are illustrated in Fig. 14.

The rate of formation of a protective oxide film on the surface of a material is strongly influenced by the nature of the aqueous medium to which it is exposed. The surface oxide layers which form on many metals and alloys, can act as barriers to dislocation activity. Consequently, in the presence of an oxide layer, a case for which the dissolution rate is slow, the PSB spacing will be small because slip localization is inhibited. By raising the dissolution rate, or by making the oxide film thinner, the barriers to slip are reduced, slip localization is favoured and PSB spacing increases. Studies on copper single crystals by Finney and Laird [36] have shown that almost all the imposed plastic strain is taken up by the PSB regions. Thus, when the PSB spacing is increased by environmental effects, each PSB carries a larger local plastic strain, leading to accelerated crack initiation. Additionally, environment alters the stability of the near surface matrix dislocation structures causing, as a result, the matrix dislocations to be transferred more easily into the PSB, further accelerating the formation of PSBs.

Aqueous environments can generally be classified as being: (a) acidic in nature ($\text{pH} < 7$), (b) neutral solution ($\text{pH} = 7$), and (c) basic solution ($\text{pH} > 7$). Each one of these categories of solutions significantly influences the chemical contribution to the mechanism of corrosion fatigue crack initiation.

Duquette [68] reported the occurrence of corrosion fatigue in acid solutions where adherent protective surface films are unstable [33]. This observation suggests that film rupture cannot be accepted as a general mechanism for corrosion fatigue. Simnad and Evans [86, 87] based on the results of their intensive investigation concluded that film rupture may be

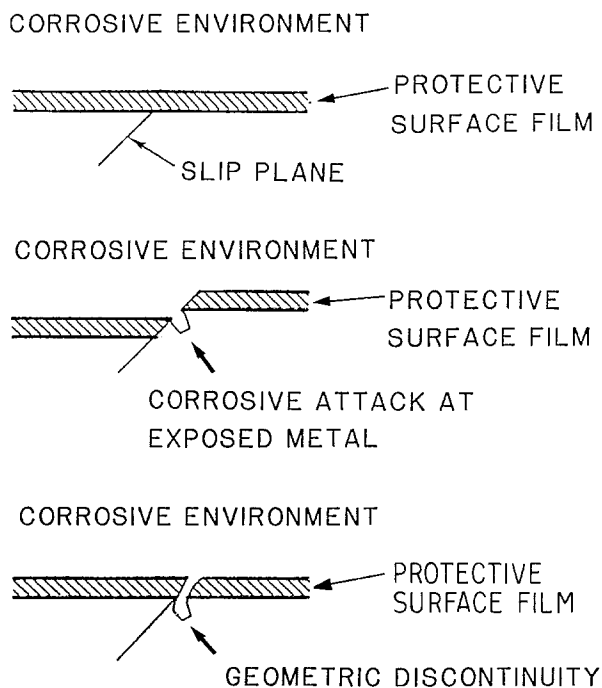


Figure 14 Mechanism of surface film rupture for environmentally enhanced crack initiation.

important in neutral solutions, and that subsequent structural changes in the metal through strain-enhanced dissolution could be involved in acid solutions with the distorted metal acting as the anode. The observation that adherent films are unstable in acidic solutions led to the conclusion that formation of a protective oxide film under these conditions is an extremely rapid process. The surface films formed were spalled off upon reaching a critical thickness, following which the mechanical parameters influenced the crack initiation mechanism [87].

Parkins [88] observed the effects of pH on crack initiation in aluminium exposed to sodium chloride solution. The effect was explained in terms of the stability of aluminium oxide films, because the solubility of aluminium oxide varies with pH. At low pH, the solubility of the aluminium oxide (Al_2O_3) is rather high and, consequently, film formation is difficult. In a neutral solution of pH = 7, the aluminium oxide is relatively insoluble and the initial oxide film protected the underlying metal until such time as the film is mechanically disrupted and fresh metal is exposed to the environment which subsequently causes crack initiation. In basic solutions, i.e. pH = 10, the solubility of the aluminium oxide increases such that lateral dissolution is less restricted and crack blunting is induced.

