CHAPTER 4

CORROSION FATIGUE

4.1 GENERAL

Corrosion fatigue is one of the forms of environmentally induced cracking. Environmentally induced cracking (EIC) is a general term for brittle mechanical failures that result from a synergism between tensile stress and a corrosive environment. Corrosion rates are usually quite low, and design stresses to cause EIC are often below the yield stress. However, when tensile stress and a corrosive environment are combined, EIC can result. EIC includes stress corrosion cracking (SCC), corrosion fatigue cracking (CFC), and hydrogen induced cracking (HIC). In any given situation, more than one of the three may be operative, further complicating analysis of failures and the determination of appropriate prevention methods. New designs and technology continually demand higher-performance alloys which must be exposed to still more severe conditions of stress, temperature, and corrosion. Modern alloys of high strength and corrosion resistance are often more susceptible to EIC. As a result, the incidence of EIC has risen rapidly in recent years.

4.2 STRESS CORROSION CRACKING, CORROSIÓN FATIGUE CRACKING, AND HYDROGEN INDUCED CRACKING

Some common characteristics of SCC, CFC, and HIC are given in Table 4.1. These characteristics must be regarded as general guidelines and sufficient care must be taken while categorising failures (Jones 1992). For example, SCC, HIC, as well as CFC may have corrosion products in the cracks
Table 4.1 Characteristics of environmentally induced cracking (Jones, 1992)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Stress corrosion cracking</th>
<th>Corrosion fatigue cracking</th>
<th>Hydrogen induced cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>stress</td>
<td>static tensile</td>
<td>cyclic with some tensile</td>
<td>static tensile</td>
</tr>
<tr>
<td>corrosive environment</td>
<td>specific to the alloy</td>
<td>any</td>
<td>any</td>
</tr>
<tr>
<td>temperature increase</td>
<td>accelerates</td>
<td>accelerates</td>
<td>increases to room temperature, then decreases</td>
</tr>
<tr>
<td>pure metal</td>
<td>more resistant</td>
<td>susceptible</td>
<td>susceptible</td>
</tr>
<tr>
<td>crack morphology</td>
<td>transgranular or intergranular branched sharp tip</td>
<td>transgranular unbranched blunt tip</td>
<td>transgranular or intergranular unbranched sharp tip</td>
</tr>
<tr>
<td>corrosion products in the crack</td>
<td>absent (usually)</td>
<td>present</td>
<td>absent (usually)</td>
</tr>
<tr>
<td>crack surface appearance</td>
<td>cleavage like</td>
<td>beach marks and/or striations</td>
<td>cleavage like</td>
</tr>
<tr>
<td>cathodic polarisation</td>
<td>suppresses</td>
<td>suppresses</td>
<td>accelerates</td>
</tr>
<tr>
<td>near maximum strength level</td>
<td>susceptible, but HIC often predominates</td>
<td>accelerates</td>
<td>accelerates</td>
</tr>
</tbody>
</table>

if the failed parts are exposed for long periods after the cracks have formed. Also, fatigue failures in vacuum or inert atmospheres are increased in some cases even by the very low corrosion rates resulting from exposure to humid air. On rare occasions, cathodic polarisation\* may move an alloy into a

\* Polarisation refers to a change in the potential of an electrode during electrolysis, such that the potential of an anode becomes more noble, and that of a cathode more active, than their respective reversible potentials. Polarisation is often accompanied by formation of a film on the electrode surface. Cathodic polarisation refers to the change of the electrode potential in the active(negative) direction due to current flow.
potential region of SCC susceptibility (Jones 1992). Failure analysis is further complicated by the fact that two or more phenomena may operate simultaneously.

SCC occurs in alloys with a static tensile stress in the presence of specific environmental conditions. Pure metals are comparatively more resistant to SCC. A specific dissolved species is often required. For example, stainless steels are susceptible in hot chlorides, brass in ammonia solutions, and carbon steel in nitrates.

CFC occurs under cyclic stresses in a corrosive environment. Susceptibility to and rate of fatigue cracking are usually increased in the presence of a corrosive environment. Both alloys and pure metals are susceptible and no specific environment is required. Macroscopic beach marks are often observed where tarnish or corrosion products accumulate during discontinuous propagation of the crack front. However, beach marks may also be caused due to differences in microplastic deformation when crack propagation is interrupted, and beach marks may be present with little or no visible corrosion.

HIC is caused by hydrogen diffusing into the alloy lattice when the hydrogen evolution reaction \(2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\) produces atomic hydrogen at the surface during corrosion, electroplating, cleaning and pickling, or cathodic protection. Although stress corrosion cracks often show more branching, SCC and HIC have a very similar appearance otherwise. HIC is accelerated by cathodic polarisation, whereas SCC and CFC are suppressed by cathodic polarisation. Figure 4.1 gives a schematic of the three types of EIC. Figure 4.2 illustrates a conceptual interrelationship of corrosion fatigue, stress corrosion, and hydrogen embrittlement (Ford 1984; Sprawls 1992). The most serious practical situations involving ductile alloy/environmental systems are in the
Fig. 4.1 Schematic of the three types of environmentally induced cracking (Jones 1992)

Fig. 4.2 Venn diagram illustrating the interrelationship of stress corrosion, corrosion fatigue and hydrogen embrittlement (Sprowls 1992; Ford 1984)

Fig. 4.3 Relative fatigue behaviour under various environmental conditions (Fuchs and Stephens 1980)
crosshatched regions, which indicate the combination of any two failure mechanisms, and especially in the centre, in which all three phenomena interact.

