Environmental Cracking—Corrosion Fatigue

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CORROSION FATIGUE (CF) is an important but complex mode of failure for high-performance structural metals operating in deleterious environments. This view is based on the likelihood of cyclically varying loads and chemical environments in service, the need for predictable long-life component performance and life extension, the universal susceptibility of pure metals and alloys to CF damage, and the time-dependent multivariable character of corrosion fatigue. For example, stress corrosion cracking (SCC) immune alloys are susceptible to CF. Corrosion fatigue has affected nuclear power systems, steam and gas turbines, aircraft, marine structures, pipelines, and bridges; CF issues are central to the behavior of many aging systems [1–3].

The objective of this chapter is to highlight modern laboratory methods for characterizing the corrosion fatigue behavior of metals in aqueous electrolytes. The principles and mechanisms of CF are summarized in the first section of this chapter, followed by discussions of experimental methods in the second section. Specimen design and loading, environment control, strain and crack size measurement, and computer automation are discussed. The emphasis throughout is on exemplary experimental methods and results, as well as on CF data analysis and interpretation. The third section of this chapter cites applications of CF data to service, the advantages and limitations of the experimental methods, and directions for research on CF experimentation. Symbols and terms are defined in the Nomenclature. This chapter, with extensive references, extends previous reviews of corrosion fatigue test techniques [4,5]. This chapter was published originally in 1995, the following literature in the Bibliography reflects new developments in Corrosion Fatigue.

Nomenclature

- $\Delta \sigma$: applied engineering true stress range in a fatigue load cycle, $\sigma_{\text{max}} - \sigma_{\text{min}}$, where $\sigma$ is load/initial cross-sectional area
- $\Delta \varepsilon_p$: true plastic axial strain range in a fatigue load cycle, $\varepsilon_{\text{pmax}} - \varepsilon_{\text{pmin}}$
- $\Delta \varepsilon_T$: true total axial strain range in a fatigue load cycle, $\varepsilon_{\text{Tmax}} - \varepsilon_{\text{Tmin}}$
- $\varepsilon$: true axial strain, $\ln (l/l_0)$
- $\varepsilon_d$: true diametral strain, $\ln (d/d_0)$

$\sigma_p$, $b$: Basquin relationship material property parameters
$\varepsilon_f$, $c$: Coffin-Manson relationship material property parameters
$N_f$: number of load cycles for specimen failure by fatigue
$N_i$: number of load cycles for fatigue crack initiation
$N_T$: transition fatigue life, or number of load cycles where the magnitudes of the elastic and plastic axial strain ranges are equal
$\Delta a/\Delta N$: macroscopically averaged fatigue crack growth rate
$a$: fatigue crack length
$N$: fatigue load cycle count
$\Delta K$: applied stress intensity factor range, $K_{\text{max}} - K_{\text{min}}$
$A$, $m$: Paris Law material property constants
$\Delta K_{\text{TH}}$: threshold stress intensity range
$R$: stress ratio, $K_{\text{min}}/K_{\text{max}}$
$\rho$: notch tip radius
$f$: loading frequency in cycles per s or Hz
$1/\omega$: time-portion of the load cycle where CF damage occurs
$K_{\text{ISC}}$: threshold stress intensity for monotonic load SCC
$da/dt$: velocity of monotonic load SCC
$E_C$: free corrosion potential
$E$: modulus of elasticity
$\Delta K_{\text{eff}}$: effective stress intensity range, $K_{\text{max}} - K_{\text{cl}}$
$K_{\text{cl}}$: stress intensity value in a fatigue load cycle where crack-surface closure contact is experimentally resolved and operationally defined
$\Delta K_0$: stress intensity range at a fixed crack length, $a_0$
$C$: constant in the $\Delta K$-control equation with units of mm$^{-1}$
$da/dt_f$: time-based crack growth rate in fatigue, often approximated by $(da/dN)(f)$