Early studies aimed at evaluating the corrosion fatigue characteristics of drawn mild steel wires exposed to potassium chloride (KCl) solutions with and without potassium chromate (K_2CrO_4) additions showed that the measured electrode potential dropped suddenly on loading [89]. The drop in potential occurred several times during the cyclic fatigue tests and was interpreted as an indication of breakdown or destruction of the protective surface film during cyclic stressing.

A subsequent investigation by Duquette and Uhlig

[92] strongly disagreed with the surface film rupture mechanism because experimental data obtained on low carbon steel specimens exposed to chloride-containing solutions revealed the existence of a critical corrosion rate associated with initiation of micro-cracks in corrosion fatigue. The corrosion rate was observed to be independent of the applied stress level (Fig. 13) [92]. Additionally, it was shown that independent of the applied stress level, low carbon steels could be cathodically protected from corrosion fatigue either above or below the fatigue limit at a potential that corresponded to that normally observed for cathodic protection. Thus, from these studies it is not clear whether the mechanical parameters alone are adequate to dominate the crack initiation mechanism. It may very well be that a critical applied stress in conjunction with a critical corrosion rate promotes the surface film rupture mechanism of microcrack initiation.

4.3. Mechanism of strain-induced dissolution of slip steps

Strain-induced dissolution of emerging slip bands was another mechanism put forth to explain early crack initiation in corrosion fatigue. For example, Whitman and Evans [93] suggested, based on a series of corrosion fatigue experiments performed on annealed and cold worked steel wire, that cracks advanced by a combination of electrochemical and mechanical action. Prior deformation was found to have no effect on the number of cycles to failure (N_f) when exposed to acid solutions. However, on application of cyclic stresses, preferential attack of the slip bands was observed and attributed to the higher energy state of atoms at the crack tip than in the specimen body. The atoms associated with dislocations are preferentially attacked because it takes less activation energy to remove these atoms from the material. The dissolution effectively unlocks otherwise blocked slip processes, accelerates extrusion-intrusion formation, and accordingly promotes premature crack initiation.

In a much later study, Masuda and Duquette observed from a series of experiments performed on polycrystalline pure copper that when anodic currents were applied, the fatigue fracture morphology changed from a mixed mode transgranular-intergranular to totally intergranular [83]. This behaviour suggests that the enhanced deformation associated with grain boundaries results in an increased corrosive attack of the grain boundaries relative to that of the emerging slip bands. The researchers observed the slip bands to be preferentially corroded with a concomitant increase in both the magnitude and the density of the emerging slip bands.

Grain boundaries tend to localize the deformation, leading to intergranular cracking by essentially the same mechanisms that operate in the region of persistent slip bands to promote transgranular cracking in single crystals. The presence of alloying additions and soluble impurities causes them to segregate to the grain boundary. The possibility that such segregation may take a variety of forms was initially suggested by Staehle [94] and is shown in Fig. 15. The precipitates

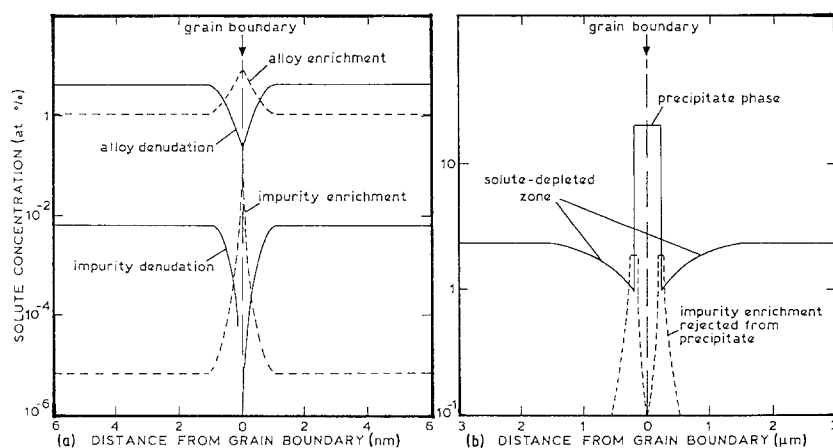


Figure 15 Schematic illustration of the solute concentration profile across the grain boundaries [94] (a) without precipitate formation, (b) with precipitate formation.