4.3 CORROSION FATIGUE

4.3.1 Definition, basic principles and mechanisms

Corrosion fatigue refers to the phenomenon of cracking in materials under the combined action of fatigue (or cyclic) loading and a corrosive (or deleterious) environment (gaseous or aqueous). This phenomenon is known to occur in many engineering alloys over a broad range of environments and has been recognised as an important cause of failure of engineering structures (Pao 1996). The combination of cyclic loading and deleterious environment both acting together is more detrimental than either acting separately. That is, repeated stressing accelerates the corrosive action and corrosive action accelerates the mechanical fatigue mechanisms. Definitions of fatigue and corrosion fatigue are given in ASTM E206-1979 and ASTM E742-1981 respectively. As per ASTM E206, fatigue is defined as the "process of progressive localised permanent structural change occurring in a material subjected to conditions which produce fluctuating stresses and strains at some point or points and which may culminate in cracks or complete fracture after a sufficient number of fluctuations". As per ASTM E742, corrosion fatigue is defined as the "synergistic effect of fatigue and aggressive environment acting simultaneously, which leads to a degradation in fatigue behaviour". The damage is often manifested as accelerated fatigue crack initiation and/or propagation.

Since most fatigue data are obtained in laboratory air, we have primarily only corrosion fatigue data available because the air environment can certainly be corrosive with relative humidity or moisture content and oxygen, the two major influencing factors. However, laboratory air fatigue data are often
used as a reference for comparing other environmental effects on fatigue. Figure 4.3 shows typical constant amplitude S-N (stress range versus number of cycles to failure) curves obtained at room temperature under four environmental conditions (Fuchs and Stephens 1980). The relative fatigue behaviour is very realistic. If air tests are taken as the reference, it is seen that vacuum can have a small beneficial effect primarily at long fatigue life. This benefit, however, depends on the material and the reference air environment. High humidity air can be quite detrimental to fatigue behaviour. This is particularly true with aluminium alloys. Presoaking fatigue specimens in a corrosive liquid followed by testing in air often causes a detrimental effect. However, the combination of simultaneous exposure to corrosive environment and repeated stressing causes the most drastic decrease in long-life fatigue strengths as shown in Fig.4.3. The relatively flat long-life S-N behaviour (called the endurance limit) that can occur in air or vacuum is eliminated under corrosion fatigue conditions. At short lives, all four test conditions shown in Fig.4.3 tend to converge. This is primarily due to insufficient time for corrosion to be effective.

The mechanisms of corrosion fatigue are not well understood. It is an electrochemical process dependent on the environment/material/stressing interaction. Some models proposed by researchers to explain corrosion fatigue mechanisms are: (i) hydrogen environment embrittlement model; (ii) passive film rupture and transient anode dissolution model; and (iii) models based on interactions between dislocations and environment based processes (Gangloff 1995; Pao 1996).

In case of corrosion fatigue, pits which act as stress raisers for cracks to initiate more readily, can form very early in life. A greater number of surface fatigue cracks usually occur under corrosion fatigue conditions and these tend to grow across grains. As the cracks get larger, they also tend to grow in Mode I perpendicular to the maximum tensile stress. Fracture surfaces
are often discoloured in the fatigue crack growth region. Very little loss of material due to corrosion occurs and thus loss of material is not a major contributing factor. Both crack initiation life and crack propagation life are reduced under corrosion fatigue conditions. Frequency effects are important and alter fatigue behaviour as a result of the time dependent nature of corrosion fatigue. Only at very short lives or high crack growth rates are frequency effects small. However, under these conditions, air and corrosion fatigue behaviour in general are similar. Corrosion fatigue also depends on how the corrosive environment is applied. For example, specimens submerged in fresh or salt water have better corrosion fatigue resistance than those subjected to a water spray, drip, or those submerged in continuously aerated water. This is due to the great importance of oxygen and the formation of oxide films in the corrosion fatigue process (Fuchs and Stephens 1980).

4.3.2 Initiation and propagation of CFC

From the viewpoint of engineering analyses, the fatigue damage process in metals consists of two stages, viz., fatigue crack initiation and fatigue crack propagation. Hence, we have two categories of laboratory corrosion fatigue tests: cycles to failure (crack initiation) tests and crack propagation tests. In crack initiation testing, specimens or parts are subjected to the number of stress or strain cycles required for CFC to initiate and subsequently grow large enough to produce failure. Such data are usually obtained by testing smooth or notched specimens. With this type of testing, however, it is difficult to distinguish between CFC initiation life and CFC propagation life. In crack propagation testing, Fracture Mechanics (FM) methods are used to determine the crack growth rates of preexisting cracks under cyclic loading. Preexisting cracks or sharp defects in a material reduce or may eliminate the crack initiation portion of the fatigue life of the component. Both types of testing are important; however, it appears that crack initiation is of more significance in
the failure process of relatively thin sections, while crack growth appears to dominate thick-section component endurance (Sprawls 1992).

In corrosion fatigue laboratory studies and component life evaluation, one important aspect is the difficulty in conceptually or experimentally distinguishing crack initiation from propagation. Many scientists and engineers consider crack initiation to be phenomenologically different from crack advance. However, in most instances, there is little evidence to support this view, and any initiation phase is merely associated with crack detection capability (Andresen 1996). Thus, 'initiation' can span the range from complete failure to 25% load drop in strain-controlled tests, to readily observable crack in visual examination, to subgrain size. All these definitions of crack initiation are arbitrary. In many cases, the processes that control propagation of long cracks (e.g., >1 mm) also control the behaviour of very short cracks (e.g., ≤ 20 μm), although there are instances where crack propagation occurs from localised corrosion (e.g., pitting or grain boundary attack), fracture of inclusions, and so on, where the processes controlling initiation differ from those that control propagation.

