Corrosion pitting and environmentally assisted small crack growth

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In many applications, corrosion pits act as precursors to cracking, but qualitative and quantitative prediction of damage evolution has been hampered by lack of insights into the process by which a crack develops from a pit. An overview is given of recent breakthroughs in characterization and understanding of the pit-to-crack transition using advanced three-dimensional imaging techniques such as X-ray computed tomography and focused ion beam machining with scanning electron microscopy. These techniques provided novel insights with respect to the location of crack development from a pit, supported by finite-element analysis. This inspired a new concept for the role of pitting in stress corrosion cracking based on the growing pit inducing local dynamic plastic strain, a critical factor in the development of stress corrosion cracks. Challenges in quantifying the subsequent growth rate of the emerging small cracks are then outlined with the potential drop technique being the most viable. A comparison is made with the growth rate for short cracks (through-thickness crack in fracture mechanics specimen) and long cracks and an electrochemical crack size effect invoked to rationalize the data.

1. Introduction

The incidence of such failures has been progressively reducing through greater recognition of the potential failure mechanisms, improvements in materials selection, informed system management, advances in inspection methodologies and establishment of international standards and codes of practice. There is now arguably a shift in emphasis in industry-related research towards improved understanding and prediction of the early stages of damage development in acknowledgement of the key role that this regime can play in determining the overall life of components and structures.

In many applications, corrosion pits act as precursors to cracking, but qualitative and quantitative prediction of damage evolution has been hampered by lack of insight into the process by which a crack develops from a pit. That perspective has changed dramatically with the advent of advanced three-dimensional imaging tools such as X-ray computed tomography (XCT) and focused ion beam machining with scanning electron microscopy (FIB-SEM) enabling unique characterization of the transition from pit to embryonic crack. In turn, this has stimulated extended application of finite-element (FE) modelling to calculation of the distribution of stress and strain around a pit. These advances in approaches to understanding the pit-to-crack transition are exciting but where a crack-tolerant approach in design is operational quantifying the growth rate of small cracks emerging from pits is a necessary adjunct.

The goal of this paper is to highlight the recent breakthroughs in characterization and understanding of the pit-to-crack transition and to outline the challenges in quantifying the subsequent growth rate of the emerging small cracks.

2. Pit-to-crack transition

The critical role of pitting in crack nucleation in power generation, aerospace, and oil and gas applications stimulated considerable effort to understand and to model quantitatively the different stages of damage development, including pit initiation, pit growth, the transition from a pit to a crack and subsequent growth of the crack [3–8]. All of these stages present challenges in life prediction modelling but most significantly the transition from a pit to a crack, as the mechanistic process was, until recently, not well characterized. Accordingly, a phenomenological approach was adopted in early predictive schemes. Specifically, a crack was assumed to initiate from a pit when two criteria were satisfied: the pit depth exceeded a threshold value, corresponding to a threshold stress or stress intensity factor, and the crack growth rate was greater than the pit growth rate [3]. Such simple rules are ideal for incorporating into predictive models and evidently must be satisfied for a crack to develop. However, the further assumption adopted in these models, that the crack has the same depth as the pit at the point of transition and by implication initiates at the pit base, had no intrinsic foundation. It was not an unreasonable perspective, because the local chemistry tends to be most aggressive at the pit base in many applications and it is almost instinctive to imagine that the stress associated with a deep pit would be a maximum at the base of the pit. However, as three-dimensional imaging reveals, the transition from a pit to a crack does not occur necessarily at the pit base. In addition, the expressions adopted in these models for the stress intensity factor at the point of transition from a pit to a crack also lacked rigour.

(a) Application of X-ray computed tomography

XCT provides an ideal non-destructive tool to investigate the three-dimensional morphology of pits [9,10] and cracks [10–20] and is based on the variation in absorption coefficients along the path of a transmitted X-ray beam [21–24]. The absorption coefficient is linked to the density and atomic number of the material within a specimen enabling visualization of defects, and thus providing quantitative information that would not be otherwise readily collected. A key advance has been the development of accessible laboratory-based instruments with resolutions ranging from 50 nm to several micrometres, albeit with a trade-off with respect
to depth of penetration. For the bench-top XCT experiments in our study [25], a SkyScan 1072 or a SkyScan 1172 desktop micro-CT X-ray scanner was used. The three-dimensional spatial resolution of the reconstructed images obtained from the SkyScan 1072 ranged from 3.5 to 7.5 µm, depending upon the magnification used (typically 70×). Spatial resolution of reconstructed images obtained via the Skyscan 1172 was of the order of 2 µm. Image analysis, visualization and three-dimensional rendering of the tomographic data were performed using a commercial software package. Inherently, there will be some loss of resolution close to the crack tip, and some of the finer detail may be missed, but in terms of the general thrust for the application in identifying the location of crack development with respect to a corrosion pit, this is non-critical.