at the grain boundaries which contribute to selective dissolution at such regions by the environment continues to be a subject of speculation. Nevertheless, it has been unequivocally demonstrated that preferential corrosion is sensitive to such segregation [95]. While equilibrium phases are precipitated at the grain boundaries, solute depletion occurs in the immediate vicinity of the grain boundary resulting in the formation of a precipitate free zone. Such locations are susceptible to preferential attack as observed in the case of age-hardened aluminium alloys [96]. Such chemical heterogeneity promotes localized corrosion in aggressive aqueous environments resulting in accelerated crack initiation. Other mechanisms based on the formation of a galvanic couple between the deformed and undeformed metal were also proposed to explain the corrosion fatigue phenomenon [93].

The strain enhanced dissolution mechanism is operative when the metal is in an active corrosion state, while film rupture is dominant when the metal is in a passive state. This observation is strengthened by the results obtained from a corrosion fatigue study on a copper-nickel alloy by Harvey *et al.* [97]. In this study, the researchers fatigued the samples while they were being polarized over a range of anodic voltages encompassing both the active and the passive corrosion regions. The degradation in fatigue life for a given increase in applied anodic potential was found to be greater in the active region than in the passive region, indicating that both the film rupture and strain enhanced dissolution mechanisms were occurring in the two regions.

In all experiments performed to support the hypothesis of strain enhanced dissolution, the materials were located in an environment which allowed the formation of a protective surface film. This fact was, for the most part, ignored by several investigators. Formation of the protective surface film accounts well for preferential corrosion occurring at emerging slip bands, because it is at these emerging slip bands where film rupture occurs.

4.4. Mechanism of surface adsorption

Liquids when adsorbed on solids, lower the surface energy of the solid and significantly alter the mechanical properties. Initial studies by Rebinder and co-workers [98, 99] revealed accelerated creep rates in metals coated with active surface agents. The

explanation put forth by Rebinder was that the surface active agent preferentially adsorbed in pre-existing microcracks on the metal surface causing them to propagate at reduced stress level. Subsequently, this mechanism was modified to include a reduction in the surface energy of atoms at the surface layer by the adsorbing species. Accordingly, the slip bands are easier to produce, and therefore, cracks are initiated earlier than in the air environment. Lynch [100], based on his extensive investigations, actually found that a reduction in surface energy enhanced plasticity and promoted early crack initiation. An alternate view proposed by Stoltz and Pelloux [101] was that adsorption reduces plasticity and promotes nucleation of cracks due to local brittle fracture. Such observations were strengthened by experiments on Al-Zn-Mg alloys which exhibited total brittle fracture when exposed to water. Because hydrogen is the only stable gaseous species present in water, failure can be attributed to hydrogen embrittlement, as no evidence of anodic dissolution or plasticity was observed [102, 103].

A reduction of the surface energy of the metal by environment adsorption fails to rationalize completely the corrosion fatigue phenomenon. Reduction in surface energy should result in the appearance of a fatigue limit in the case of steels. However, no observable fatigue limit was actually observed. In general, interpretations of corrosion fatigue crack initiation based on the Rebinder or surface energy lowering effect were accepted more in the Soviet Union than elsewhere. Researchers in England and in Europe favoured a different explanation for the Rebinder effect. These researchers ascribed the reduction of creep strength to an environmental dissolution of the strong adherent surface oxide by the liquid environment [102-105]. In the absence of a liquid environment, the oxide film serves as a barrier to dislocation egress and, consequently, exerts sufficient back stress on the slip planes to strengthen the metal. Aggressive environments particularly acids, dissolve the film and allow slip processes to occur more easily at the surface (Fig. 16). Although this mechanism may be a contributing factor in a number of metal-environment combinations, it cannot be accepted as the mechanism to explain the Rebinder effect as a similar effect has been observed to exist in gold where oxide films do not exist.

