

CORROSION OF STRESSED COMPONENTS

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ABSTRACT

Many engineering components operate under the combined influence of service stresses and deleterious environment. For better life prediction and to prevent failures, it is necessary to understand the mechanical behaviour of materials under conjoint action of stress and environment. Depending upon the metal-stress-environment system, the operating mechanism that would affect the life of the component may differ. Some of these mechanisms are discussed in this paper. Typically, the life limiting factor of engineering materials in corrosive environments have been identified as stress corrosion cracking, damage in components due to the presence of hydrogen, corrosion fatigue and fretting corrosion. In this paper, each of these phenomena has been discussed with respect to their mechanisms, methods to quantify the damage and ways to prevent or control them. Developments in fracture mechanics have been used as an effective tool in assessing the material's resistance to fracture. Application of fracture mechanics techniques to predict the fracture behaviour of materials in aggressive environments has been discussed along with the conventional techniques.

INTRODUCTION

Engineering components are often required to perform in severe environmental conditions. The interaction of the stresses (service or residual) on the component with the chemical species of the aggressive environment is expected to adversely influence the mechanical properties of the material. Over time, these conditions can cause defects in the component parts that would eventually lead to failure. The aggressiveness of the corrosive environment to cause such failure varies with different materials, and, in general, with no visual indication of corrosion or impending failure. Nevertheless, intercrystalline or transcrystalline cracks can penetrate the component, leading to eventual break-up. Stress corrosion failures are thus particularly insidious form of failure, often occurring without visible sign of corrosive damage or mechanical strain at stresses considered to be *safe* when judged by performance in air.

Although degradation of material due to corrosion is a slow time-dependent phenomenon, incorporating its influence in design concepts for structural integrity assessments is a challenging task. If the corrosion attack proceeds fairly slowly and at a reproducible and predictable rate, a 'corrosion allowance' may be built into the design, so that a safe material thickness remains at all points after the anticipated lifetime of the structure. Typical phenomena that may be addressed in this way include dissolution of steel in acid media and elevated temperature oxidation. A limitation of this approach is the accuracy of the predictive tools or 'corrosion models' available. If the corrosion attack is

localised and propagate rapidly once initiated, e.g. pitting and crevice corrosion, it is normal to design so that attack can never initiate. This requires appropriate material selection. The simplest approach to materials selection is to rely on previous experience, although it is essential to understand the operating environment, so that changes between past and future service regimes can be accounted for. Where previous successful experience does not exist, materials testing may be required to demonstrate fitness for purpose. Laboratory testing, typically to recreate the principal components of the service environment, by increasing temperature, the concentration of certain environmental species or by forcing electrochemical changes, may not necessarily create the exact service conditions.

The results of stress corrosion related failures can be of minor importance, as in the failure of such articles as tea urns, or disastrous such as the explosion of boilers damaged by caustic embrittlement. The peculiar aspect is that there is no fixed recipe to solve the problem. Even though some guidelines or approaches can be suggested, the problem has to be treated case to case basis. In order to analyse and prevent such failures, it is important to understand the environment-material system and the micromechanisms involved. Some of such stress-corrosion related failure modes and their micromechanisms are discussed here.

STRESS CORROSION CRACKING

Stress-corrosion cracking (SCC) relates to the environmental degradation of the mechanical integrity of structural components. Stress-corrosion failures are well known in a variety of industries such as electrical power generation including nuclear, aircraft, petrochemical, and underground pipeline transmission systems. In order for a component to undergo SCC a combination of 3 factors must be in place, a susceptible material, a corrosive environment and an appropriate level of tensile stress. Figure 1 is a Venn diagram showing the intersection of these three factors and resultant SCC. Environments that cause SCC are usually aqueous and can be condensed layers of moisture. Also, an environment that causes SCC in one alloy system may not cause SCC in another alloy. Changing the temperature, the degree of aeration and/or concentration of ionic species may alter the *safe* environment into one that causes SCC failure. Even an alloy that is immune in one heat treatment may be susceptible to SCC in another. Due to these factors SCC is very complex and alloy-environment specific. A partial list of alloy-environment combinations that are commonly observed to trigger SCC is given in Table 1.^[1]

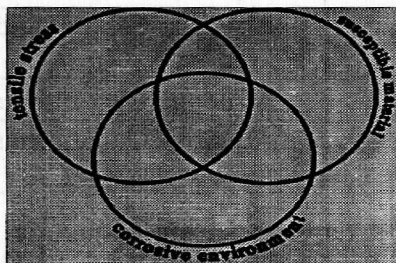


Fig. 1: Venn diagram illustrating the factors that control the onset of stress corrosion cracking.

In general, SCC is observed in alloy-environment combinations that result in the formation of a film on the metal surface. These films may be passivating layers, tarnish films or dealloyed layers. In many cases, these films reduce the uniform corrosion rate. As a result, SCC is of greater concern in corrosion resistant alloys exposed to aggressive aqueous environments.

Stress Corrosion Cracking Mechanisms-an Overview

Many different mechanisms have been proposed to explain the synergistic corrosion – stress interaction that causes failure, and there may be more than one process that would cause SCC. However, the SCC mechanisms can be categorized into two main variants. They are (i) *active path dissolution* and (ii) *hydrogen embrittlement (HE)*. This is schematically represented in Fig. 2. In active path dissolution (otherwise called anodic mechanism), crack advance occurs by a localized corrosion process during which metal is actually dissolved (corroded) locally from the tip of an advancing crack. In the second mechanism, hydrogen gas, made available by an electrochemical process, actually absorbs into the metal and reduces the cohesive energy of the solid. Hydrogen embrittlement is differentiated from the *first* in that there is no requirement of metal dissolution for crack advance to occur. Each of these crack advance mechanisms can result in two different metallurgical classifications of cracking, intergranular SCC and transgranular SCC. A typical intergranular and transgranular stress corrosion cracks are shown in Fig. 3. However, a specific mechanism must attempt to explain the crack propagation, fractographic evidences and the mechanism of formation of cracks.

Table 1 : Alloy – Environment systems that are prone to SCC

<i>Alloy</i>	<i>Environment</i>
Carbon steel	Hot nitrate, hydroxide, and carbonate/ bicarbonate solutions
High strength steels	Aqueous electrolytes, particularly when containing H ₂ S
Austenitic stainless steels	Hot, concentrated chloride solutions; chloride containing steam
High Ni alloys	High purity steam
Aluminium alloys	Aqueous Cl ₂ , Br ⁻ and I ⁻ solutions
Titanium alloys	Aqueous Cl ₂ , Br ⁻ and I ⁻ solutions; organic liquids; N ₂ O ₄
Magnesium alloys	Aqueous Cl ⁻ solutions
Zirconium alloys	Aqueous Cl ⁻ solutions; organic liquids, I ₂ at 350°C

The mechanisms of SCC require certain sequential events for sustained crack propagation leading to failure. That is a sequence of chemical reactions and process is required, and the rate limiting step of these events will determine the rate of crack growth. Some of the potential rate determining steps is

- Transport of chemical species to the crack tip
- Reactions in the solution near the crack
- Surface adsorption of species at/near crack tip
- Surface diffusion
- Surface reaction
- Absorption into the bulk of the material
- Bulk diffusion of species into the plastic zone of advancing crack
- Chemical reactions in the bulk metal
- Rate of interatomic bond rupture