The techniques were applied to the pitting and cracking of steam turbine disc steel, the failure of which can be catastrophic as the turbines are spinning at 50 Hz. A 3NiCrMoV disc steel was investigated. This steel exhibited extensive pitting and stress corrosion cracking (figure 1) when exposed at a service stress of 90% of the 0.2% proof stress ($\sigma_{0.2}$) to a deliberately aggressive simulated condensate at 90°C, designed to develop damage in a modest time scale. The pit geometry tended to be broadly similar to those encountered for such steels in less aggressive environments [26] but with increased purity of the solution the pits tended to be deeper relative to their opening (as shown later, a factor that should lead to greater likelihood of crack initiation near the crack mouth in the lower conductivity solution). Service experience indicates pits tend to grow deep relative to their mouth opening and have a similar macrogeometry to those developed in the laboratory. However, detailed comparison with pits in service at the microtopographical level has not been undertaken.

Longitudinal sections of about 2 mm thickness (close to the penetration limit for the instrument) were used to acquire transmission X-ray images over 180° of rotation of the sample with an 11 s exposure/projection, and a 0.9° rotation step creating 200 two-dimensional transmission X-ray images in total. The images characterizing the transition from pits to cracks are best illustrated by figure 2. Figure 2 shows a three-dimensional rendering of attenuation data of several cracks emerging from a single bullet-shaped (U-shaped in cross section) pit of 681 µm depth after 7173 h exposure. Pits and cracks can easily be visualized by making the bulk of the material transparent. A more comprehensive image of the pit and cracks can be seen in the electronic supplementary material, video S1. The most notable observations are that pit A is deeper than the cracks, multiple cracks are evident, and these cracks tend to be irregular in character (a common feature of small crack growth). Electronic supplementary material, video S1,
Figure 2. Multiple crack evolution from a corrosion pit showing a scanning electron microscopy (SEM) image (a) and an XCT image (b) of a steam turbine disc steel specimen stressed at 90% \( \sigma_{0.2} \) and exposed to simulated condensate at 90°C for 7173 h [25] (see electronic supplementary material, video S1, for additional visualization). (Online version in colour.)

Also provides better visualization of the coalescence of crack 3 and crack 4 within the bulk of the specimen (the coalescence is not evident on the surface of the specimen depicted in the SEM image).

While this provided ground-breaking imaging of pits and cracks, systematic investigation of a number of such pits with cracks revealed that about 50% had pits deeper than the cracks and about 50% the converse. This led to uncertainty as to the location around the pit from which the crack actually initiated and whether this was variable or localized to a particular region.

To capture the very early stages of crack development, it was necessary to expose specimens for much shorter times. Accordingly, the test protocol was repeated as for the longer exposure tests, but the specimens were removed at shorter exposure periods of 171, 668 and 2209 h. Pits were apparent at 171 h, but with no associated cracks. A pitted area of a specimen that had been exposed for 668 h is shown in figure 3. This three-dimensional tomographic image is best perceived as looking at the surface skin of the pit and crack as viewed from inside the material, or viewing a replica from underneath. Figure 3, supported by the electronic supplementary material, video S2, indicates that cracks have initiated on the walls of the pits near the pit mouth. It is readily seen that pit B extends well beyond the depth of crack 2.

Visualization of pits and cracks after 2209 h exposure (figure 4) reinforces the perspective that crack initiation occurs predominately at the pit mouth rather than at the pit base. In figure 4, three cracks can be seen that clearly developed at or near the mouth of three different pits. In one case, there is an example of a crack bridging two pits, most likely involving coalescence of individual cracks from the adjacent pits.

Numerous pits and cracks at different exposure times were examined, with overwhelming evidence that the vast majority of cracks emanated at or just below the pit mouth. For example, of the 30 pits containing cracks observed on the 668 h specimen, 86% had cracks that had initiated at the mouth of the pit. This percentage increased as the applied stress decreased, and at an applied stress of 50% \( \sigma_{0.2} \), there were no cracks from the base at all. An argument can be put that cracks initiated from the base, extending initially around the periphery of the pit, and the higher growth rate at the base resulted in dissolution of that portion of the crack, but not towards the mouth where the pit growth rate is lower. This would create the appearance of near-surface cracks that were shallow relative to the depth of the pit. The counter against this is twofold: pit growth rates decrease with depth, and it seems unlikely that the crack could initiate when the pit growth rate is relatively high, but then be overwhelmed by the pit when the growth rate of the pit is actually lower. Additionally, for the tests at the relatively short exposure times at the highest applied stress and also for those at the lower applied stress (for which the pit is deeper and the growth rate is
Figure 3. Internal view of the pit-to-crack transition within a steam turbine disc steel specimen stressed at $90\% \sigma_{0.2}$ and exposed to simulated condensate at $90^\circ$C for 668 h (the surface of the sites rendered on the left are shown in the SEM image on the right for comparison). Two pits are imaged showing crack initiation on the pit wall near the pit mouth [25] (see electronic supplementary material, video S2, for more detail). (Online version in colour.)