Kramer and Demer [105] modified the Rebinder

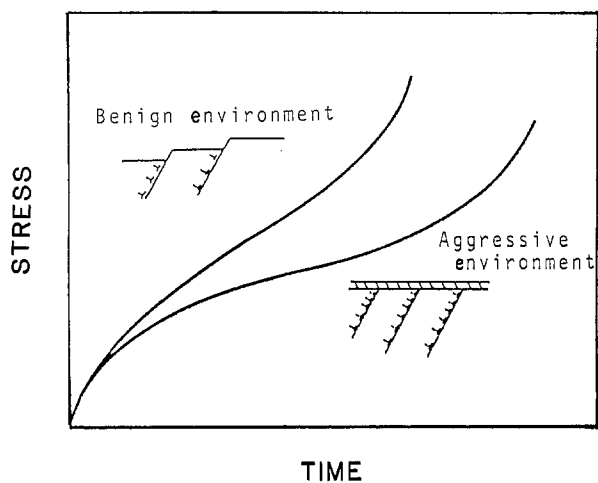


Figure 16 Schematic illustration of oxide film-dislocation interaction and the resultant creep curves for (a) adherent oxide film, (b) oxide film removed by the environment [33].

mechanism. In this modified mechanism the weakening effect is associated with a chemical adsorption process and the rate of removal of the entire metal surface by dissolution is the controlling process. The dissolution either removes or unlocks the dislocation pile-ups thereby inducing additional slip.

5. Summary and concluding remarks

The large body of literature reviewed in this paper presents the cross-section of views, models and experimental results that have been developed over the years by several investigators in the general field of corrosion fatigue. The increasing belief that all structures have inherent defects that serve as potential sites for crack initiation has in recent times stimulated studies predominantly on crack propagation. Thus any importance to an understanding of environmental effects on fatigue crack initiation have been largely left to the academic community.

The literature suggests that crack initiation in aqueous environments is extremely complex because of the very large number of variables some of which include the nature of the aqueous medium, corrosion interactions, pH levels, alloy chemistry, processing treatments, intrinsic microstructural effects, and test variables such as frequency, waveform, temperature and stress intensity levels. As all experimental investigations lack detailed and systematic control of each and every variable (a practical impossibility due to the size of the matrix) comparison of results from different sources becomes tedious, confusing and often contradicting. Often there are as many contradictions as there are agreements to any specific model or mechanism. While large experimental programmes can be devised, it appears that what is immediately required is separation of each individual aspect that promotes aqueous corrosion fatigue and establishing its validity and/or importance in a wide variety of systems. Thus, experiments need to be designed with care and caution in an attempt to understand the specific phenomenon at the microscopic and submicroscopic levels.

Little attention has been focused on the role played by surface films in the crack initiation process. The nature, thickness and type of film may complicate

interpretation of test results from one set of data to another. These broad observations lead the authors to the conclusion that future work must not attempt to promote or develop a uniform model for fatigue crack initiation, but must in fact provide the phenomena observed for a specific alloy/environment system. The development of several sophisticated analytical techniques has definitely stimulated the possibility of arriving at a basic understanding of crack initiation processes. It is hoped that cross-pollination of ideas among researchers combined with experiments aimed at resolving the several anomalies will serve as a catalyst for better understanding of the complex environmentally influenced phenomena.