In routine low- and high-cycle fatigue crack initiation testing, complete fracture of a small specimen is generally the failure criterion. Approximately 30 to 40% of the low-cycle fatigue life and about 80 to 90% of the high-cycle fatigue life measured by cycles to failure involve nucleation of the dominant fatigue crack that eventually causes failure (Sprawls 1992). Low-cycle fatigue is the regime characterised by high overstress. The commonly accepted dividing line between high-cycle and low-cycle fatigue is considered to be between $10^4$ and $10^5$ cycles. In practice, this distinction is made by determining whether the dominant component of the strain imposed during cyclic loading is elastic (high-cycle) or plastic (low-cycle), which in turn depends on the properties of the metal as well as the magnitude of the nominal stress. Normally, strain-controlled tests (constant strain amplitude) are used in case of
low-cycle fatigue. Either constant load amplitude or constant deflection tests are used in case of high-cycle fatigue.

4.3.2.1 Fracture mechanics based CFC growth curve

Results of fatigue crack growth rate tests for many metallic materials have shown that complete $da/dN$ versus $AK$ curves have three distinct regions of behaviour where $a$ is the crack length, $N$ is the number of fatigue load cycles, and $AK$ is the crack tip stress intensity factor range; $da/dN$ gives the crack growth rate. The three regions of a typical crack growth curve in metals is shown in Fig.4.4. In Region II, the crack growth curve is represented by the power law equation $da/dN = C(AK)^n$, where $C$ and $n$ are constants for a given material and stress ratio (Sprawls 1992). In an aggressive environment, the CFC growth curve can be quite different from the curve for inert environment. Crack growth curve in an aggressive environment is also shown in Fig.4.4.

Corrosion fatigue crack growth is normally thought of in terms of the applied stress intensity related to some apparent threshold for stress corrosion cracking, $K_{ISCC}$, under static loading. The conventional view is that either CFC or SCC dominates at various levels of stress intensity factor (SIF), and finally at higher values of SIF, i.e., at values of SIF approaching the fracture toughness of the material, $K_{IC}$ or $K_C$, steady load cracking becomes important. McEvily and Wei (1972) have categorised CFC growth as falling into one of the three types of behaviour illustrated in Fig.4.5. In Type A behaviour, there is a synergistic interaction of cyclic and corrosive crack growth mechanisms at all but very rapid rates of crack growth, where the mechanical aspects are dominant because cracking occurs more rapidly than chemical and/or transport processes involved in corrosion fatigue. With Type B response, there is no environmental effect below the threshold $K_{ISCC}$ observed in sustained load crack growth studies. Above $K_{ISCC}$, sustained load crack growth contributes substantially to the cyclic crack growth component. Type C response is
intermediate to the extremes of Types A and B and is the behaviour which is typical of most alloy-environment systems. The behaviour tends to be similar to that of Type A systems below $K_{isc}$.

Fig.4.4 Corrosion fatigue crack propagation rate as a function of the crack tip stress intensity factor (Sprowls 1992)
Fig. 4.5 Three types of corrosion fatigue crack growth behaviour (McEvily and Wei 1972)

Fig. 4.6 Venn diagram of variables contributing to EiC (Andresen 1996)
4.4 VARIABLES INFLUENCING CORROSION FATIGUE

Wei and Speidel have listed a large number of variables that influence corrosion fatigue behaviour (Wei and Speidel 1972). The variables are listed in three categories – mechanical, metallurgical, and environmental. Andresen also has listed the variables under these categories (Andresen 1996). Pao has listed the variables in four groups – mechanical, geometrical, metallurgical, and environmental (Pao 1996). The variables considered by these researchers are given in Table 4.2. Figure 4.6 shows a Venn diagram of the variables contributing to EIC. The extensive list emphasises the complexity of corrosion fatigue behaviour. With such a large number of variables, a complete evaluation of all the factors involved cannot be justified economically. In most studies, all but a few of these are held constant while those of primary importance to the investigators are varied. When evaluating and comparing data from different sources, it is important to know all of these variables so that proper evaluations and comparisons can be made. For example, some results may appear, at first glance, to be contradictory. However, when all the variables are considered, this apparent contradiction can be explained and taken into account. Because of the contribution of many variables to corrosion fatigue crack advance (or EIC in general), attention to experimental details is greatly rewarded. Unless the multidisciplinary nature of the studies on EIC is recognised, most efforts would produce seriously misleading results or outright confusion, which perhaps is the main reason for the slow progress in quantifying and understanding CFC.

4.4.1 Effect of mechanical variables

4.4.1.1 Cyclic frequency

Cyclic load frequency is the most important variable that influences corrosion fatigue for most material, environment, and stress intensity conditions. The rate of environmental cracking above that produced in vacuum
Table 4.2 Variables influencing corrosion fatigue (Andresen 1996; Pao 1996; Wei and Speidel 1972)