Figure 4. Internal view of pits and cracks in a specimen exposed to simulated condensate at $90^\circ$C for 2209 h; the surface of the site rendered in (b) is shown in the SEM image (a) for comparison [25] (see the electronic supplementary material, video S3, for greater detail). (Online version in colour.)

lower), a higher proportion of cracks at the base would be projected and this is not observed. Hence, it is reasonable to deduce that the observation of cracks shallower than the pit depth reflects preferential initiation local to the pit mouth.

The rationale for cracks initiating preferentially near the pit mouth is discussed in the context of the FE analysis. At later exposure times, the proportion of pits with cracks deeper than the pit progressively increases. Here, the perspective is that cracks developing near the pit mouth coalesce, and the rate of growth of these coalesced cracks subsequently increases with respect
to the pit growth rate. An example of two cracks about to coalesce is shown in figure 5 and the
electronic supplementary material, video S4.

In this application, generation of H$_2$S from dissolution of MnS inclusions in the pit is
considered to be the main driving force for pit propagation, supported by enrichment of chloride
concentration in response to an increase in the metal ion concentration. These two factors would
tend to make the chemistry at the pit base more aggressive, which is reflected in the evolution
of bullet-shaped geometry of the pits as the pit depth increases. The question then arises: why
should the crack develop near the pit mouth rather than near the pit base, as might be expected
from a chemical and electrochemical perspective? A mechanics-based explanation appeared by
default to be the most plausible explanation. To substantiate that perspective, FE analysis of the
stress and strain associated with a corrosion pit was undertaken.

(b) Finite-element analysis

The details of the FE analysis are described elsewhere [27]. In brief, the corrosion pit is located
at the mid-point of a cylindrical rod (simulating the tensile test) stressed remotely in tension.
Mesh density is increased around the pit to minimize uncertainty in calculation of local stress
and strain. The pit geometries examined included hemispherical pits typical of shallow pits and
bullet-shaped pits typical of deeper pits.

The results were a revelation. For pits with a depth-to-width aspect ratio similar to or greater
than that of a hemispherical pit, the stress was a maximum near the pit mouth at low applied
stresses, but became a minimum near the pit mouth at stresses commensurate with the onset of
plastic deformation. In essence, the reduced constraint to plastic flow near the pit mouth resulted
in a redistribution of the maximum in stress away from the pit mouth. By implication, the crack
initiation process was not linked to stress directly but to local plastic deformation. As the pit
depth increased and the geometry evolved to ‘bullet-shaped’ increased localization of plastic
strain concentration to the pit mouth was apparent. This observation explains why decreasing
applied stress reduces the likelihood of a crack emanating at the pit base. For a lower applied
stress, the pit size has to be greater to achieve the threshold stress/strain criterion for transition to
a crack. As pits get deeper, a bullet-shaped geometry becomes more prevalent as such a geometry
more readily constricts mixing of bulk and pit solution, and the pits that survive exhibit that
geometry. The focus on mechanics does not preclude a key role for the environment; it is an
environment-induced crack growth process after all. In this case, sulfide species diffusing out of
the pit will be present near the mouth, but at reduced concentration compared with the pit base. It
Figure 6. FE analysis highlighting localization of plastic strain just below the mouth of a corrosion pit (a). An increment of material is removed denoted by the grey region to simulate pit growth (b) and the new strain distribution then calculated (c) [27]. The average change in strain, used to estimate the strain rate, was calculated from numerical data rather than reading off the colour chart as the latter can be deceptive and affected by noise—it can appear to decrease with pit removal in this particular image.

is the competitive balance between pit and crack growth rate that matters and the local mechanics shifts that balance in favour of crack growth at a location near the pit mouth.

The FE analysis also stimulated a step-changing idea on the role of pits as precursors to cracks. Specifically, it was realized that if plastic strain is localized in this fashion and the pit is growing in an otherwise static stress field, then the growing pit was itself generating dynamic plastic strain. Because stress corrosion cracking is most readily initiated by dynamic plastic strain, this was an exciting new concept. The question then was whether the strain rate would be in the domain relevant to stress corrosion cracking? In a further advance of the FE analysis, the growing pit was simulated by incremental removal of material while retaining the plastic wake history from previous increments (exemplified by figure 6). Remarkably, the strain rate calculated, about $3 \times 10^{-8} \text{ s}^{-1}$, correlating the change in strain with measured pit growth rate, was precisely in the domain where stress corrosion cracking would be most likely, typically in the range $10^{-5} \text{ s}^{-1}$ to below $10^{-9} \text{ s}^{-1}$ (though the range of susceptibility is dependent on the material–environment combination) [28].