References

1. M. E. FINE, *Met. Trans.* **11A** (1980) 365.
2. S. SURESH and R. O. RITCHIE, *Int. Metals Rev.* **29**(6) (1984).
3. N. THOMPSON and N. J. WADSWORTH, *Metal Fatigue Adv. Metal Phys. (Phil. Mag. Suppl.)* **7** (1958) 72.
4. T. H. ALDEN, Report no. 62-RL-2923, General Electric Research Laboratory (1962).
5. D. H. AVERY and W. A. BACKOFEN, "Fracture of Solids", edited by D. C. Drucker and J. C. Gilman (Interscience, New York, 1963) p. 339.
6. J. C. GROSSKREUTZ, *J. Appl. Phys.* **34** (1963) 372.
7. J. C. GROSSKREUTZ and P. WALDOW, *Acta Metall.* **11** (1963) 717.
8. K. U. SNOWDEN, *ibid.* **11** (1963) 675.
9. C. LAIRD and G. C. SMITH, *Philos. Mag.* **8** (1963) 1945.
10. M. J. MAY and R. W. K. HONEYCOMBE, *J. Inst. Metals* **92** (1963-64) 41.
11. J. C. GROSSKREUTZ, Sagamore Conference, Fatigue-An Interdisciplinary Approach, edited by J. J. Burke, N. L. Reed and V. Weis (Syracuse University Press, 1964) p. 27.
12. B. L. RITTER and N. L. GRANT, "Thermal and High Strain Fatigue" (Institute of Metals, London, 1967) p. 80.
13. J. C. GROSSKREUTZ and G. G. SHAW, "Fracture 1969" Proceedings of the Second International Conference on Fracture, Brighton, 1969 (Chapman and Hall, London, 1969) p. 602.
14. W. J. PLUMBRIDGE and D. A. RYDER, *Metall. Rev.* **136** (1969) 119.
15. J. C. GROSSKREUTZ, *Phys. Status Solidi* (1970).
16. D. J. DUQUETTE, "Corrosion Fatigue - Chemistry Mechanics and Microstructure", NACE-2, edited by O. F. Devereux *et al.* (1972) p. 12.
17. "Corrosion Fatigue", University of Newcastle, *Met. Sci.* **13** (1979).
18. H. MUGHRABI, R. WANG, K. DIFFERT and U. ESSMAR, "Fatigue Crack Initiation by Cyclic Slip Irreversibility in High Cycle Fatigue", International Conference in Quantitative Measurement of Fatigue Damage, Dearborn, Michigan (1982).
19. Z. S. BASINSKI, R. PASCUAL and S. J. BASINSKI, *Acta Metall.* **31** (1983) 591.
20. M. E. FINE and R. O. RITCHIE, Fatigue and Microstructure, edited by M. Meshii (American Society of Metals, Metals Park, Ohio, 1979) p. 245.
21. P. H. FRITH, *J. Iron Steel Inst.* **159** (1948) 385.
22. W. A. WOOD, "Fatigue in Aircraft Structures" (Academic, New York, 1956).
23. H. E. FRANKEL, J. A. BENNETT and W. A. PENNINGTON, *Trans. ASM* **52** (1960) 257.
24. W. A. WOOD, S. COUSTAND and K. R. SARGART, *Acta Metall.* **11** (1963) 643.
25. P. R. SWANN, F. P. FORD and A. R. C. WESTWOOD, (eds) "Mechanisms of Environment Sensitive Cracking of Materials" (Metals Society, UK, 1977).
26. H. H. ATKINSON, *J. Appl. Phys.* **30** (1959) 637.