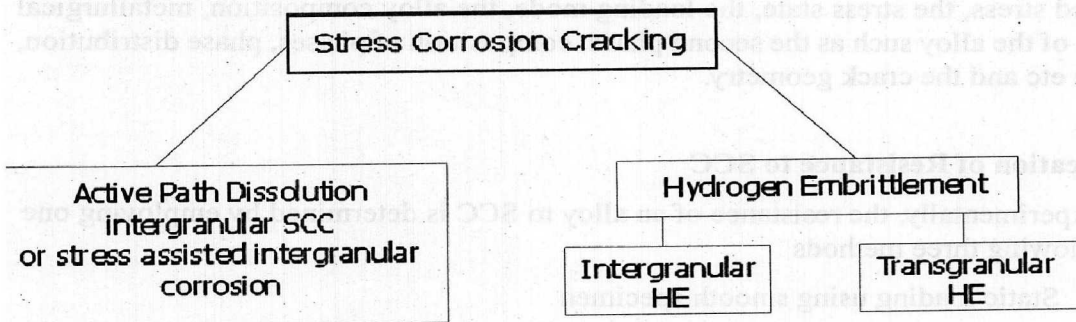


Fig. 2 : Variants of stress corrosion cracking mechanisms

Any change in the environment that modifies the above rate determining steps will have a dramatic influence on crack propagation. In aqueous solutions, the rate of adsorption and surface reactions is usually very fast compared with the rate of mass transport. As a result bulk transport into this region or reactions in this region is believed to be the rate limiting steps. In gaseous environments, surface reactions, surface diffusion, and adsorption may be rate limiting as well as the rate of bulk transport to the crack tip.^[2-3]

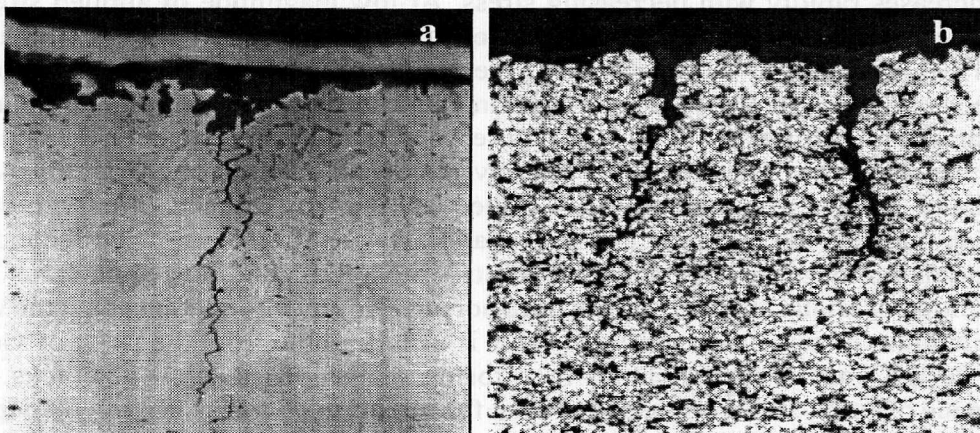


Fig. 3: Typical (a) intergranular and (b) transgranular stress corrosion cracking

Several different environmental parameters are known to influence the crack growth rate in aqueous environments. These parameters include, temperature, pressure, solute species, solute concentration, pH of solution, electrochemical potential, solution viscosity and stirring or mixing of solution. Altering any of these parameters may alter the rate of the rate controlling steps. Generally, the environment at the occluded sites, such as crack tip will be significantly different from the bulk solution. If the alteration to the bulk environment allows formation of SCC favorable environment at the crack tip, then crack propagation will be promoted. If the changes in the bulk environment cannot maintain this local crack tip environment then the crack propagation will stop. In addition to environmental parameters stated above, stress corrosion crack propagation rates are influenced by the magnitude of the applied stress, the stress state, the loading mode, the alloy composition, metallurgical condition of the alloy such as the second phase, composition of phases, phase distribution, grain size etc and the crack geometry.

Quantification of Resistance to SCC

Experimentally, the resistance of an alloy to SCC is determined by employing one of the following three methods

- Static loading using smooth specimen
- Static loading using precracked specimen
- Slow strain rate testing

Using statically loaded smooth specimens

In this method, various predetermined static stress (or load) levels are applied on a smooth specimen in the environment and the time to failure is measured. A plot of applied stress versus the time to failure will be as shown in Fig. 4. It may be noted that the time to failure increases rapidly with decreasing stress. At low magnitude of applied stresses, a threshold value (σ_{th}) can be determined where the time to failure approaches infinity. Alternatively, the time to failure for any given magnitude of applied stress can also be determined as shown in Fig. 4. These experiments can be used to determine the maximum stress that can be applied to avoid SCC failure, to determine an inspection schedule or to evaluate the influence of metallurgical and environmental changes on SCC. However, this conventional smooth specimen testing is inadequate in many respects. Firstly, it does not distinguish between the initiation and propagation stages of crack growth. Secondly, this approach inherently recognizes only two points – the initial condition of no crack and the final condition of totally cracked body. It does not provide any information about the velocity and acceleration of crack as it grows.^[4] This is unacceptable from the point of view of a modern design code which includes monitoring of the progression of cracks for the maintenance of safety. Finally, the actual time for initiation of cracks is strongly dependent on a number of parameters. If a crack like flaw or a crevice is present in the material, then the time to initiate a crack may be reduced dramatically.

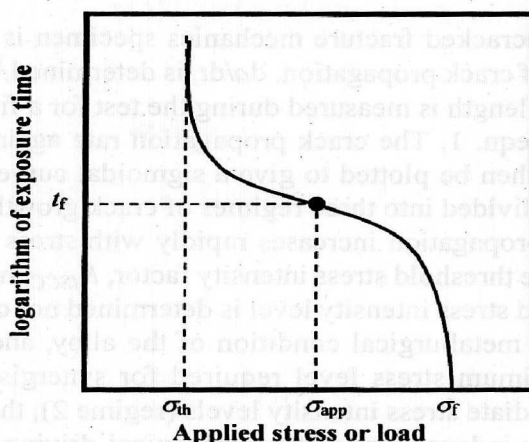


Fig. 4: Schematic of typical time to failure as a function of applied stress during SCC

Using precracked specimen

This method uses fracture mechanics based principles to predict the fracture resistance of an alloy under stress corrosion cracking conditions. In the presence of a pre-existing defect, the stress distribution ahead of the crack will be different from that of the bulk material and the stresses near the crack tip may exceed 30% of the material. Irwin^[5] showed that the crack tip stresses can be described by a single crack tip characterising parameter known as the stress intensity factor (SIF) K . The SIF is related to the service stresses and the component geometry as in eqn 1.

$$K = \sigma \sqrt{\pi a Y} \quad \dots(1)$$

where σ is the service stress, a is the crack length in the component and Y is the geometry function. The variation of σ ahead of a crack tip is given in Fig. 5. It can be appreciated that K characterizes the stress field. K is the crack driving parameter, and when the value of K approaches a critical value, crack extension will take place. This method will thus provide a critical value of this crack driving force, denoted as K_{ISCC} , a measure of resistance of the material to SCC. The subscript I denote the applied load being in tension, in the crack opening mode.