Thus, a totally new perspective on the role of pitting in stress corrosion crack initiation has been introduced. Instead of just associating a pit with an aggressive local chemistry and a stress–strain concentrator, as conventionally assumed, it is necessary now to consider the additional and perhaps critical role of the growing pit providing the dynamic strain that is so important for developing stress corrosion cracks.

(c) Advanced microscopy

While the induced dynamic strain concept is fundamental, the observation of cracks emanating near the pit mouth cannot be assumed to have generic applicability as the location of crack initiation would be expected to be a sensitive function of pit geometry and the local pit chemistry. In addition, the pit may have significant microtopographical features reflecting the impact on
corrosion activity of local variation in material microchemistry, microstructure, inclusions and constituent particles. Examples of these can be found in the work of Burns et al. [29] in relation to constituent particles in aluminium alloys and of Ma et al. [30] with respect to elongated inclusions in carbon steel. Neither of these observations precludes the possibility that cracks may initiate near the pit mouth, but the specific location around the pit where cracking initiates will be topographically sensitive. Refinement in FE analysis is being undertaken at the National Physical Laboratory, UK, in which three-dimensional digital reconstruction of real pits will be used as the basis for the analysis. However, it is not simply microtopographical features that matter. There can be major differences in macropit geometry from one metal–environment system to another. Thus, for stainless steels in chloride environments, the pits tend to be bulbous shaped with a pit mouth opening that is constrained as this encourages the retention of the specific local chemistry in the pit necessary for pit stability. The question then is where would the cracks initiate from in such a system?

The opportunity to explore this came from a separate investigation into the performance of 316L stainless steel in an oilfield environment (50 000 ppm chloride solution of pH 4.5) at 110°C in which the test solution was saturated with a gas mixture of 1% H₂S in CO₂ at 100 kPa [31]. Stress corrosion cracks in this system were always initiated at corrosion pits. In this study, three-dimensional imaging of a pit with emerging cracks (Figure 7) was undertaken using FIB-SEM (Zeiss Auriga 60 FIB microscope).

FIB microscopes produce three-dimensional structures using a tomographic approach in which successive thin slices of the material are cut or milled by the FIB, and a scanning ion or electron beam technique is used to image, or to map, characteristics of the surface revealed by the removal of each slice. The images acquired can then be combined in a stack to produce a three-dimensional representation, interpolating between like features on adjacent images. FIB-SEM not only enables high spatial resolution of features, but also reveals atomic number contrast (highlighting dealloyed zones around corroded pits for example) and, in principle, can be combined with energy dispersive X-rays for three-dimensional elemental analysis or with electron backscatter diffraction (EBSD) for information on three-dimensional grain structure and crystal misorientation associated with deformation. For the pit with cracks in 316L stainless steel, the material was milled away in 50 nm increments using a gallium ion beam.

The results (Figure 8 and the electronic supplementary material, video S5) were dramatic, showing that cracks appeared to develop in the thinned section of steel undercut by corrosion with linkage to corrosion fissures formed by attack of slip lines introduced in the near-surface during grinding. Clearly, the undercut would be expected to localize stress and strain in the remaining cross section. While not replicating the fine details of this pit in FE analysis, we have shown previously for a pit with a truncated spheroid (somewhat bulbous) geometry that localized...
Figure 8. SEM images from two different FIB slices, formed by gallium ion milling to a depth of 20 µm, showing a corrosion pit mouth at the top of the image with cracks emanating from it [31]. Image (a) highlights corrosion fissures formed at slip lines while the pronounced undercutting and thinning of the top surface is apparent in (b) (see also the electronic supplementary material, video S5). The darker region apparent around the pit (associated with a lower atomic number) is primarily associated with preferential dissolution of iron from the iron–chromium–nickel alloy. (Online version in colour.)

plastic deformation would be predicted in the region of the undercut at the stresses relevant to this experiment. At first sight, this would seem to further support the perspective that the cracks develop preferentially near the pit mouth. However, we have not studied this systematically in this case. In addition, highly localized dissolution features have been observed to develop elsewhere in a pit, including the pit base [31], though no cracks were apparent in that location. Hence, there has to be caution in predicting the location of embryonic crack development from a pit but certainly the traditional perspective that the pit base is the primary site has been shown to have no intrinsic foundation.