<table>
<thead>
<tr>
<th>Mechanical variables</th>
<th>Geometrical variables</th>
<th>Metallurgical variables</th>
<th>Environmental variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>- maximum stress or stress intensity factor ($\sigma_{\text{max}}$ or $K_{\text{max}}$)</td>
<td>- crack size and shape</td>
<td>- alloy composition</td>
<td>- temperature</td>
</tr>
<tr>
<td>- cyclic stress range or stress intensity range ($\Delta \sigma$ or $\Delta K$)</td>
<td>- component size and geometry</td>
<td>- distribution of alloying elements and impurities</td>
<td>- type of environment (gaseous, liquid, liquid metal etc.)</td>
</tr>
<tr>
<td>- cyclic load frequency ($f$)</td>
<td></td>
<td>- microstructure and crystal structure</td>
<td>- partial pressure of damaging species in gaseous environments</td>
</tr>
<tr>
<td>- stress ratio ($R$)</td>
<td></td>
<td>- heat treatment</td>
<td>- concentration of damaging species in aqueous or other liquid environments</td>
</tr>
<tr>
<td>- cyclic load wave form (constant amplitude loading)</td>
<td></td>
<td>- mechanical working</td>
<td>- electrochemical potential</td>
</tr>
<tr>
<td>- load interactions in variable amplitude loading</td>
<td></td>
<td>- preferred orientation of grains and grain boundaries (texture)</td>
<td>- pH</td>
</tr>
<tr>
<td>- state of stress</td>
<td></td>
<td>- mechanical properties (strength, fracture toughness etc.)</td>
<td>- viscosity of the environment</td>
</tr>
<tr>
<td>- residual stress</td>
<td></td>
<td></td>
<td>- coatings, inhibitors etc.</td>
</tr>
</tbody>
</table>
generally increases with decreasing frequency. Frequencies exist above which corrosion fatigue is diminished. The dominance of frequency is directly related to the time dependence of the mass transport and chemical reaction steps required for environmental cracking (Sprowls 1992). It is impossible to predict the frequency range at which corrosion fatigue is severe, because of the numerous chemical processes. It is also difficult to extrapolate short-term (high-frequency) laboratory crack growth rate data in order to predict long-term component performance. Since the effect of frequency is associated with the environmental effects, at high frequencies, there is less time for environmental action, which means that the crack growth rate per cycle approaches that found in dry air. Vosikovsky has investigated frequencies from 0.01 Hz to 10 Hz and has found that decreasing the frequency caused a critical crack growth rate, \(\frac{da}{dN_{CR}}\), to increase (Vosikovsky 1975). The effect of cyclic frequency on corrosion fatigue crack propagation in salt water is shown in Fig.4.7. Below the value of critical crack growth rate, \(\frac{da}{dN_{CR}}\), the \(\Delta K - \frac{da}{dN_{CR}}\) curve was the same for all frequencies and above this value, the \(\Delta K - \frac{da}{dN_{CR}}\) curves tended to approach asymptotically the in-air behaviour at crack growth rates near \(10^{-5}\) m/cycle. An extremely important point to keep in mind is that the data developed for high \(\Delta K\) levels above \(\frac{da}{dN_{CR}}\) cannot be reasonably extrapolated to low \(\Delta K\) levels when such environmental effects are present. If the upper portions of the dotted or dashed curves in Fig.4.7 were extrapolated downward, very conservative and unrealistic estimates of actual behaviour would be made. Scott and Silvester (1975) found that decreasing the frequency from 10 Hz to 1 Hz had little effect on crack growth rate but decreasing it to 0.1 Hz and 0.05 Hz resulted in crack growth rates about four to five times those in air, when \(\Delta K\) was about 20 MN/m\(^{3/2}\) at stress ratio \((R) = 0.1\), and in sea water at 20°C. Below this \(\Delta K\) level, there was no significant frequency effect. Figure 4.8 shows the effect of frequency for an AISI 4340 steel in a water vapour environment at 585 Pa (Pao et al 1979). Data for tests
Fig. 4.7 Effect of cyclic frequency on corrosion fatigue crack propagation in salt water (Vosikovsky 1975)

Fig. 4.8 Effect of cyclic frequency in AISI 4340 steel (Pao et al 1979)
in Argon are also included in the figure for comparison. These data cover $\Delta K$ from 15 to 45 MN/m$^{3/2}$ at a load ratio $R = 0.1$. The corresponding $K_{\text{max}}$ values are below the apparent $K_{\text{SCC}}$ (approximately 55) for this water vapour pressure. Figure 4.8 clearly shows that the environmental effect is much more pronounced at lower cyclic frequencies than that at higher frequencies as the fatigue crack growth rates at 0.1 Hz are more than an order of magnitude higher than those obtained at 10 Hz.

4.4.1.2 Stress amplitude

In general, a low amplitude of cyclic stress favours relatively long fatigue life, permitting greater opportunity for involvement of the environment in the fatigue process. However, environmental interaction may be insignificant unless the strain rate is in a critical range for SCC in certain alloy/environment systems. Stress amplitude must be considered together 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 time sufficient for the corrosion processes to do significant damage (Sprawls 1992).

4.4.1.3 Stress intensity

Corrosion fatigue crack growth rates generally increase with increasing stress intensity; however, the precise dependence varies markedly. For example, materials that are extremely environment-sensitive, such as ultra high strength steel in distilled water, are characterised by high crack growth rates that are influenced less by $\Delta K$. It is always important to examine the entire relevant $\Delta K$ regime, not assuming the observed enhancement at a specific $\Delta K$ (Sprawls 1992; Andresen 1996).
4.4.1.4 Stress ratio

The rates of corrosion fatigue crack propagation generally are increased by higher stress ratios. Increased stress ratio at constant $\Delta K$ results in increased crack tip strain and strain rate, enhanced film rupture, and therefore increased corrosion fatigue crack propagation.