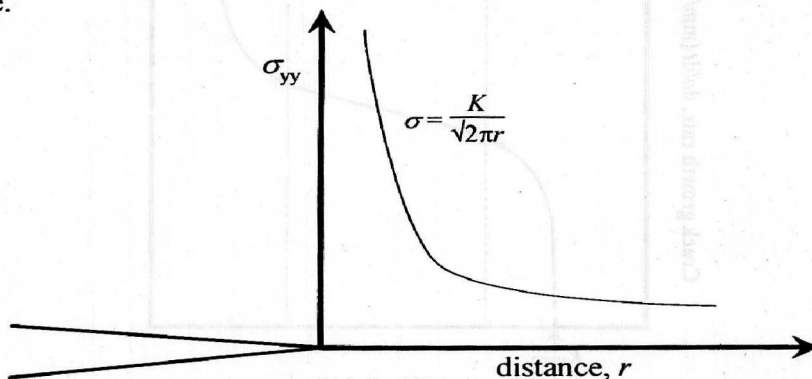


Fig. 5 : Variation of SIF, K , with distance ahead of crack tip

In this test method a precracked fracture mechanics specimen is subjected to a constant load and the actual rate of crack propagation, da/dt , is determined.^[6] If the load conditions are known and the crack length is measured during the test for a fixed sample geometry, K can be calculated using eqn. 1. The crack propagation rate against K data for the entire duration of the test can then be plotted to give a sigmoidal curve as illustrated in Fig. 6. Such a plot may be sub-divided into three regimes of crack growth as shown in the figure. In regime 1, the crack propagation increases rapidly with stress intensity factor. At low levels of SIF, below some threshold stress intensity factor, K_{ISCC} , no crack propagation will take place. This threshold stress intensity level is determined not only by the alloy but also by the environment and metallurgical condition of the alloy, and presumably, this level corresponds to the minimum stress level required for synergistic interaction with the environment. At intermediate stress intensity levels (regime 2), the crack propagation rate is steady and is virtually independent of the mechanical driving force. This steady state region is characteristic of the alloy-environment combination and is representative of rate limiting environmental processes such as mass transport of environmental species to the crack tip. In regime 3, the crack propagation again increases rapidly and approaches the fracture toughness of the material K_{IC} ^[7]. Here the high stress levels (contributing to the high level of K) is primarily responsible for driving the failure in comparison to the contribution of the environment.

The applied stress during the K_{ISCC} experiments can be varied in a number of fashion. In the test method described above, the K value will increase progressively as the crack growth takes place. Alternatively, the load can be made to decrease with a predetermined constant crack opening. Sometimes, a special tapered specimen is used such that the load is approximately constant with the crack growth. Each of these methods has its advantages and disadvantages. Commonly, most of the SCC failures occur under constant load conditions such that the K increases as the crack propagates. As a result the method described above is found to be in common use.

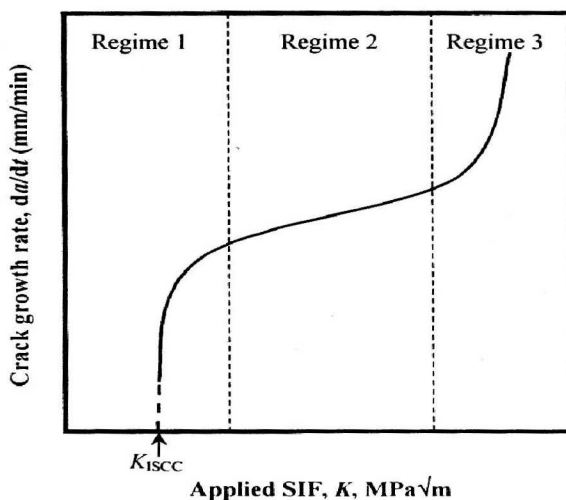


Fig. 6 : Typical crack propagation rate as a function of K during SCC

Slow strain rate testing

SCC tests are sometimes performed by slowly increasing the load or strain on either a smooth or a precracked cylindrical specimens exposed to a corrosive environment.^[8] The low strain rate enables the environment to initiate SCC damage. The decrease in mechanical properties between exposed and unexposed samples at the same strain rate is again a measure of the SCC susceptibility. These tests are preferred if a relative assessment of the susceptibility of alloys to SCC is required or to study the influence of metallurgical variables on susceptibility of an alloy to SCC. However, the application of data obtained from these tests to the actual in-service crack propagation rate predictions is unreliable.

Prediction, Diagnosis and Control of SCC

As SCC is strongly influenced by the mechanical, metallurgical and environmental factors, the predictive/diagnostic methodology should contain the required information. Prior knowledge of stress distribution in the component, chemical species of the operating environment and the metallurgical condition of the material are the pre-requisites for the prediction and control of SCC. A generalized methodology to control the SCC is given in Fig. 7.

Mechanical approaches to control SCC

In most of cases, SCC results from the presence of residual stresses in components. In such cases, thermal stress relief, especially with the welded fabrication is beneficial. Limitations related to the availability of large furnaces to accommodate the component, however, restrict the application of stress relieving treatment. In some cases, components distort at relatively at high temperatures (about 650°C for mild steels and 800°C for austenitic stainless steels). A partial stress relief at lower temperature than that required for full stress relief can be adequate in these cases where the residual and operating stresses can be reduced below the threshold stress. A locally applied heating on large structures can also be beneficial. The following example in Table 2 ^[9] illustrates the beneficial effect of stress relieving for 1hr on mild steel into boiling nitrate solution.

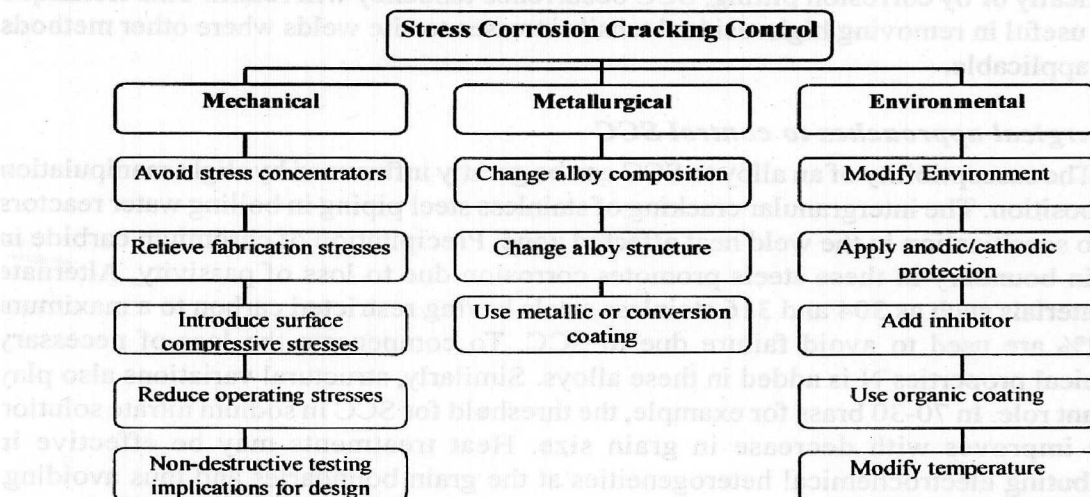


Fig. 7 : Methodology to control SCC

Table 2 : Effect of low temperature annealing on SCC of mild steel in boiling nitrate solution

Stress relieving temperature (°C)	Time for appearance of first crack (h)	No. of cracks after 500h	% stress relief
As welded	5	12	0
250	15	7	15
300	60	5	27
350	200	1	40
400	-	0 (1600h)	47
600	-	0 (1600h)	95

Another way to control SCC through mechanical route is to provide surface compressive stress. In this method, shot peening and grit blasting are frequently employed to reduce the onset of environmental assisted cracking. Following example in Table 3 [10] illustrates the beneficial effect of peening of mild steel exposed in boiling nitrate solution.