3. Small crack growth from pits

When inspection and maintenance is inherently challenging, such as in deep water oil and gas production, a crack-tolerant philosophy is not feasible, and design is conservative, within economic constraints, and based on selecting materials for the operational conditions that are resistant to crack initiation. Understanding the role of pitting in cracking is then focused on identifying the conditions for which pitting might occur and assessing the probability of those pits transforming to cracks, with implications for test exposure period for example. In other applications, including power plant and aerospace, cracks are anticipated to develop during service as the plant, structure or component ages. Reliable life prediction and intelligent maintenance scheduling are then the primary issues in ensuring structural integrity and are based generally on long crack growth rate data (obtained using fracture mechanics specimens with crack lengths typically greater than 1 mm) coupled with service experience. For long cracks, standards for measuring environment-assisted crack growth rates are well established [32]. There is a wealth of data for key industrial sectors, and there is a degree of confidence in their engineering application, the latter coupled with advanced monitoring and non-destructive inspection techniques. However, in relation to the growth rate of small cracks emerging from corrosion pits (here we adopt the Ritchie and Lankford’s definition of a small crack [33] to distinguish from through-thickness short cracks in fracture mechanics specimens), there are no standards that guide the measurement process; simply recognition that the growth rate may be different from that for long cracks, that the rate will be sensitive to local electrochemistry, near-surface microstructure and mechanical properties, as well as loading conditions, and that the time spent in the small crack regime may constitute a significant fraction of life. The major challenge is the slow growth of small cracks, which impacts on
test duration, and the time and loading rate dependence of environment-assisted cracking that constrains the adoption of accelerated testing. The development of high-resolution measurement techniques combined with understanding of the key factors that impinge on growth rate then becomes critical.

(a) Small crack growth from pits: measurement techniques

There are different approaches to measurement of the growth rate of small cracks from corrosion pits, including crack-front marking, replicas, optical methods and potential drop techniques, but all have limitations. For some alloys, it is possible to obtain a measure of crack shape and determine an average crack growth rate in the small surface crack regime by varying the loading sequence, causing a change in the crack-tip deformation characteristics, and thereby delineating the crack front [29]. The fracture surface is then examined after the test, and an estimate of the crack growth rate as a function of depth made by correlating the crack-front marking with the periodicity of the load change. The viability of the method rests on demonstrating that the step-change in loading has only an immediate transient effect, and the subsequent growth rate is not affected (e.g. through modification of the crack-tip electrochemistry or crack-tip mechanics). The ‘beach’ marks must be discernible. This will be alloy dependent and may not be achievable in aggressive environments or when the cracks are of the size of the pit or below.

Measurement of crack size can also be undertaken using replicas [34] after removal of the specimen from the environment. However, the process of drying out and re-exposing the specimen can have the undesirable consequence of perturbing the nature of oxide film, the corrosion potential, and the local chemistry each time a measurement is made and this renders the reliability of the data potentially uncertain.

While XCT has been used for qualitative examination of cracks, there are challenges in quantifying crack size at different exposure times to determine crack growth rates. Issues of beam source, specimen thickness, maintaining exposure conditions constant when growth rates are small represent a challenge. In principle, it is possible, but the range of useful applications are currently constrained.

The most common method for measuring growth rates in small surface cracks is by visual observation of surface crack length using optical microscopy, supported now with advanced digital technology that enables both high resolution and automation of the measurement process. However, visual observation may be constrained by corrosion product obscuring the crack. Surface crack-opening displacement analysis (based on digital image correlation) is an extension of optical measurement but has the same visibility constraint and involves more extensive analysis. Inherently, in both cases, an assumption about crack shape has to be made to relate the surface measurement to crack depth. While cracks will tend to be semicircular as the length progressively increases, there is less confidence in assigning a crack shape when the crack front is not continuous, for example, when the crack depth is less than the pit depth.

Direct current potential drop (DCPD) or alternating current potential drop (ACPD) methods are widely used and measurement is easily automated. Here, a constant or alternating current is applied to the specimen and the change in potential drop across the pit and crack measured by probes located symmetrically on opposite sides of the crack and as close as possible to maximize resolution. The increase in potential drop as the crack grows is associated with an increase in the surface area of the crack and therefore not a direct measure of crack dimensions; a specific geometry of the crack has to be assumed. A weakness with respect to any potential drop method applied to cracks emerging from corrosion pits is that it is only valid if the pit is not growing, because any loss of material could contribute to a change in potential drop. This is not an unreasonable assumption for pits created artificially as described below, which tend to be non-propagating when removed from the environment and re-immersed. However, that will be system dependent and will be influenced by the exposure conditions. An additional weakness comes when several cracks develop in the early stages before a dominant coalesced crack emerges as the potential drop method responds only to the change in area (resistance) and derivation...
of crack size is then inherently uncertain. Nevertheless, if the crack develops and propagates subsurface before breaking the surface, then this will be detected by the potential drop method in advance of any optical detection.