4.4.1.5 Ripple load cracking

A special case of corrosion fatigue cracking is 'ripple load cracking'. 'Ripple loading' refers to a loading profile where relatively small amplitude cyclic loads are superimposed on a large sustained load. A typical ripple load profile is schematically shown in Fig.4.9 where the stress ratio often exceeds $R = 0.90$. The significance of ripple load cracking is its relation to SCC, where the applied load is assumed to be constant. However, in the real world, structures rarely experience a constant load condition, but are actually subjected to a combination of very small amplitude cyclic loads and a large constant load. A typical example is offshore platform structures. Under ripple loading conditions, if a structure is designed solely based on the SCC threshold without considering the possibility of ripple loads, cracking or fracture may occur prematurely. Pao (1996) has approached ripple load cracking as high stress ratio corrosion fatigue.

4.4.2 Effect of environmental variables

Besides the obvious concern of primary species (such as NaCl concentration for salt water) in corrosion fatigue, small amounts of contaminants are also a key variable. For example, relative to vacuum, crack growth is accelerated by factors of 3 and 25 for moist air and highly purified low-pressure hydrogen gas respectively. Small additions of oxygen to the hydrogen environment essentially eliminate the brittle corrosion fatigue component to crack growth (Andresen 1996). In aqueous environments, the
effects of bulk ionic concentration and pH are often quite pronounced, although dissolved oxidants are often of greater consequence (e.g., dissolved oxygen, hydrogen peroxide, and copper and iron ions), as are contaminants (e.g., dissolved sulphur, chloride, lead, mercury). The primary role of oxidising and reducing species, especially dissolved oxygen and hydrogen, is in shifting the corrosion potential. The environmental effect is less at lower temperatures. In the case of humid air, there are two reasons for the decreased crack growth rates: (a) colder air can contain less water vapour, and (b) the reaction kinetics are slower at lower temperatures.

4.4.2.1 Effect of cathodic protection and electrode potential

Electrode potential strongly influences rates of corrosion fatigue crack propagation for alloys in aqueous environments. Controlled changes in the potential of a specimen can result in either complete elimination or dramatic increase of fatigue cracking. The precise influence depends on the mechanism of the environmental effect and on the anodic or cathodic magnitude of the
applied potential. A protection level of 0.2 V to 0.3 V more negative than the free corrosion potential will reduce the corrosion rate of carbon steel by 99 per cent (Jones 1971). On this basis, common recommended levels for adequate protection of steel structures are near -0.85 V Cu/CuSO₄, -0.78 V SCE (Standard Calomel Electrode), or -0.80 V Ag/AgCl. Overprotection to potentials less than -0.78 V SCE can be detrimental and can increase crack growth rates to levels above those observed under free corrosion conditions at intermediate levels of \(\Delta K\), especially at frequencies below 1 Hz. Generally, for ferrous alloys that crack by hydrogen embrittlement when stressed in aqueous solutions, corrosion fatigue is increased by high cathodic polarisation. During studies on cathodically protected steel tubular joints in sea water environment, it was observed that the crack growth rate in free corrosion conditions was about two times the growth rate in air. For cathodic protection at -1.05 V (over-protection), the growth rate was approximately six times higher (Dover and Wilson 1984). Electrode potential should be monitored and, if appropriate, maintained constant during corrosion fatigue experimentation. 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 (Sprowls 1992).

4.4.2.2 Crack tip chemistry under cathodic protection

The environmental effects related to corrosion fatigue of steel in sea water are primarily: possibility of corrosion (dissolution of iron), hydrogen uptake in the steel (from corrosion process or cathodic protection), and precipitation of heavy soluble compounds in the crack (corrosion products or calcareous deposits). All these depend on the chemistry in the crack, the primary parameters being the electrochemical potential of the steel surfaces, the pH of the solutions, the oxygen concentration and the ion concentration in the solution.
Under free corrosion, the corrosion process promotes the crack initiation. The liquid in the crack is renewed periodically by the pumping effect and especially at low $R$ values, the crack is virtually emptied for each stress cycle. Under these conditions, it can be reasonably assumed that the pH, oxygen concentration and corrosion potential are nearly the same inside and outside the crack, with only a small tendency to accelerated corrosion at the crack tip and a minimal tendency to hydrogen evolution. Hydrogen embrittlement is however possible in long cracks with a low pH or at high stress intensities with hydrogen sensitivity.

By cathodic polarisation of a steel surface, there will be a pH increase at the surface due to oxygen reduction and/or hydrogen evolution. The increase in pH promotes the precipitation of calcium carbonate at pH above about 8.4 and magnesium hydroxide at pH above 9.5. The cathodic potential, on the other hand, promotes hydrogen evolution and hydrogen uptake in the steel (Maahn 1986). Due to the precipitation of calcareous deposits inside the mouth of the crack, there is a wedging effect with consequent reduction in the effective stress intensity range. This is found to result in slower crack growth rates at low stress levels. It is generally recognised that calcareous deposit precipitation increases with increasing temperature. The higher the cathodic current density, the greater the electrolyte pH adjacent to the metal surface and, as a result, the thicker the calcareous film (Hopkins and Monahan 1986). Figure 4.10 shows a simplified illustration of the chemistry within a fatigue crack under cathodic protection. Crack closure effects are found to be significant in crack retardation during overload periods which occur under random load conditions (Maahn 1986). The presence of a substantial density of weld defects can affect the mechanism of crack growth. The overall effect of cathodic protection on corrosion fatigue life is difficult to predict and this would explain the wide scatter in lives of cathodically protected joints of offshore steel structures.
Reactions responsible for the formation of mineral deposits:

\[ \text{HCO}_3^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-} \]
\[ 2\text{OH}^- + \text{Mg}^{2+} \rightarrow \text{Mg(OH)}_2 \]
\[ \text{CO}_3^{2-} + \text{Ca}^{2+} \rightarrow \text{CaCO}_3 \]
\[ \text{CO}_3^{2-} + \text{Mg}^{2+} \rightarrow \text{MgCO}_3 \]