Table 3 : Effect of shot peening and grit blasting of surface on SCC

Type of plate	No. of cracks	Time tested (h)	Min. time for cracking (h)
Butt welded (as weld)	7	210	48
Butt welded (shot peened)	210	840	-
Patch welded (shot peened)	48	1320	-

It must be noted here that the compressive stresses introduced by such mechanical means will penetrate to the depth of about 0.1mm. If this surface layer is removed either mechanically or by corrosion pitting, SCC occurrence tendency will return. This technique is quite useful in removing high residual tensile stresses to site welds where other methods are not applicable.

Metallurgical approaches to control SCC

The susceptibility of an alloy to SCC can be greatly influenced by slight manipulation of composition. The intergranular cracking of stainless steel piping in boiling water reactors is due to sensitization in the weld heat affected zone. Precipitation of chromium carbide in the grain boundary in these steels promotes corrosion due to loss of passivity. Alternate pipe materials such as 304 and 316 stainless steels having restricted carbon to a maximum of 0.02% are used to avoid failure due to SCC. To compensate the loss of necessary mechanical properties N is added in these alloys. Similarly, structural variations also play important role. In 70-30 brass for example, the threshold for SCC in sodium nitrate solution greatly improves with decrease in grain size. Heat treatments may be effective in redistributing electrochemical heterogeneities at the grain boundaries and thus avoiding/minimizing the intergranular SCC. Thus solution treatment of stainless steels to redissolve the carbides and eliminate chromium depletion at previously sensitized grain boundaries is

reported to provide beneficial effect in boiling water reactor environment. Redistribution of grain boundary segregates on precipitates is one of the main reasons for the superior resistance of 18Ni maraging steel to SCC in chloride environments.

Environmental control of SCC

It is well established that the SCC will take place within a range of potential in an alloy-environment system. These sensitive ranges are schematically shown in Fig. 8 by shaded area. These potential ranges, if avoided by director potential/current to the system or by the use of suitable inhibitors, may alleviate SCC tendencies to a considerable extent. If SCC is associated with the ingress of hydrogen into the metal, attempts should be made to avoid the occurrence of potential below which hydrogen evolution reaction takes place. The cases frequently observed with the cracking of high pressure gas/oil transmission lines, are excellent examples of occurrence of SCC due to poor control of cathodic protection system applied from outside.^[10] A proper care should be taken to maintain the required potential to avoid SCC. Inhibitors added to the environment also play a beneficial role in controlling SCC. However, the types of chemical species involved in promotion of SCC and the crack potential range must be considered in selecting the right choice of the inhibitor.

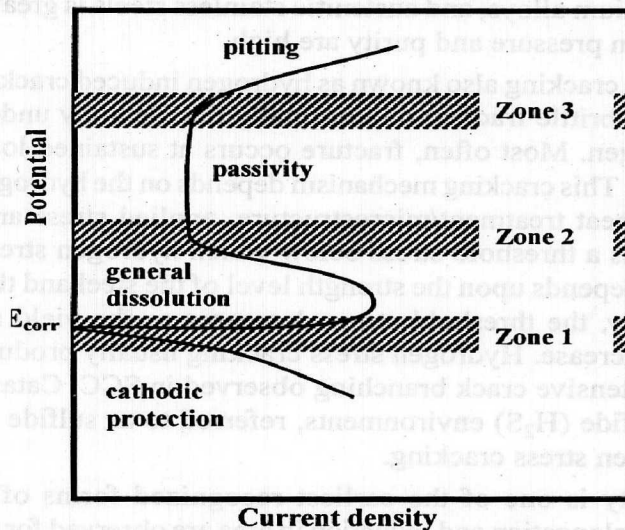


Fig. 8 : Schematic illustrating positions of sensitive zones for SCC

HYDROGEN DAMAGE

Hydrogen damage is a form of environmentally assisted failure that results most often from the combined action of hydrogen and the residual or applied tensile stress. Even though this is a sub-set of the SCC, due its various forms and frequent occurrence in industry it deserves a separate discussion. Hydrogen damage specific to alloys manifests itself in many ways, such as cracking, blistering, hydride formation and loss of tensile ductility.^[11] For many years, all these failures are improperly termed as 'hydrogen embrittlement'. The term *improper* is used here as hydrogen embrittlement demonstrates certain classical failure

features which may not be exhibited in various other forms of hydrogen related damages. Depending upon the susceptibility of the alloy system, source of hydrogen, conditions of failure and the mechanisms involved, various forms of hydrogen damage are possible. They are

- hydrogen embrittlement
- hydrogen attack
- microperforation
- hydrogen stress cracking
- blistering
- degradation in flow properties
- loss in ductility
- shatter cracks, flakes, fish eyes
- hydride formation

In the above classification the first three classes on the left hand side are grouped together and commonly called as hydrogen embrittlement since the failure mode in all these three cases exemplify the typical hydrogen embrittlement.

Hydrogen embrittlement normally occurs during plastic deformation of alloys in contact with hydrogen containing gases or hydrogen evolving corrosion reactions and is therefore strain rate dependent. Degradation of mechanical properties of ferritic steels, nickel base alloys, titanium alloys, and austenitic stainless steels is greatest when strain rate is low and the hydrogen pressure and purity are high.

Hydrogen stress cracking also known as hydrogen induced cracking or static fatigue, is characterized by the brittle fracture of a normally ductile alloy under sustained load in the presence of hydrogen. Most often, fracture occurs at sustained loads below the yield strength of the material. This cracking mechanism depends on the hydrogen fugacity, strength level of the material, heat treatment/microstructure, applied stress and temperature. For many steels there exists a threshold stress below which hydrogen stress cracking will not occur. This threshold depends upon the strength level of the steel and the hydrogen bearing environment. Generally, the threshold stress decreases as the yield strength and tensile strength of the alloy increase. Hydrogen stress cracking usually produces a sharp singular crack in contrast to extensive crack branching observed in SCC. Catastrophic cracking of steels in hydrogen sulfide (H_2S) environments, referred to as sulfide stress cracking, is a special case of hydrogen stress cracking.

Loss in ductility is one of the earliest recognized forms of hydrogen damage. Significant decrease in elongation and reduction in area are observed for many alloys exposed to hydrogen. This mode of failure is often observed in low strength alloys and the extent of loss of ductility depends upon the hydrogen content of the material.

Hydrogen attack is a high temperature form of hydrogen damage that normally occurs in carbon and low alloy steels exposed to high pressure hydrogen at high temperatures for a prolonged exposure. Hydrogen enters into the steel and reacts with carbon either in solution or as carbides to form methane gas; this may result in the formation of cracks and fissures or may simply decarburize the steel resulting in a loss of strength. However, this form of damage is temperature dependent, with the threshold temperature of approximately 200°C. Blistering occurs predominantly in low strength alloys when atomic hydrogen diffuses to internal defects, such as non-metallic inclusions and precipitates as molecular hydrogen.

Presence of a molecular hydrogen can attain such a high values that localized plastic deformation of the alloy occurs, forming a blister that often ruptures.

Shatter cracks, flakes and fisheyes are features common to hydrogen damage in forgings, weldments and castings. They are attributed to hydrogen pick up during melting operations when melt has high solubility for hydrogen than the solid alloy. During cooling from the melt, hydrogen diffuses to and precipitates in voids and discontinuities, producing features that result from decreased solubility of hydrogen in the solid metal. In many aspects, these features are comparable to blistering and can be considered as a special case of that class.