It will be apparent that a combination of methods, such as DCPD and optical, are the most useful in making a reasonable estimate of crack propagation rate in the small crack regime.

Whether using optical or potential drop methods in laboratory testing, it is important to control the location of crack initiation to enable positioning of crack measurement techniques for optimum crack size resolution. In that context, generation of a single pit of defined size in the centre of the test specimen is ideal. There are several methods of achieving this including the galvanostatic droplet technique, coating with a defect and exposing to an aggressive solution or stepping the potential and current, but for corrosion-resistant alloys the droplet technique enables greatest control of pit depth and is most repeatable [35]. An example of a test set-up is shown in figure 9.

A single droplet of solution (volume $\approx 2$ ml and typically $0.1$ M NaCl) from a capillary tip with outer diameter of 0.47 mm and inner diameter of 0.13 mm is placed near the centre of the gauge length and the specimen polarized anodically. The principle is relatively simple. When an anodic current greater than the passive current is applied to the specimen under galvanostatic (constant current) control in a chloride environment, the potential of the electrode will move in a positive direction until it reaches the pitting potential. A pit will initiate at the pitting potential and, as a result, the potential will drop rapidly to below the pitting potential for new pit development, preventing additional pits from forming. Careful consideration is required in selection of the polarization current and chloride concentration: if the applied current is too small, then a pit may not initiate or the initiated pit may arrest as the pit area increases; if the applied current is too large, then multiple pits may form and patchy corrosion may occur. Once the polarization current has been optimized, the desired depth of pit is achieved by controlling the polarization time. Using this method, pits in stainless steels can be produced with a variation in depth less than 10% of the target value. A typical image of a corrosion pit, with relatively long crack to make it most apparent, is shown in figure 10.

Having obtained measurements from optical techniques or from the variation of potential drop with time the question then is how to extract information about the crack depth, $a$, because neither technique measures it directly. This is especially true when cracks exist on either side of the pit and the individual crack depth is smaller than the pit depth such that there is no continuity of the crack front. When there is a continuous crack front (the crack depth exceeds the pit depth) Newman [36] suggests, from fractographic observations and fracture mechanics-based analysis [40], that it is reasonable to assume a semicircular crack shape in estimating the crack depth

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**Figure 9.** Image of galvanostatic droplet process for pre-pitting [35]. (Online version in colour.)
from either optical or DCPD measurements, though it will not be ideal in the early stage of crack development immediately after the continuous crack front is established.

(b) Mechanical driving force for small cracks

It is recognized that fracture mechanics concepts that link crack size and stress through the stress intensity factor $K$ (assuming small-scale yielding) or the $J$ integral (elastic–plastic conditions where macroscopic yielding is significant) are inherently limited when the crack size is of the scale of the microstructure and continuum mechanics no longer applies. Estimating the local variation in the mechanical driving force as a small crack propagates through a complex microstructure may be achievable perhaps in model systems using FE crystal plasticity modelling, and this can be informative, but this is not practical from an engineering perspective. In reality, there is no ready replacement for the continuum mechanics approach and $K$ or $J$ is usually adopted but with a recognition that this is on a pragmatic, empirical, basis.

In that context, an expression for $K$ has been derived for the case of semicircular cracks by Newman [36] that can be applied to pits when the crack front is continuous and the crack depth exceeds the pit depth. However, for a crack smaller than the pit depth, there is no explicit $K$ solution and this needs resolution.

(c) Crack size and crack growth rates

Most of the effort in characterizing the growth of small cracks has been under cyclic loading conditions. A distinctive feature of the fatigue crack growth of small cracks is the characteristically oscillatory nature of the growth rate especially in surface measurement of crack length (figure 11a, where the crack depth, $a$, has been calculated assuming the crack is semicircular [37]), as observed in many other studies [38]. This oscillatory behaviour reflects the sensitivity of the crack growth rate to local variations in microstructure, with the crack alternately slowing down and speeding up. With DCPD (figure 11b), which responds to the change in area of the crack, the oscillations in growth rate are less marked (by comparison with the growth rate based on surface length measurement), because the crack front extends over a number of microstructural regions and local variations in growth rate are smoothed out to an extent. This smoothing is even more pronounced for a short crack (through-thickness crack in fracture mechanics specimens that is short in length), because the length scale for the crack-front is orders of magnitude greater than the microstructural dimensions.
Figure 11. Comparison of fatigue crack growth rates for small, short and long cracks in a 12Cr martensitic stainless steel (FV 566) tested at 90 °C in air with a loading frequency of 1 Hz and stress ratio of 0.05; (a) small crack depth determined using optical technique and (b) using DCPD. \( a_p \) and \( a_i \) represent the pit depth and final crack depth, respectively, and \( a_i \) is the initial crack depth for the short and long crack growth rate tests [37]. (Online version in colour.)