27. J. C. GROSSKREUTZ, *Phys. Status Solidi* **47** (1971) 11.
28. C. LAIRD and D. J. DUQUETTE, "Corrosion Fatigue — Chemistry, Mechanisms and Microstructure", NACE-2, edited by O. F. Devereux *et al.* (1971) p. 88.
29. N. THOMPSON, N. J. WADSWORTH and N. LOUAT, *Philos. Mag.* **1** (1956) 113.
30. J. V. SHARP, *ibid.* **16** (1963) 77.
31. P. J. E. FORSYTH and C. A. STUBBINGTON, *J. Inst. Metals* **83** (1954–55) 395.
32. *Idem, ibid.* **86** (1956–57) 339.
33. *Idem, ibid.* **86** (1957–58) 90.
34. A. H. COTTRELL and D. HULL, *Proc. R. Soc.* **A242** (1957) 211.
35. W. A. WOOD and R. L. SEGALL, *Bull. Inst. Metall.* **3** (1957) 160.
36. J. M. FINNEY and C. LAIRD, *Philos. Mag.* **31** (1975) 339.
37. D. HULL, *J. Inst. Metals* **86** (1958) 425.
38. R. C. BOETTNER, A. J. McEVILY, Jr and Y. C. LIN, *Philos. Mag.* **10** (1964) 95.
39. D. I. GOLLAND and P. L. JAMES, *Acta Metall.* **15** (1967) 1889.
40. N. F. MOTT, *ibid.* **6** (1958) 195.
41. A. J. McEVILY, Jr and E. S. MACHLIN, "Fracture" (Wiley, 1959) p. 450.
42. A. J. KENNEDY, *Philos. Mag.* **6** (1961) 49.
43. P. G. PATRIDGE, *Acta Metall.* **13** (1965) 517.
44. D. F. WATT, *Philos. Mag.* **14** (1966) 87.
45. P. NEUMANN, *Acta Metall.* **17** (1969) 1219.
46. A. N. MAY, *Nature* **185** (1960) 303.
47. *Idem, ibid.* **186** (1960) 573.
48. C. ROBERTS and A. P. GREENOUGH, *Philos. Mag.* **12** (1965) 81.
49. D. F. WATT, J. D. EMBURY and R. K. HAM, *ibid.* **17** (1968) 199.
50. M. P. E. DESVAUX, *Z. Metallkde* **61** (1970) 206.
51. M. P. E. DESVAUX and P. CHARSELEY, *Mater. Sci. Engng* **4** (1969) 221.
52. J. C. GROSSKREUTZ, *J. Electrochem. Soc.* **7** (1970) 940.
53. C. LAIRD, "Metallurgical Treatises", edited by J. K. Tien and J. F. Elliott (Metallurgical Society of AIME, 1981).
54. M. R. LIN, M. E. FINE and T. MURA, *Acta Metall.* **34** (1986) 619.
55. J. D. ESHELBY, *Proc. R. Soc.* **241A** (1957) 376.
56. *Idem, ibid.* **252A** (1959) 561.
57. C. LAIRD and A. R. KRAUSE, "Inelastic Behavior of Solids", edited by M. F. Kanninen, W. F. Adler and A. R. Rosenfield, (McGraw Hill, 1970) p. 691.
58. W. H. KIM and C. LAIRD, *Acta Metall.* **26** (1978) 241.
59. D. S. KEMSLEY, *J. Inst. Metals* **85** (1956) 420.
60. J. PORTER and J. C. LEVY, *ibid.* **89** (1960) 86.
61. R. C. BOETTNER, C. LAIRD and A. J. McEVILY, Jr, *Trans. ASME* **233** (1965) 379.
62. E. A. STARKE, Jr and G. LUTJERING, "Fatigue and Microstructure", edited by M. Meshii (American Society for Metals, Metals Park, Ohio, 1979) p. 275.
63. R. C. BOETTNER, A. J. McEVILY, Jr and Y. C. LIU, *Philos. Mag.* **10** (1984) 95.
64. T. S. SUDARSHAN and M. R. LOUTHAN, Jr, *Int. Metals Rev.* **32** (3) (1987) 121.
65. B. P. HAIGH, *J. Inst. Metals* **18** (1917) 55.
66. D. J. McADAM, Jr, *Proc. ASTM* **26** (1926) 224.
67. D. WHITMAN and U. R. EVANS, *J. Iron Steel Inst.* **165** (1950) 79.
68. D. J. DUQUETTE, "Fatigue and Microstructure", edited by M. Meshii (American Society for Metals, Metals Park, Ohio, 1979) p. 336.
69. R. JOHNSON, A. McMINN and B. TOMKINS, "Proceedings Third International Conference on Mechanical Behavior of Materials" University of Cambridge (Pergamon, Oxford, 1979) p. 371.