Microperforation by high pressure hydrogen occurs at extremely high pressures of hydrogen near room temperature. Microperforation occurs predominately in steels. This form of hydrogen damage manifests itself as a network of small fissures that allows permeation of gases and liquids.

Degradation in flow properties in hydrogen environments has been found at ambient temperatures for iron and steel, and at elevated temperature for several alloy systems. The steady state creep rate under constant load has been observed to increase in the presence of hydrogen in some nickel base alloys.

Hydride formation produces embrittlement in magnesium, tantalum, niobium, zirconium etc and in other less common metals and alloys. Degradation of mechanical properties and cracking of these metals are due to the precipitation of metal hydride phases. Hydrogen pickup often results from welding, heat treating, charging from corrosion processes, or during melting of alloy.

Determination of Resistance to Hydrogen Embrittlement

The only ASTM standards for hydrogen embrittlement testing are F 519^[12] and F326.^[13] These standards are based on (i) not putting hydrogen into the steel by keeping the hydrogen in the plating bath at acceptably low levels and (b) using mechanical tests to ensure that the amount of residual hydrogen after baking is below the acceptable levels.

The standard F 326 covers an electronic hydrogen detection instrument procedure for the measurement of plating permeability to hydrogen, a variable that is related to the hydrogen absorbed by the steel during plating and to the hydrogen permeability of the plate during post plate baking. A specific application of this method involves controlling cadmium plating processes in which the plate porosity relative to hydrogen is critical, such as for high strength steels.

The standard F 519 is employed to evaluate the hydrogen generating potential of fluid (specifically aircraft maintenance chemicals) and the hydrogen embrittlement control during electroplating processes. Various specimen types as in SCC are recommended and the acceptable level of hydrogen is determined by a go/no-go situation established by the failure of a sustained loaded, stressed specimen baked at a particular temperature and time,.

Other than the above specified standard procedures, following tests are commonly used in laboratory to investigate the susceptibility of the material to hydrogen embrittlement.

Cantilever beam test

A constant load is applied to the precracked V-notched specimen subjected to a bending load via a moment arm. The notch area of the specimen is enclosed by a chamber containing the environment. Specimen is subjected to a constant load for a predetermined duration. SIF (K) for the test geometry is calculated and the time to failure is noted. Time to failure is plotted against the K , and the lower limit of resultant curve is the threshold stress intensity for hydrogen embrittlement, K_{IHE} . Other methods of loading or use of non-rectangular specimen geometries are also in practice following the ASTM standard E 399. [14]

Wedge opening load test

This method employs the application of constant wedge or crack opening displacement. The actual stress intensity as a function of crack length, load and specimen geometry is calculated. As the crack extends, the stress intensity decreases due to relaxation of the load until crack arrest occurs. Crack growth is monitored using strain gauges or by optical methods. The specimen is maintained under these conditions for about 5000h to establish the threshold value, K_{IHE} .

Contoured double cantilever beam test

This method is used to measure the crack growth rate at a constant SIF. The specimen geometry (contoured double cantilever) simplifies the SIF calculation such that SIF is proportional to the applied load and independent of the crack length. This method is also used to study the stress history effect of that produces an incubation time before hydrogen stress cracking.

Other test methods such as rising step load test, [15-16] disk pressure method and slow strain rate tensile test [17] are also sometimes used. Readers are directed to refer the respective references for more details.

Prevention and Control of Hydrogen Embrittlement

The potential for hydrogen embrittlement must be evaluated before any prevention and control process are implemented. The sources of hydrogen must be examined with regards to three possibilities: the manufacture of the alloy, the manufacture and processing of the part and the environmental service condition. A source of condition and sufficient stress must exist for hydrogen embrittlement to occur. If either of condition is eliminated, hydrogen embrittlement will not occur.

From the control viewpoint, attempt must first be made to eliminate the hydrogen and to ensure that no hydrogen is introduced during manufacture and processing part. It can then be anticipated that no problem will exist in service. Attention must be given to potential hydrogen embrittlement failures due to the presence of residual stresses. Source of residual stress must be identified or an assumption of a high residual stress must be considered during design. This must be ensured especially for welded structures.

CORROSION FATIGUE

A component has said to have failed by fatigue when it disintegrates or collapses after having been subjected to a number of cycles of alternating stress. Usually no obvious damage or deterioration of its service capability can be observed throughout the majority of the loading cycles. In corrosive environments, susceptible materials can fail even more quickly due to corrosion fatigue. Corrosion fatigue cracking is not limited to certain metallurgical conditions of the metal or to critical environmental species, as are other forms of environmentally assisted cracking. Classical corrosion fatigue, stress corrosion cracking and hydrogen embrittlement failures are separated by a spectrum of behaviours separated by a large number of factors such as metallurgical condition of the material, method and magnitude of stress, and the electrochemistry of the metal-environment system. Figure 9 shows a conceptual interrelationship of corrosion fatigue, stress corrosion and hydrogen

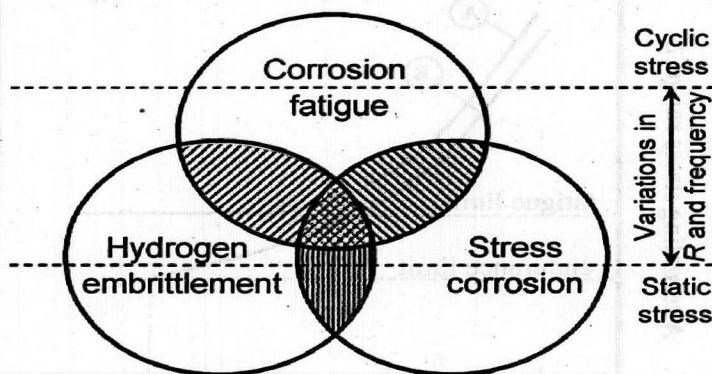


Fig. 9 : Venn diagram illustrating interrelationship among corrosion fatigue, HE and stress corrosion

embrittlement.^[18] The most serious practical situations involving ductile alloy/environment systems are in the crosshatched regions. These regions indicate the combination of any two failure mechanisms. In the centre, all three phenomena interact, which is the representative of many practical situations. For example, in corrosion fatigue and SCC, a surface pit can act as a stress raiser and will start the crack initiation process. Electrode potential and pH at the crack tip will be significantly different from those on other exposed surfaces. High pH conditions at the crack tip can lead to metal dissolution and crack tip blunting which will eventually reduce the stress concentration. In contrast, low pH conditions favour hydrogen generation and, consequently increase the risk of HE. Reduction in local ductility associated with HE will sharpen the crack tip, thereby increasing the stress concentration effect. This will trigger synergistic SCC and/or corrosion fatigue. For materials that exhibit classical active-passive behaviour, passivation is more conducive under static rather than dynamic conditions. For the latter, frequency of cyclic loading is often one of the critical factors that influences the corrosion fatigue. Conversely, for corrosion control, cathodic protection generally mitigates corrosion fatigue and SCC but increases the probability of HE if the material-environment combination is favourable. Thus it is apparent that a complex relation exists between corrosion fatigue, SCC and HEC.^[19-21]

Quantification of Corrosion Fatigue Resistance

The conventional approach to corrosion fatigue acknowledges the applied stress amplitude, $\Delta\sigma$, as the crack driving force, while the time dependence of fatigue is characterized by the time or number of cycles to failure. The concept of the S-N curve and the Coffin – Manson relationship are examples of this category.