The Newman solution for \( K \) [36] was used for these small crack data assuming a continuous crack front at all crack lengths, so there may be uncertainty when the crack was small compared with the pit. Although the small crack growth data appear to indicate scatter, it is important to recognize that it is the average growth rate and the repeatability of the average growth rate that matters in terms of the spread of data. Assigning an upper bound to all the data points, as has been undertaken [38], would be inappropriate because that presupposes there is a probability that a crack growth rate close to the upper bound is sustainable. This is not the case as there is no crack path through the material that would allow this upper bound growth rate; there will always be obstacles to crack growth in the small crack regime that will cause transient crack growth retardation. Alternative treatments to that of Newman [36] exist that introduce a short crack ‘correction’ factor to the expression for \( K \) in an empirical fashion, most notably by El Haddad et al. [39], so that \( K \) is then a function of \( \sqrt{a + a_0} \), where \( a_0 \) is the crack depth correction factor. This short crack correction worked particularly well in describing the dependence of the fatigue limit on pit size for the FV 566 martensitic stainless steel [40]. The same value of the correction factor (82 µm) was applied to the small crack growth rate data of figure 11 and did show consistency with the
Figure 12. Comparison of fatigue crack growth rates for small, short and long cracks in a 12Cr martensitic stainless steel tested at 90°C in aerated 300 ppb Cl\(^-\) and 300 ppb SO\(_4\)^{2-}\) at 90°C. The rise time and fall time in all cases was 20 min, but, in some tests, a hold time of 100 min at maximum load was included but without any observable effect. The stress ratio was 0.05. Oscillatory crack growth was observed for the small crack tests at low ΔK and low growth rates; in this case, the associated symbol represents the average growth rate [36]. (Online version in colour.)

The measurements of figure 11 were all made in a relatively benign environment. It is well established [42,43] that a crack size sensitivity of growth rate can arise in aqueous environments owing to enhanced crack-tip electrochemical kinetics in a short crack compared with a long crack. However, there are few coherent studies comparing small, short and long crack growth rates in aqueous environments under the same controlled conditions. Nevertheless, the results of a recent corrosion fatigue study [37] highlight the distinct features of each, as summarized in figure 12. In this investigation, a 12Cr martensitic stainless steel was subjected to low-frequency fatigue with load rise and fall times each of 20 min in a solution of aerated 300 ppb Cl\(^-\) and 300 ppb SO\(_4\)^{2-}\) at 90°C, representing normal water chemistry in a steam turbine system under hot start-up conditions.

It is not readily possible at this loading frequency to follow the progressive development of the crack continuously because of the very slow time-based growth rate at the lowest ΔK. In long crack growth measurements, this is often overcome by step-increases in the load to achieve a higher ΔK with the crack extension then monitored for a period at each ΔK value. However, when the crack is small the applied stress is often close to the limit for macroscopic yielding, and there is little scope for increasing the stress. Accordingly, the most effective approach is to monitor the crack growth for a small amount of crack extension and then either initiate a new test with an increased initial pre-crack length or extend the crack length an increment by fatigue at a higher frequency before restoring normal loading conditions.
The short crack growth rate was determined by a conventional method of pre-cracking a single edge notched tensile specimen at low ΔK and machining off the stop surface to leave a specimen with a short fatigue pre-crack before then exposing to the environment and testing as normal. The enhanced crack growth rate for the short crack at ΔK ≤ 20 MPa m$^{1/2}$ (corresponding to a crack length of 271 µm) is remarkable, and distinct from any effect of reduced crack closure compared with the long crack. The relatively high crack growth rate can be rationalized readily based on the greater ease of crack-tip electrochemical polarization for a short crack, compared with a long crack, in low-conductivity solution. For a long crack, the more noble potential associated with the external surface exposed to aerated solution has no impact on the crack-tip potential as the large potential drop associated with a long crack in low-conductivity solution electrochemically decouples the crack tip from the external surface. The solution in the crack will be oxygen-free because of rapid consumption and poor replenishment (although the stress ratio is small, so that the crack is almost completely closed each cycle, the rate of crack opening is very slow and the kinetics of oxygen reduction very rapid). Hence, the crack-tip potential will be the low value associated with de-aerated solution and by implication the most tenable mechanism for crack advance is hydrogen-assisted fatigue. For a short crack, the crack solution will also tend to be de-aerated, but the potential drop will be much smaller in this case, enabling coupling to the external surface exposed to aerated solution resulting in a more noble crack-tip potential. Although the more noble potential might seem to imply a mechanism of cracking based on anodic dissolution, it is considered that the increased crack-tip acidification upon anodic polarization enhances electrochemical generation of hydrogen and absorbed hydrogen then facilitates the fatigue process [37].