Calcium Carbonate  Magnesium Carbonate  Magnesium Hydroxide

Fig. 4.10  Simplified illustration of chemistry within a fatigue crack under cathodic protection (Hopkins and Monahan 1986)
4.4.2.3 Temperature

Because temperature may influence the environment/metal surface reactions as well as the many transport processes involved in corrosion fatigue, temperature can be expected to affect corrosion fatigue crack growth rates. In many environment/alloy systems, corrosion fatigue crack growth rates increase with increasing temperature. That is, the corrosion fatigue cracking process is thermally activated (Pao 1996).

4.4.3 Effect of other variables

4.4.3.1 Cyclic waveform

While cyclic load waveform has little effect on the fatigue crack growth rates in benign environments, available data indicate that corrosion fatigue crack growth rates in aggressive environments may be highly dependent on the shape of the cyclic load waveform. Environment-enhanced effects on fatigue crack growth rates can be substantial if the cyclic waveform consists of a significant period of rising load. The longer the load rise time during each load cycle, the greater the influence of an aggressive environment.

4.4.3.2 Notches and surface roughness

Stress raisers such as notches and surface roughness increase susceptibility to corrosion fatigue. Severe notches have a greater effect on the fatigue life than does corrosion alone. Figure 4.11 shows that corrosion has lesser effect on the reduced properties of notched than on smooth fatigue specimens (Speidel 1977). The corrosion fatigue endurance data given in Fig.4.11 are for 13% Cr steel. The specimens were subjected to rotating bending test at mean load zero, frequency 50 Hz, and temperature 23°C. Surface roughness by preexposure to a corrosive environment is well known to degrade subsequent fatigue life. Cracks have often been observed to initiate
from corrosion pits, which again serve as surface stress concentrators. In any alloy system, corrosion reduces the stress amplitude and shortens the time or number of stress cycles to failure, as shown in Fig.4.11.

**4.5. CORROSION FATIGUE TEST METHODS AND TECHNIQUES**

Andresen (1996), Gangloff (1995) and Sprowls (1992) have given details regarding corrosion fatigue test methods/techniques for specific environments, environmental cell design, crack detection and measurement etc. Details regarding corrosion fatigue testing techniques dealing with high
cycle corrosion fatigue, low cycle corrosion fatigue, FM methods for CFC propagation, and small crack corrosion fatigue methods are also discussed in these references. Details regarding corrosion fatigue experiments in marine environments only are discussed in the following sub-section.

4.5.1 Corrosion fatigue experiments in marine environments

General kinds of aqueous solutions are used to simulate marine environments in corrosion fatigue experiments. These include fresh natural sea water, sea water with organic species removed (usually shipped to an inland laboratory site), synthetic sea water solutions such as ASTM standard synthetic sea water (ASTM 1990), brackish waters and sodium chloride solutions. In comparing results obtained by different investigators or in using data to provide design guidelines for particular service applications, it is important to remember that these variations in water composition may have a significant influence on the corrosion fatigue behaviour. Bogar and Crooker (1979) emphasise the importance of using natural sea water in studies of corrosion fatigue crack growth. They used 3.5 per cent sodium chloride, ASTM synthetic sea water and natural sea water in a comparative study of two steels and an aluminium alloy. Their results showed that these three types of solutions can produce different results, with crack growth rate variations of up to a factor of three under comparable loading. Neither of the saline solutions commonly used in laboratory studies are direct substitutes for natural sea water. This environmental difference should be kept in mind when evaluating and comparing data.

In most marine environment corrosion fatigue experiments, the specimen test section is totally immersed in the aqueous solution. Sometimes, the solution is dripped or sprayed on to the specimen surface. With the latter methods, the surface may be kept moist continuously or it may be allowed to become alternately wet and dry for certain periods. Immersion is usually
achieved by enclosing the specimen test section with a chamber through which water is flowed. The flow rate is typically just fast enough to ensure a constant supply of well-aerated water with minimal contamination and to avoid stagnant conditions. In some cases, however, the flow rate is fast enough to examine the effects of increased water velocity on the corrosion fatigue process. The corrosion chamber and associated fittings, flow lines, reservoirs and pumps are normally made from plastic (non-metallic) material to avoid introduction of undesired metallic ions into the water and to prevent possible unintended galvanic effects.

Most fatigue experiments are conducted at ambient temperatures of about 20°C to 25°C. In some cases, however, higher or lower temperatures are used by either heating or chilling the water reservoir. Most corrosion fatigue tests are carried out at ambient atmospheric pressure, although some tests have been done at high pressures to simulate conditions that may be encountered in deep waters. Typically, sea water will have 5 ppm to 10 ppm dissolved oxygen, 30 ppt to 35 ppt salinity and 7.8 to 8.2 pH level (Jaske et al 1981). Variations within these ranges generally are expected to have little influence on corrosion fatigue behaviour. However, larger variations or values outside of these ranges may significantly affect corrosion fatigue.

pH is a measure of acidity or alkalinity of a solution. The effects of pH on corrosion vary from metal to metal, but, in general, more acidic waters are more corrosive. Sea water, normally with a pH value of 8.2, is mildly alkaline. Variations in pH can affect the formation and growth of calcareous deposits and the stability of other protective films. Variations in pH result from corrosion reactions, sea life and dissolved oxygen.