The S - N Curve Approach

The first systematic research on fatigue was carried out by Wöhler ^[22] between the years 1852-1871. He showed that the fatigue life, i.e. number of cycles to failure N or N_f was primarily dependent on the applied stress range, S . Fatigue life was seen to increase with decrease in the applied stress range, resulting in the typical S-N curve as shown in Fig. 10.

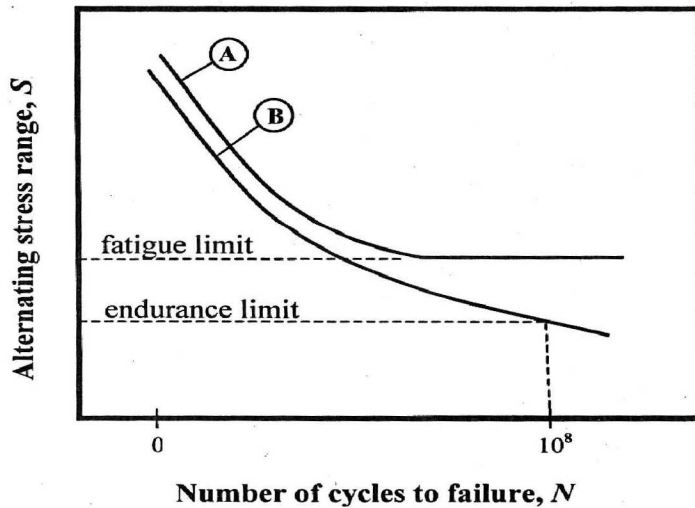


Fig. 10 : Typical S-N curves for (A) strain ageing materials, and (B) non-strain ageing materials

As shown in Fig. 10, there are two types of S-N curves. In one case (curve A), usually derived for strain ageing materials such as steels, a sharp *knee* is demonstrated at a particular value of stress range known as fatigue limit. The fatigue life is effectively infinite below this fatigue limit stress range. In another case (curve B), produced by non strain ageing materials, no such sharp fatigue limit is apparent. However, for design purposes, an endurance limit is defined for such materials as the value of stress range at which the fatigue life is 10^8 cycles. A general definition of the fatigue limit is that it represents the highest stress level at which the competitive processes of dislocation multiplication, cyclic hardening and strain ageing are at equilibrium.^[23] If S-N type data from the above fatigue limit is plotted using logarithmic axes, then is seen that they fall on a straight line which could be represented by the equation

$$\log \Delta\sigma = -\alpha_1 \log N_f + \log C_1$$

$$N_f^{\alpha_1} \Delta\sigma = C_1 \quad \dots(2)$$

where α_1 and C_1 are constants. Such a equation can then be used to predict the failure of

components in an environment under a specified stress amplitude, provided the specimens used to generate the S-N curve are exact replicas of the component and experience conditions comparable to them.

Mean stress can represent an important test variable in the evaluation of material's fatigue response. Hence various empirical relations have been developed to calculate the equivalent stress range at a non-zero mean stress from that at a zero mean stress, for a given fatigue life. The Goodman, Gerber and Soderberg relations^[24] are examples of such empirical equations.

The Coffin-Manson Relationship

Failure of a component, as characterized by the S-N curve, is essentially under load controlled cycling. However, in practical situations, a structure may be subjected to strain or position controlled cycling, for example due to temperature fluctuations, and undergoes failure under such circumstances. Coffin^[25] and Manson^[26] were pioneers in presenting experimental data from constant plastic strain range ($\Delta\epsilon_p$) tests. They proposed what is known as the Coffin-Manson relationship to deal with such strain controlled situations which can be written as

$$N_f^{\alpha_2} \Delta\epsilon_p = C_2 \quad \dots(3)$$

in similarity to eq. 2, where α_2 and C_2 are constants.

In fact, it is believed that it is the plastic strain existing locally in a specimen which determines its fatigue behaviour. When testing under stress controlled cycling, the applied strain range decreases or increases (depending upon whether the material cyclically hardens or softens) and hence it can be argued that data from strain controlled tests are more suitable for correlating fatigue behaviour and fatigue properties.

Equation 3 has been found to provide a good fit for data from a wide range of alloys.^[27] A value of $\alpha_2 \approx 0.5$ has been proposed to be valid for many materials, while C_2 , termed as the fatigue ductility coefficient has been often to be of the same order as the true fracture strain ϵ_f obtained from tensile tests.^[28]

Specific effects of corrosive media on S-N curve behaviour / low cycle behaviour are discussed later.

Inadequacies of the Conventional Approach

Engineering design is still largely based on failure data produced by the conventional approach. Conventional smooth specimen testing still provides important informations on crack initiation and the initial stage of propagation. However, in spite of its usefulness, the conventional approach is inadequate in many respects as stated previously. It does not provide any link between the micromechanisms of crack propagation that have been advanced and the fatigue of materials. Hence the basic aspiration of explaining fatigue from fundamental considerations is not fulfilled.

Differential Approach to Quantification of Fatigue Resistance

In the differential approach to quantification, the rate of the fatigue crack growth, da/dN (N = no. cycles), is expressed as a function of the SIF range, ΔK , (ΔK = difference of

maximum and minimum value of K). In an inert or benign environment, if the rate of fatigue crack growth per cycle, da/dN , is plotted in logarithmic scales against the stress intensity factor (SIF) range, ΔK , attending the fatigue loading cycle, then for the entire range of fatigue crack growth rates, from 10^{-8} to 10^{-3} mm/cycle in a typical instance, a sigmoidal curve, shown schematically in Fig. 11, is obtained. Such a plot may be sub-divided into three regimes of crack growth as shown in the figure. In regime A, a non-linearity is observed as the ΔK approaches a minimum value. This minimum value is called the threshold ΔK , designated ΔK_{th} , and represents the crack driving force below which crack growth is virtually undetectable. Regime A is therefore known as the threshold regime. In regime B, also called the Paris regime (after the proponent of the equation below) the crack growth follows a power law relationship [29]

$$\frac{da}{dN} = C \Delta K^m \quad \dots(4)$$

where m varies with the situation. In the above equation, ΔK for any component can be related to $\Delta \sigma$ through a relation of the form

$$\Delta K = \Delta \sigma \sqrt{\pi a Y} \quad \dots(5)$$

In regime C, the linearity of the curve breaks down as the maximum load in the fatigue cycle approaches the load sustainable for a given fracture toughness of the material for the instantaneous crack length.