At ΔK ≤ 10 MPa m$^{1/2}$, the small crack growth rate is low and similar to or just above that in air, though uncertainty in assigning K-values precludes too definitive a statement. There is clear indication of an apparent ‘threshold’ ΔK above which there is a rapid acceleration of growth rate to a value similar to that projected by extrapolation of long crack growth rate data but below that for short cracks, i.e. there is no electrochemical crack size effect for the small crack. The absence of such an effect implies a greater net anodic current associated with the combination of the small crack and the corrosion pit (albeit essentially passive) to the extent that the current exceeds the threshold value below which crack-tip polarization is achievable. Testing at a greater concentration of chloride should extend the electrochemical crack size effect to greater depths and enhanced crack growth for the small crack relative to the long crack would be anticipated. This prediction is borne out by results from parallel stress corrosion cracking tests [37] but confirmation for cyclic loading conditions would be merited.

(d) Near-surface properties to be considered

For the data presented in figures 11 and 12, the specimens were ground to a very fine finish and then stress relieved in vacuum. For more general applications, it is necessary to consider the additional impact on crack initiation and growth of gradients in near-surface microstructure, mechanical properties and residual stress induced by the machining and grinding processes. Machined and ground surfaces will often exhibit a near-surface microstructure (figure 13) that is characterized by a very small grain size on the scale of nanometres, perhaps 50–100 nm, with a depth that is dependent on surface preparation history [31,44]. Slip lines can also be observed to extend to depths of about 20 µm. Associated with this highly deformed and nano-crystalline microstructure will be significant changes in mechanical properties with strength levels much greater than the bulk owing to the small grain size and dislocation structure. In addition, in the absence of stress relief, there can be large near-surface residual stresses as exemplified in figure 14.

Although this is an area studied for some time by those seeking to optimize surface properties, for example to improve wear resistance [45], it is only comparatively recently that awareness of the impact of surface preparation on near-surface properties has spread to the corrosion and cracking community [46–49]. The complex nature of the changes at the surface makes it more difficult to predict the location of crack initiation at a corrosion pit and the extent to which local
conditions will control the propagation rate. While advanced testing to elucidate the effect of near-surface variables on crack growth is pertinent, complementary FE crystal plasticity modelling is important in providing a more fundamental understanding of the interaction between the crack and the microstructure.

4. Summary

Understanding the early stages of damage development in environment-assisted cracking and focusing on characterizing the crack propagation rate will provide a much more informed basis for design and lifetime prediction.

The advent of XCT and FIB-SEM combined with FE analysis has provided radical insights with respect to the pit-to-crack transition. A critical advance has been to recognize that a growing pit in a static stress field can generate dynamic plastic strain locally, a step-change in thinking in relation to initiation of stress corrosion cracks.

Figure 13. Transverse cross section of 316L stainless steel coarse ground to Ra 0.8 µm. EBSD grain reference orientation colour scale map superimposed on a grey-scale image quality map [29]. The misorientation colour scale (in degrees) is shown below the image. The arrows define the region with no indexable EBSD patterns. Step size is 0.1 µm.

Figure 14. Residual stress of 316L stainless steel as a function of depth longitudinal (L) and transverse (T) to the long axis of the specimen for two different surface finishes (fine, corresponding to Ra 0.2 µm, and coarse, 0.8 µm) using the incremental hole drilling technique [29]. The open symbols show the corresponding values obtained via X-ray diffraction. (Online version in colour.)
The location of crack initiation from a pit will depend critically on local conditions of stress, strain and material characteristics. The traditional idea that the cracks emanate from the pit base, while not excluded, has no intrinsic basis.

Measurement of growth rates of small cracks emerging from pits when the time-based growth rate is very low is a major challenge because of constraints in accelerated testing in aqueous solution and an inherently costly process. There is no ideal technique for measuring the crack size but the potential drop method in combination with optical observation (in the absence of obscuration by corrosion product) is perhaps the most viable technique.

There is evidence of accelerated growth rates for short cracks under fatigue loading that can be attributed to an electrochemical crack size effect that is quite distinct from issues of crack closure. For small cracks, a similar effect is projected and observed in stress corrosion cracking studies but not in testing in the very low-conductivity solution adopted for fatigue loading in simulated steam turbine condensate.

Further work is required to account for the effect of near-surface microstructure, hardness and residual stress on the location of crack initiation from corrosion pits and the subsequent rate of propagation.

FE crystal plasticity modelling combined with FIB-EBSD for three-dimensional characterization of grain structure would provide more fundamentally based insight with respect to small crack growth and its relation to the microstructure.

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