CF: corrosion fatigue
SCC: stress corrosion cracking
HCF: high-cycle fatigue
LCF: low-cycle fatigue
FCP: fatigue crack propagation
HEE: hydrogen environment embrittlement
H: atomic hydrogen
HCP: hexagonal-closed-packed
LEFM: linear elastic fracture mechanics
SN: stress range versus life
CP: cathodic polarization
cpm: cycles per minute
Mode I: applied load perpendicular to the crack plane and growth direction [6–8]
Mode II: applied load parallel to the crack plane and the crack growth direction

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2 CORROSION TESTS AND STANDARDS MANUAL

Mode III applied load parallel to the crack plane and perpendicular to the growth direction

νe Poisson’s ratio for isotropic elastic deformation, often taken as 0.33

LVDT Linear Variable Differential Transformer

EPD electrical potential difference

BASIC PRINCIPLES

Fundamentals of Corrosion Fatigue

Definition

Corrosion fatigue is defined as the sequential stages of metal damage that evolve with accumulated load cycling, in an aggressive environment compared to inert or benign surroundings, and resulting from the interaction of irreversible cyclic plastic deformation with localized chemical or electrochemical reactions. Environment-enhanced fatigue is a modern term; however, corrosion fatigue is traditionally used when emphasizing electrochemical environments. Mechanical fatigue experiments and analyses, detailed in recent textbooks [6–8], provide the basis for understanding CF.

Stages of Corrosion Fatigue

CF damage accumulates with increasing load cycle count (N) and in four stages: (1) cyclic plastic deformation, (2) microcrack initiation, (3) small crack growth to linkup and coalescence, and (4) macrocrack propagation. A cardinal principle is to design a CF experiment to isolate and quantitatively characterize one of these four stages. The methods in this chapter are organized as follows: (1) smooth specimen life for high cycle fatigue (HCF) described by ∆σ versus Nf data, (2) smooth uniaxial or notched specimen life for low cycle fatigue (LCF) described by ∆εp versus Nf or ∆K/√ρ versus Nf, respectively, and (3) fatigue crack propagation (FCP) kinetics described by da/dN versus the fracture mechanics ∆K.

Mechanisms

It is important to understand damage mechanisms in order to correctly interpret and extrapolate laboratory CF data. Similar to SCC, the mechanism for CF may involve hydrogen embrittlement; film rupture, dissolution and repassivation; enhanced localized plasticity; interactions of dislocations with surface dissolution, films or adsorbed atoms; and complex combinations of these processes [9–16]. The contribution of each mechanism is controversial and depends on metallurgical and environment (thermal and chemical) variables. While providing significant insight, existing mechanism-based models are generally not capable of accurately predicting CF behavior beyond the range of laboratory data.

Hydrogen environment embrittlement (HEE) is an important mechanism for CF crack propagation in ferritic and martensitic steels, as well as aluminum, titanium, and nickel-based alloys exposed to gases and electrolytes within order of 100°C of ambient temperature [15–21]. This hypothesis is supported by extensive but circumstantial evidence, and is most readily accepted for high-strength alloys in strong hydrogen-producing environments. In HEE atomic hydrogen chemically adsorbs on strained-clean initiation sites or crack surfaces as the result of electrochemical reduction of hydrogen ions or water. (Adsorbed hydrogen is also produced by the reactions of H2, H2O, C2H2, or H2S molecules with metal surfaces.) Hydrogen production follows mass transport within the occluded crack (pit or crevice) solution, crack tip dissolution, and hydrolysis of cations for local acidification; and precedes hydrogen diffusion by lattice, interface, or dislocation processes in the initiation-volume or crack tip plastic zone. Fatigue damage is promoted by hydrogen-affected lattice bond decohesion, grain or dislocation cell boundary decohesion, enhanced localized plasticity, or metal hydride formation (in materials such as HCP titanium-based alloys). Hydrogen-enhanced CF cracking is either intergranular or transgranular, with the latter involving dislocation substructure, low index crystallographic planes, or interfaces.