70. B. D. WESTCOTT, *Mech. Eng.* **60** (1938) 813.
71. R. N. PARKINS, "Corrosion Fatigue" edited by R. N. Parkins and Y. M. Kolotyokin (Metals Society, UK, 1980) p. 36.
72. D. J. DUQUETTE and H. H. UHLIG, *Trans. ASM* **61** (1968) 449.
73. H. SPAHN, "Corrosion Fatigue", NACE-2 (1972) p. 40.
74. H. KITAGAWA, T. FUJITA and K. MIYAZAWA, "Corrosion Fatigue Technology", ASTM STP 642 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1978) p. 98.
75. K. ENDO, K. KOMAI and P. IMASHIRO, *Bull. J. SME* **20** (1977) 513.
76. J. CORNET and S. GOLAN, *Corrosion* **15** (1959) 262.
77. G. D. LEHMANN, *Engineering* **122** (1926) 837.
78. A. M. BINNIE, *ibid.* **128** (1929) 190.
79. P. MEHDIZADEH, R. L. McGLASSON and J. E. LANDERS, *Corrosion* **22** (1966) 325.
80. H. P. CHU and J. G. MACCO, "Corrosion Fatigue Technology", ASTM STP 642 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1978) p. 223.
81. M. LEVY and J. L. MORROSSI, *ibid.*, p. 300.
82. R. EBARA, T. KAI and K. INOUE, *ibid.*, p. 155.
83. H. MASUDA and D. J. DUQUETTE, *Met. Trans.* **6A** (1975) 87.
84. E. F. SMITH III, R. JACKO and D. J. DUQUETTE, in "Effect of Hydrogen on Behavior of Materials", edited by I. M. Bernstein and A. W. Thompson (Metallurgical Society of AIME, 1976) p. 218.
85. D. J. McADAM Jr and G. W. GEIL, *Proc. ASTM* **41** (1928) 696.
86. M. T. C. SIMNAD and U. R. EVANS, *J. Iron Steel Inst.* **156** (1947).
87. U. R. EVANS and M. SIMNAD, *Proc. R. Soc. Ser.* **188A** (1947) 372.
88. R. N. PARKINS, "Corrosion Fatigue", Proceedings of the First USSR-UK Seminar on Corrosion Fatigue of Metals, edited by R. N. Parkins and Y. H. Kolotkyku, Lvov, USSR (The Metals Society, London, 1984).
89. A. J. GOULD and U. R. EVANS, *J. Iron Steel Inst.* **156** (1947) 531.
90. O. F. DEVERAUX, J. DRESTY and B. KOVACS, *Met. Trans.* **2A** (1971) 3225.
91. H. N. HAHN and D. J. DUQUETTE, *ibid.* **10A** (1979) 1453.
92. D. J. DUQUETTE and H. H. UHLIG, *Trans. ASM* **62** (1969) 839.
93. D. WHITMAN and U. R. EVANS, *J. Iron Steel Inst.* **165** (1950) 72.
94. R. W. STAEHLE, in "Mechanical Behavior of Materials", edited by K. J. Miller and R. F. Smith, Vol. I (Pergamon, Oxford, 1980) p. 93.
95. E. D. HONDROS and C. LEA, *Nature* **289** (1981) 663.
96. J. C. SCULLY, "The Fundamentals of Corrosion", 2nd Edn (Pergamon, Oxford, 1975).
97. D. P. HARVEY II, T. S. SUDARSHAN, M. R. LOUTHAN Jr and R. E. SWANSON, *J. Mater. Energy Systems* **7** (1985) 269.
98. P. A. REBINDER and E. K. VENSTREM, *Z. Fiz. Khim.* **26** (1952) 12.
99. V. LIKTMAN, E. SHCHUKIN and P. A. REBINDER, "Physicochemical Mechanisms of Metals" (Academy of Sciences, Jerusalem, 1963) p. 12.
100. S. P. LYNCH, "Mechanisms of Environment Sensitive Cracking of Materials" (The Metals Society, London, 1977) p. 201.
101. R. E. STOLTZ and R. M. PELLOUX, *Met. Trans.* **3A** (1972) 2433.
102. D. PHILLIPS and N. THOMPSON, *Proc. Phys. Soc. Lond.* **63B** (1950) 39.
103. S. HARPER and A. COTTRELL, *ibid.* **63B** (1950) 331.
104. R. ROSCOE, *Nature* **133** (1934) 912.
105. I. KRAMER and L. DEMER, *Prog. Mater. Sci.* **9**(3) (1961) 195.

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