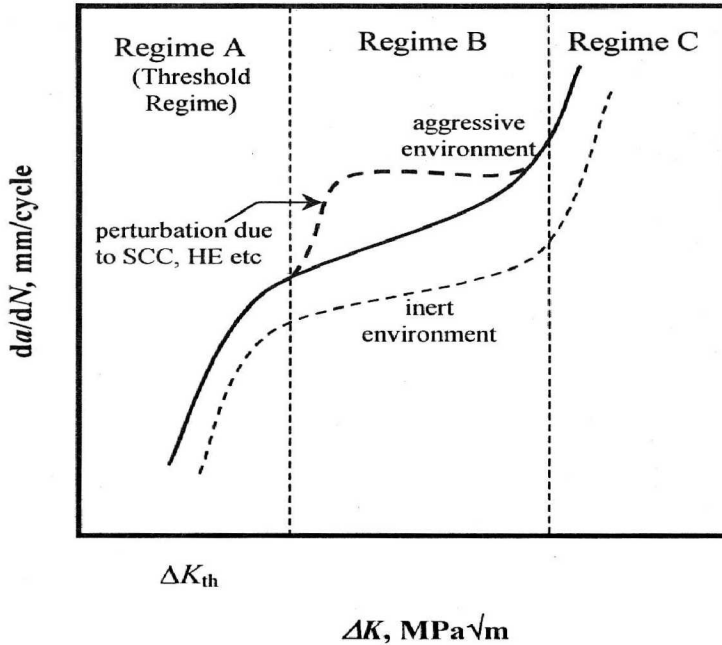


Fig. 11: Typical corrosion fatigue crack growth rate curve showing three regimes. Note the change in behaviour from inert environment

In an aggressive environment, crack growth may be quite different from the pure fatigue behaviour depending upon the sensitivity of material to the environment and the occurrence of various static stress fracture mechanisms as shown in Fig. 11. The environmental effects are quite strong above some threshold for SCC and may be negligible below this level. In addition, factors such as frequency, stress ratio and waveform can influence the crack growth behaviour in aggressive environment very strongly. Detailed influence of these factors on the corrosion fatigue behaviour is discussed subsequently.

Factors influencing Corrosion Fatigue Behaviour

The corrosion fatigue behaviour of a material is strongly influenced by the environmental composition, load frequency, stress intensity range, stress ratio and electrode potential in aqueous environment.

For any given material, the fatigue strength (or life) at a given value of applied stress generally decreases in the presence of an aggressive environment.^[30, 31] This effect will, however, vary with different material-environmental combination. A corrosive environment, in general, will reduce the crack initiation time by localized attack, thereby forming a stress concentrator. The environment also affects the probability of fatigue crack initiation, crack growth rate or both.

A low amplitude of cyclic stress favours relatively long fatigue life, permitting greater opportunity for the environment to get involved in the fatigue process. However, environmental interaction in certain alloy-environmental systems will be insignificant unless the strain rate is in the critical range for SCC. Stress amplitude must be considered along with mean stress and frequency. Low stress levels may allow more time for environmental interaction, but if the frequency is high, the crack tip may not be exposed to the environment for a sufficient time to cause significant damage. In case of differential growth rate behaviour, it is incorrect to assume that the three regimes for benign environment in Fig. 11 simply shift to higher crack growth rates at all ΔK levels. Although such a behaviour may actually occur as shown in Fig. 11, for absence of environment or inert environment for certain alloy-environment system for example, aluminium/dry air, the crack growth behaviour will be complex.

The frequency of cyclic loading is the most important variable that influences the corrosion fatigue behaviour of most materials. Generally, corrosion-fatigue strength will decrease as the cycle frequency is decreased. The effect is most prevalent at frequencies less than 10Hz.

However, it is difficult to predict the frequency range at which the corrosion fatigue will be severe due to numerous chemical reactions involved. It is also improper to extrapolate short term (high frequency) crack growth data to predict the long-term component performance.

Literature provides some qualitative guidelines on the effect of frequency on corrosion fatigue. Crack growth in environmentally sensitive materials stressed above K_{ISCC} , proceeds at rapidly increasing rate with decreasing frequency. Frequency effect should be predicted through the interaction of static load data throughout each cycle ^[32]. Stress ratio (K_{min}/K_{max}) also affects the corrosion fatigue crack growth behaviour. The growth rates will generally increase with increasing stress ratio. Increased stress ratio at constant ΔK , results

in increased crack tip opening crack tip strain and strain rate, enhanced film rupture, and therefore increased corrosion-fatigue crack propagation.^[33]

Similar to the effect of loading frequency, electrode potential also strongly influences the corrosion fatigue crack growth rates. Controlled changes in the potential can result in complete elimination or dramatic increase of fatigue cracking. The precise influence depends on the mechanism of the environmental effect and the anodic or cathodic magnitude of the applied potential. For ferrous alloys that crack by hydrogen embrittlement, corrosion fatigue crack growth is increased by high cathodic polarization from free corrosion potential.^[34-35] Electrode potential control can suppress the corrosion fatigue for alloys that crack through anodic dissolution/film rupture or anion adsorption mechanisms.^[36] For example, corrosion fatigue of austenitic stainless steels in chloride solutions at elevated temperature is suppressed by polarization active to the critical potential for SCC. Electrode potential should be monitored and maintained throughout corrosion fatigue testing. Apparent effects of variables, such as the dissolved oxygen content of the solution, flow rate, ion concentration, and alloy composition on corrosion fatigue, can often be traced to changing electrode potential.

FRETTING CORROSION

Fretting corrosion is due to the combined action of an aggressive environment and relative small amplitude motion between two surfaces, one of which is metallic (see Fig. 12). A normal stress is present between the two surfaces so a rubbing action is present. A wear scar is usually present during fretting.^[37-39] Usually, such a condition exists in machine components that are considered fixed and not expected to wear. Typical examples are press fit bearings on shafts and discs on a shaft bolted together, lap joints and rivets on airplane wings are other examples. The problems caused by fretting are loss of fit, seizure of the component and initiation of fatigue cracks from the fretting site. The following conditions must exist for fretting corrosion to occur,

- a high normal load between the two surfaces
- relative motion between the two surfaces (as low as 3 or 4 nm)
- an aggressive environment to promote corrosion.

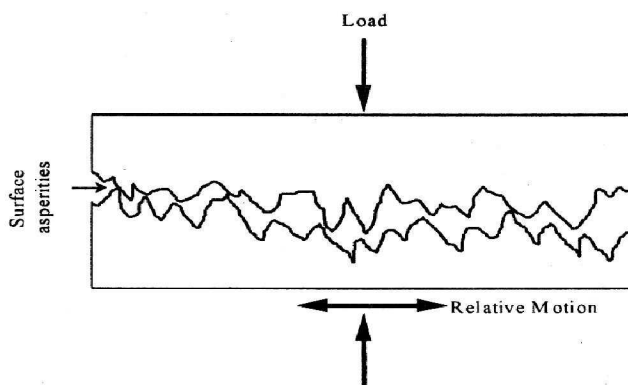


Fig. 12 : Schematic showing fretting fatigue in mating surfaces

On δ microscopic scale, the mating surfaces are rough and consist of features called asperities. These features will come into physical contact during relative movement of the surfaces, and will be responsible for load transfer and friction. Presence of the corrosive environment will further aggravate the situation.

Fretting corrosion is thought to be promoted by three possible mechanisms, (1) wear-oxidation mechanism, (2) oxidation-wear mechanism and (3) delamination due to wear.

In the wear-oxidation process, the material wears and produces small particles of heavily worked and fractured material. A schematic diagram to indicate this mechanism is shown in Fig. 13. The asperities under load plastically deform and weld together to form a contact. Further relative motion increases the stress and friction and the weld fractures, creating small amounts of debris. In this condition, the small particles of metal debris are very active and corrode rapidly to produce oxide. The oxide is normally very hard. The oxide can stay within the fretting area and produce rapid wear by micromachining of fresh soft metal surface. A second possibility is that the oxide leaves the fretting region and loss of fit results.