A second mechanism for CF is based on damage by passive film rupture and transient anodic dissolution at a surface initiation site or crack tip. This model was developed with several necessary empirical elements to predict CF propagation in carbon and stainless steels in high-temperature pure water [22,23], and is sometimes applied to titanium and aluminum alloys in aqueous chloride solutions. Localized plastic straining, described by continuum mechanics or dislocation plasticity, ruptures the protective film. Crack advance occurs by transient anodic dissolution of metal at the breached film, and at a decreasing rate while the surface repassivates pending repetition of this sequence. The increment of CF growth depends Faradaically on the anodic charge (transient current-time integral) passed per load cycle. Charge is governed by clean-repassivating surface reaction kinetics for the CF-sensitive alloy microstructure in occluded crack solution, and by the time between ruptures given by local strain rate and film ductility. As with the hydrogen mechanism, film rupture modeling is complex and controversial; confirming data exist [22,23], but other research shows the model to be untenable for specific alloy/environment systems [24].

Several CF mechanisms were proposed based on interactions between dislocations and environment-based processes at initiation sites or crack tip surfaces. For example, in-situ transmission electron microscopy and dislocation modeling show that adsorbed hydrogen localizes plastic deformation in several pure metals and alloys [25]. Second, reaction-product films are not capable of extensive plastic deformation relative to the underlying metal, and may cause CF damage by one or more processes, viz: (1) interference with the reversibility of slip, (2) localization of persistent slip bands, (3) reduction of near-surface plasticity leading to reduced or enhanced CF depending on the cracking mechanism, (4) localization of near-surface dislocation structure and voids, or (5) film-induced cleavage [14,15,26–28]. Adsorbed cations could similarly affect fatigue [29]. Finally, anodic dissolution may eliminate near-surface work hardening and hence stimulate fatigue damage [30]. These mechanisms have not been developed and tested quantitatively.

Factors Controlling Corrosion Fatigue

Two considerations are central to understanding the effects of mechanical, metallurgical, and chemical variables
on CF. The influences of electrolyte composition, conductivity, pH, electrode potential, temperature, viscosity, and biological activity are governed by the mass transport and electrochemical reaction conditions within occluded pits, crevices, or cracks, including the role of strain in creating reactive clean surfaces [31,32]. Second, CF can be time-dependent. Crack growth is often rate-limited by one or more of the slow steps in the mass transport and crack surface reaction sequence; slow loading rates enhance CF damage [17]. Increased crack tip strain rate is deleterious when the extent of per-cycle electrochemical reaction is promoted [22–24].2

Variables that affect CF were reviewed elsewhere [15–17]. Important factors are cited here to illustrate important CF test methods and to guide data interpretation.

**Mechanical Variables**

An important issue is the influence of an electrochemical environment on the cyclic deformation behavior of metals [14,33–35]. As illustrated by the data in Fig. 1 for a carbon-manganese steel in high-temperature water, environment does not typically affect the relationship between stresses and strains derived from the maximum tensile (or compressive) points of steady-state (saturation) hysteresis loops [36]. Such loops should relate to elastic and plastic deformation prior to substantial CF microcracking. CF data of the sort shown in Fig. 1 are produced by either stress or total strain controlled uniaxial fatigue experiments, identical to the methods developed for measuring purely mechanical cyclic stress-strain data [8,37]. While macroscopic constitutive properties may not be environment sensitive, slip localization can be affected by electrochemical reactions [14,33].

**Mechanical Driving Forces**

Considering smooth specimens, the ranges of applied stress or plastic strain control the fatigue or CF responses of metals for HCF and LCF conditions, respectively. For HCF, smooth specimen CF life increases with decreasing elastic stress range, at cycles in excess of the transition fatigue life, $N_T$, according to the Basquin equation

$$\Delta\sigma = \sigma_f' (N_T)^{-b}$$  \hspace{1cm} (1)

and due to decreasing globally plastic strain at cycles less than $N_T$, according to the Coffin-Manson equation for LCF

$$\Delta\varepsilon_p = \varepsilon_f' (N_T)^{-c}$$  \hspace{1cm} (2)

Alternatively, Eq 1, divided by $E$ to relate $N_T$ to elastic strain range ($\Delta\sigma/E$), is added to Eq 2 in order to relate $N_T$ to total applied strain range, the sum of the elastic and plastic strain ranges.