Most corrosion fatigue experiments in marine environments are carried out under free-corrosion conditions. It is desirable to measure the free-corrosion potential during such experiments, but often this is not done. In some
experiments, the specimens are anodically or cathodically polarised. Anodic polarisation usually is employed in studies to examine the influence of accelerated corrosion rates on the corrosion-fatigue-damage process. Cathodic polarisation is used to simulate the effects of commonly used cathodic protection methods on corrosion fatigue performance. Usually, potential is maintained potentiostatically in laboratory studies and variations in applied current density are monitored during the course of testing. In some cases, cathodic polarisation is provided by coatings such as zinc, or by sacrificial anodes connected to the specimen. Since the electrochemical potential can significantly influence corrosion fatigue behaviour, it is important to take this variable into account in evaluating data.

The difficulty found in service in applying uniformly the optimum cathodic potential, between -0.7 V and -0.8 V, leads to the situation where one should expect some regions of an offshore structure to be over protected. This has prompted the study of the effect of over protecting up to -1.1 V, in S-N and corrosion fatigue crack growth studies of structural steel. In many tests, the influence of over cathodic protection on crack growth at certain $\Delta K$ (range of stress intensity) levels has been to increase the crack growth up to 4 times the growth in air, whereas the S-N data show the air performance to be restored by correct or over protection (Dharmavasan and Dover 1988).

The effect of test time (and test frequency) is again complex mainly because the effect of environment on crack growth behaviour is not general, i.e., the crack growth rate is not influenced to the same degree by the environment at all values of $\Delta K$ (Dharmavasan and Dover 1988). Thus, in certain types of S-N tests, the crack growth regime critically affected by the environment may occupy only a small part of the total crack growth process. This would lead, in these cases, to a very small influence of the environment on test life and apparently no effect on fatigue life due to test time, frequency etc.
The conclusion of such tests is, therefore, only valid for the particular test specimen geometry and mode of loading, and is not general.

Loading history can have a significant influence on crack growth behaviour in corrosive environments. Since most real structures are subjected to variable amplitude loading spectra in actual service, loading history effects are important to consider. Variable amplitude loading will not only alter the plastic zone size and residual stress fields, but may also alter the mechanism of crack growth in aggressive environments. Frequency and wave form are important to consider. Generally, decreased frequencies accelerate crack growth rates in aggressive environments. Wave form is an important consideration in water-steel systems, but has only a small influence in aluminum-water systems (Wei and Speidel 1972).

4.6 BASIC PROCEDURE FOR PREDICTION OF FATIGUE CRACK GROWTH IN TUBULAR JOINTS

Prediction of corrosion fatigue crack growth in tubular joints using fracture mechanics consists of a fracture mechanics solution for the stress intensity modification factor, \( Y \), and a suitable numerical representation of the corrosion fatigue material response. Deriving stress intensity factors for cracks in tubular joints is difficult due to the complex component and crack geometries, and the nonlinear distribution of stresses around the cracked regions. A diverse range of approaches are reported in the literature, e.g., empirical crack growth based methods, application of boundary conditions to simple plate solutions, and the use of solid 3-D and line spring finite element analyses. The solutions are conveniently expressed in terms of the nondimensional stress intensity modification factor, \( Y \). In tubular joints, crack growth in the depth direction, i.e., through the thickness of the member, is of primary significance, because the joint begins to lose load carrying capacity rapidly once the member (chord or brace) wall has been breached. A solution for the \( Y \) factor for the deepest point of the crack is often sufficient to obtain a realistic fatigue life.
estimate, although some approaches produce stress intensity factors for other locations along the crack front. Assuming a solution for $Y$ is available for a given component and crack geometry, the stress intensity factor range, $\Delta K$, for a crack of depth, $a$, subject to a fatigue stress range, $\Delta \sigma$, may be found from the equation

$$\Delta K = Y \Delta \sigma \sqrt{\pi a}$$  \hspace{1cm} \ldots (4.1)$$

An empirical crack growth relationship such as the Paris Law may be used to determine an instantaneous crack growth rate in response to the applied range of stress intensity factor:

$$\frac{da}{dN} = C (\Delta K)^m$$  \hspace{1cm} \ldots (4.2)$$

The terms $C$ and $m$ represent the material response to the fatigue loading in the given environment. The numerical values of both of these constants are sensitive to many variables such as environment, load waveform, material condition, cyclic frequency etc. and therefore must be obtained experimentally by testing a standard specimen of the required material in the required environment and subject to the required fatigue loading. The $K$ calibration of the standard specimen is known, so $C$ and $m$ can be determined by measuring crack growth rates in response to a range of $\Delta K$ values, and fitting the data to Equation 4.2. In aggressive environments, it is often necessary to approximate the growth rate data in a piecewise linear fashion, so that several pairs of $C$ and $m$ values are required to describe the material response over the full range of applied $\Delta K$.