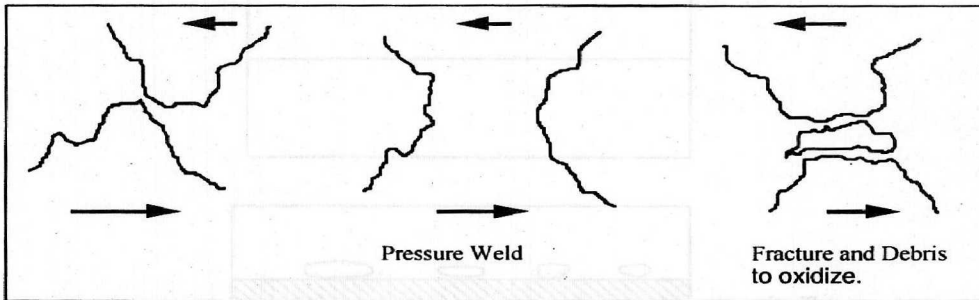


Fig. 13 : Schematic of wear-oxidation process inducing fretting fatigue

The second mechanism is just opposite of the first. Here, oxidation of the surface occurs first. The oxide is then removed when contact during fretting is made. This is schematically shown in Fig. 14. The debris in this case is hard oxide particles. The exposed metal surface rapidly reoxidizes and the process continues. The hard particles either wear the surface more if contained in the contact region or escape.

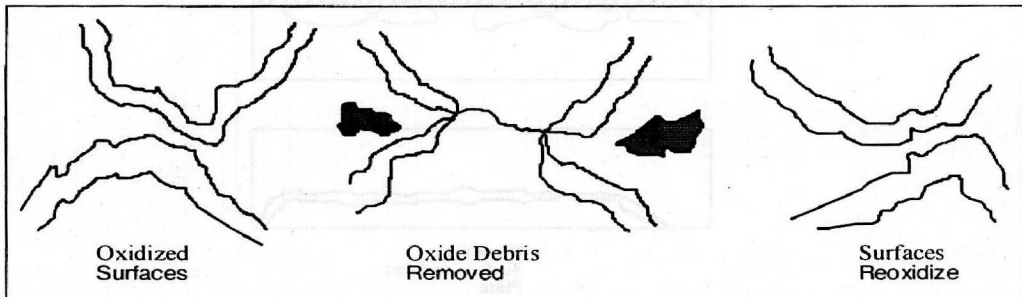


Fig. 14 : Schematic of oxidation-wear process inducing fretting fatigue

In delamination theory of wear, small platelets of material are detached from the surface of the material. This occurs because the highest stresses are developed inside the material some 10 to 20 nm below the surface. This initiates subsurface cracks which run parallel to the surface initially, but eventually come to the surface when the friction between the two surfaces overcomes the stress at the thin neck of the plate. At this stage, a thin plate is lifted from the surface. The presence of the aggressive environment acts to accelerate the process by aiding crack growth and again oxidizing the active metal surfaces. The mechanism is schematically shown in Fig. 15.

In this figure, the plastic contact zones are shown shaded. The voids initiate below the plastic zone, usually at second phases in the alloy. With further fretting exposure, the voids grow parallel to the surface and eventually connect to the surface when the friction between the plate and the opposing surface is greater than the fracture stress for the small neck of material connecting the plate to the surface. The fresh surface exposed is highly active and cracks exist for solution to penetrate into. Today, the delamination theory is widely accepted to control fretting.

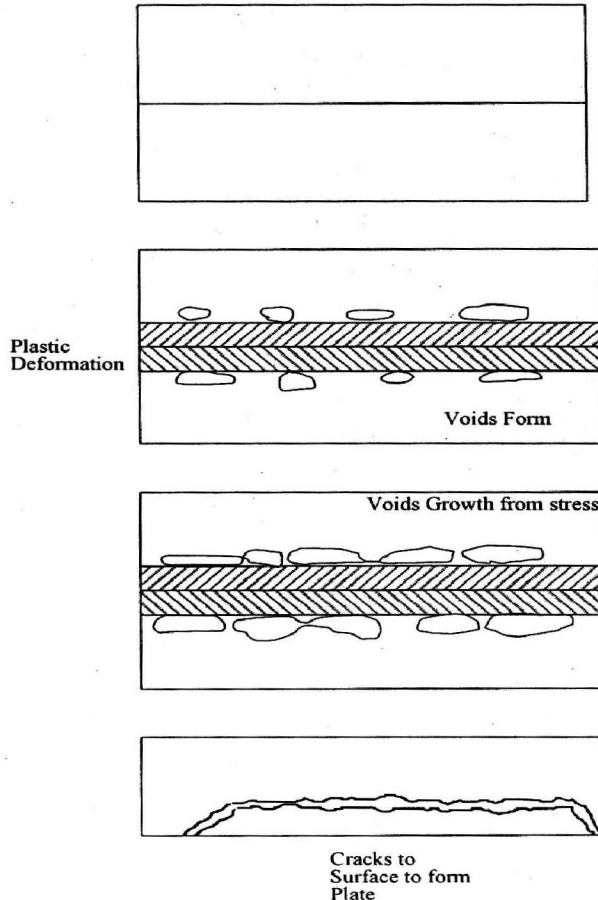


Fig. 15 : Schematic showing delamination theory of wear leading to fretting fatigue

Medical implants are thought to be subject to fretting due to the small amplitude of motion between the screw-head and fracture plates. The problem in this case is that metal ions not usually detached are released into the human body during fretting. If the body is sensitive to them then a rejection reaction will occur and remedial action must be taken. Today, Ti-6Al-4V is the metal of choice for implants. It has excellent corrosion resistance in human body which is roughly 5% NaCl solution.

Fretting can influence other processes such as fatigue. The relative motion between the two surfaces can generate cyclic stresses, stretching one region more than another. A typical example is a rivet in an airplane wing where the wing is stretched but the rivet is not. The surface damage induced by fretting can then initiate the fatigue crack. Fretting decreases the fatigue life of parts operating under fatigue loading.^[40] This process is then termed fretting fatigue to indicate its role in crack initiation.

Fretting can be minimized or eliminated in many cases, by one or more of the following.

- i. Increasing the hardness of contacting surfaces. This may mean increasing the hardness of both or just one of the components. Surface hardening treatments such as shot peening, nitriding, chrome plating and carburizing are often found to be beneficial.
- ii. Increasing the friction between the mating members by roughening or by plating will also minimize fretting.
- iii. Lubricate the mating surfaces to stop the friction. Sometimes, application of anti-fretting components will help.
- iv. Generally, materials that oxidize easily and form tenacious oxides are problems. These include aluminum and its alloys and titanium. Increase the amplitude motion in such cases.
- v. Applying phosphate coatings to exclude air or applying anaerobic sealants or adhesives to increase the tightness of the fit.
- vi. Increasing the fit interference, which reduces slippage by increasing the force on mating components. Use gaskets or sealants between parts.
- vii. Switching to materials with more fretting resistance is an alternative solution.

CONCLUDING REMARKS

In this paper, a brief discourse on behaviour of materials under conjoint stress - corrosive environments has been given. Various types of failures, their mechanisms, quantification methods and the methods to minimize the adverse effects have also been discussed. However, considering the complex nature of the issue, a specific problem has to be dealt with caution, taking into consideration all the metallurgical, mechanical and environmental conditions. The content of this paper will give some direction to handle such situations. Another approach to understand the complex material-stress-aggressive environment behaviour, is to get exposed to typical case studies of failure and get acquainted with fracture surfaces. Some of them are presented in vol. 12 of 9th edition and vol. 10 of the 8th edition of Metals Handbook, and the ASM source books and technical reports on failure analysis. In closure it may be said that although engineering failures occur due to stress-corrosion related issues, a majority of them can be averted with the better application of knowledge at hand.

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