The material property parameters for HCF and LCF ($b$, $c$, $\sigma_f'$, and $\varepsilon_f'$) depend on metallurgical, environmental, and time variables. Data in Fig. 2 show that the HCF life of AISI 4140 steel is degraded by aerated neutral NaCl solution, compared to similar fatigue lives for dry and moist air as well as deaerated chloride [38,39]. The data in Fig. 3 show that distilled water and aqueous 3% NaCl similarly degrade the LCF resistance of an unrecrystallized precipitation-hardened aluminum alloy [35]. The Basquin and Coffin-Manson relationships are generally obeyed for fatigue in electrochemical environments; however, multiple power law segments may occur. Critically, the HCF endurance limit or

![FIG. 1—The nil effect of environment on the cyclic stress-strain response of a C-Mn steel in moist air and pressurized water at 288°C [36]. Data are represented as true stress—true total strain range.](image1)

![FIG. 2—The deleterious effect of aerated aqueous chloride solution on the HCF life of smooth specimens of tempered martensitic AISI 4140 steel. Symbols with horizontal arrows indicate that CF failure has not occurred after 107 load cycles [36].](image2)
threshold stress range can be eliminated by the action of the electrolyte, as illustrated in Fig. 2. A common explanation for this effect is pitting-based CF crack initiation. Rates of CF crack propagation are uniquely defined by the linear elastic fracture mechanics stress intensity factor range that combines the effects of applied load, crack size, and geometry \[17,40\]. The similitude principle states that fatigue and CF cracks grow at equal rates when subjected to equal values of \(\Delta K\) \[6–8\]. The \(da/dN\) versus \(\Delta K\) relationship may be complex; however, an effective approach is based on a power (or Paris) relationship of the form \[41\]

\[
da/dN = A \Delta K^n
\]  

\(\Delta K\) is limited to stress intensity changes above zero because compressive loads do not cause appreciable crack tip plastic strain and damage. The material properties \((A\) and \(m))\) depend on environmental and time variables. For metals in vacuum and moist air, FCP is described by a single power law and an apparent threshold stress intensity range below which \(da/dN\) tends to zero \[42\]. More complex cracking behavior is observed for CF, as illustrated for aqueous chloride solution-enhanced FCP in titanium (Fig. 4) and advanced aluminum-lithium-copper alloys (Fig. 5) \[43,44\]. Note the complex \(\Delta K\)-dependence of \(da/dN\) for FCP in chloride solution, but not vacuum or moist air. Environmental effects on Paris regime FCP have been characterized broadly; however, data on near-threshold CF \((da/dN < 10^{-6}\) mm/cycle) are scarce \[16,42\].

Crack closure can strongly affect fatigue and CF \[45\]. This phenomenon is based on crack surface contact during unloading, critically at stress intensity levels above zero and applied-positive \(K_{\text{min}}\) values. Crack wake contact is caused by corrosion debris, plasticity, crack path roughness, or phase transformation products; each mechanism may be sensitive to aqueous environmental reactions \[6\]. To account for closure, \(da/dN\) is correlated with an effective stress intensity range that is defined operationally as the difference between applied \(K_{\text{max}}\) and the \(K_c\) level where surface contact is resolved (see Data Analysis and Evaluation in this chapter).

\[\Delta K\text{, Stress Intensity Range, MN m}^{-3/2}\]

\[
a/\Delta N, Crack Growth Rate, In 10^{-8}\text{mm/cycle} \times 10^{18} \]  

\(\Delta K\) is calculated assuming a sharp crack of length and geometry equivalent to the notch. This method is a reasonable alternative to a finite element or Neuber analysis of notch strain, but only for crack-like notches of the sort shown by the insert in Fig. 6 \[7\].