A fatigue life prediction can be obtained by integrating Equation 4.2, usually numerically, over a large number of crack growth increments between an assumed initial defect size and the crack size when the failure criterion is reached. This approach is adequate for prediction under constant amplitude
loading, but complicated when variable amplitude loading is considered. Austin and Dover (1995) have presented a method of analysis suitable for corrosion fatigue life prediction using variable amplitude WASH (Wave Amplitude Stress History) sequences. In variable amplitude corrosion fatigue, it is not appropriate to use the equivalent stress range as the fatigue stress range in Equation 4.1, since more than one value of $m$ is required to characterise the material response data. It is necessary to reduce the random load signal to a stress range probability distribution (SRPD) by cycle counting, and determine an equivalent growth rate by summation of the individual growth rates. A probability distribution of stress intensity factor ranges defined as $(\Delta K_i, P(\Delta K_i))$ may be obtained from the SRPD, the current crack size, $a$, and the appropriate $Y$ factor using the relations:

$$\Delta K_i = \Delta \sigma_i Y \sqrt{\pi a} \quad \ldots (4.3)$$

$$P(\Delta K_i) = P(\Delta \sigma_i) \quad \ldots (4.4)$$

where there are $i$ discrete ranges in the stress range probability distribution. A crack growth rate for each individual $\Delta K_i$ may then be calculated from the constants $C_j, m_j$ pertinent to the Paris Law segment under which the particular $\Delta K_i$ lies.

$$\frac{da}{dN_i} = C_j (\Delta K_i)^{m_j} = C_j (\Delta \sigma_i Y \sqrt{\pi a})^{m_j} \quad \ldots (4.5)$$

An instantaneous total growth rate for the current crack size, $a$, and all $i$ is obtained by summation of the individual growth increments, $\Delta a_i$, associated with a period of random cycling totalling one virtual cycle, so that,

$$\frac{da}{dN_{\text{total}}} = \frac{\sum_{i=1}^{k}(\Delta a_i)}{1} = \sum_{i=1}^{k}\left\{ \sum_{j=1}^{i} C_j (\Delta \sigma_i Y \sqrt{\pi a})^{m_j} P(\Delta \sigma_i) \right\} \quad \ldots (4.6)$$
where there are \( k \) discrete ranges in the SRPD, and the material response is characterised by \( l \) linear segments. It should be noted that the summation index \( i \) is conditional depending on whether the stress intensity factor range \( \Delta K_i \) lies under the current Paris segment \( j \). In practice, each crack growth increment would be made over a longer period of cycles, the length of which would depend on the magnitude of the growth rate and on the accuracy required. Where the stress history is nonstationary, a unique SRPD needs to be determined for each cyclic interval in the prediction. In the case of multi-sea state WASH sequences, the sea state statistics can be used in conjunction with the sequence of sea states to define the SRPD for each interval from

\[
P(\Delta \sigma_i)_{\text{total}} = \sum_{j} \left( \frac{\text{NSS}_j}{\text{NSS}_{\text{total}}} P(\Delta \sigma_j)_j \right)
\]

where there are a total of \( \text{NSS}_{\text{total}} \) sea states in the interval, of which \( \text{NSS}_j \) are sea state \( j \). This method can be used to carry out variable amplitude corrosion fatigue crack growth predictions, once suitable material response data and a solution for the \( Y \) factor have been determined.

4.7 PREVENTION OF CORROSION FATIGUE FAILURES

Several methods can be used to prevent or circumvent the detrimental effects of corrosion fatigue on structural performance. These methods may be easy to identify, but their implementation may be difficult or expensive. The effectiveness of a given method or a combination of methods depends on the particular material-environment system under consideration. Some methods that are currently in use to prevent or circumvent the detrimental effects of corrosion fatigue on the performance of structural components are listed below (Barsom and Rolfe 1987; Fuchs and Stephens 1980):
• **Isolate the environment and the material.** This can be accomplished by placing a barrier between the environment and the material. Barriers that have been used include metallic coatings (e.g., zinc, chrome), organic coatings (e.g., paint), inorganic coatings (e.g., glass), ceramic and rubber liners, and cladding. Proper care must be exercised in selecting a particular protection method/material. For example, zinc and cadmium coatings are anodic to steels and have produced improved corrosion fatigue resistance. Chromium and nickel are cathodic to steels and electrolytic plating with these materials is undesirable. Under service conditions of many components and structures, it is difficult or may be impossible for coatings to retain complete continuity. Broken or disrupted coatings can eliminate the beneficial effects.

• **Alter the severity of the environment.** This can be accomplished by chemically removing the aggressive constituents in the environment, by increasing the pH of the environment, or by decreasing the temperature, flow rate, and concentration of the environment.

• **Apply cathodic protection.** This can be accomplished by externally imposed negative potential or a galvanically generated potential. Sacrificial anodes are frequently used for cathodic protection of structures.

• **Alter the surface characteristics of the material.** This can be accomplished by inducing favourable compressive stresses on the material surfaces that are exposed to the environment. Compressive surface stress can be induced by using induction hardening, shot peening, cold working, nitriding etc. These favourable compressive stresses may not minimise corrosion fatigue crack initiation or general corrosion but could significantly decrease and possibly eliminate crack propagation.

• **Substitute a more resistant material.** In general, materials that are resistant to a given environment are available. However, care should be exercised in the selection process to ensure that the substitute material possesses all the other properties that are essential for its use in the particular application.

• **Do not relate water or salt water corrosion fatigue resistance of steels to ultimate tensile strength.** Many carbon and low alloy steels have similar corrosion fatigue strengths in water and salt water and thus high strength steels may not be advantageous unless surface compressive self-stresses and/or protective coatings are used. Long-
life corrosion fatigue strengths in water and salt water can vary from about 5 to 40 per cent of the ultimate strength.

- Do not overlook the deleterious effects of humidity on fatigue resistance, particularly in aluminium alloys.

- Design the components to prevent the initiation or the propagation of cracks to a critical size. For a given material/environment system, this can be accomplished by using relevant data for designing the structural components properly against corrosion fatigue damage or establishing inspection procedures and inspection intervals that would ensure the safe operation of the structure in the environment of interest.