CF crack formation in notched specimens is most effectively characterized by the notch-root plastic strain range calculated by Neuber’s method, elastic-plastic finite elements, or fracture mechanics approximation \[7,8\]. The latter approach is illustrated in Fig. 6, showing the results of over 100 experiments with C-Mn and alloy steels in aqueous chloride solution compared to moist air \[8,46–48\]. The load cycles to produce 1 mm of fatigue crack extension, measured optically, increase with decreasing \(\rho \Delta K\), an estimate of notch root \(\Delta\varepsilon_p\), for air and chloride solution. At fixed \(\Delta K/ \rho\), Ni is reduced by chloride exposure at free corrosion, relative to fatigue in moist air. An endurance limit is observed for moist air, but not this CF case. Cathodic polarization (CP) restores a portion of the moist air fatigue initiation/early growth life, as discussed in an ensuing section.

Loading Frequency (Frequency Domain Issues)—Slow frequency CF experiments may be necessary because of mass transport and electrochemical reaction rate limitations on
damage, but are challenging because of prolonged test time. The generally deleterious effect of decreasing $f$ on smooth specimen CF life is illustrated in Fig. 7 for an LCF case involving a C-Mn pressure vessel steel, corroding freely in high-temperature water with varying dissolved oxygen levels between 0.01 and 8 ppm. (The free corrosion potential for these steel CF specimens increases as the dissolved oxygen concentration increases.) For fixed $\Delta \varepsilon$, the ratio of $N_f$ for fatigue in water to that for air, each at 270°C, declines with decreasing average total strain rate (proportional to frequency) [36]. LCF lives are rate-independent for fatigue in laboratory air at low to moderate temperatures where creep is minimal.

Frequency effects on CF crack propagation have been characterized broadly and modeled based on the HEE and film rupture mechanisms [16–18,22–24]. FCP rates are $f$-independent for alloys in moist air, inert gases such as N$_2$ or Ar, or vacuum at low to moderate temperatures. For CF, there are three possible frequency responses: (1) purely time-dependent, where $da/dN$ increases with decreasing frequency proportional to $(1/\alpha f)$, (2) cycle-time-dependent, where $da/dN$ increases with decreasing frequency proportional to $(1/\alpha f)^\beta$ with $\beta$ on the order of 0.5, and (3) cycle-dependent, where $da/dN$ is environmentally enhanced but frequency-independent. The parameter $\alpha$ gives the proportion of the load-cycle time that produces CF damage, and is often taken as 2 for a symmetrical cycle, since environmental cracking may not occur during unloading [16]. An alternative model of the frequency effect considers that...
electrochemical reactions occur throughout the entire load-cycle [17]. A single alloy/environment system can exhibit each da/dN-f relationship, depending on ∆K, f, and alloy composition, as illustrated for aged 7000 series aluminum alloys (AA) (Fig. 8) and steels (Fig. 9) [18,49–51]. These plots illustrate the two usual ways of presenting frequency-dependent CF da/dN data, with the abscissa as either log (f) or log (1/αf). The f range where da/dN is most circle-time dependent varies with mass transport and reaction kinetics that are material-environment sensitive.

Time-dependent cracking is observed for high-strength SCC-prone alloys when K_{max} in the fatigue cycle is above K_{ISCC} and da/dt is rapid. This case, illustrated in Fig. 8 for AA7079 at f < 1 Hz and for AA7075 at f < 0.001 Hz, is modeled by linear superposition of SCC da/dt and inert environment da/dN data [49,52,53]. Cycle-time-dependent CF (or cyclic stress corrosion cracking) involves substantial CF at ∆K levels that are below K_{ISCC} or where da/dt is slow. This

response is illustrated for AA7017 and AA7475 (Fig. 8) in seawater and acidified NaCl, respectively, and for two steels in neutral NaCl with cathodic polarization (Fig. 9), each at fixed ∆K and R [18,50,51]. In both systems, β is 0.3 to 0.6. Note (Fig. 9) that cycle-time-dependent da/dN achieves a plateau or saturation level at slow frequencies below a critical value that depends on steel composition. The third case, f-independent CF, is illustrated for AA7075 in 80°C chloride solution (Fig. 8) and for the two steels at high frequencies in NaCl at 25°C (Fig. 9) [49,51]. This response (true corrosion fatigue) is often observed at low ∆K, at high loading frequencies, or for alloys that resist environmental cracking. In some cases CF da/dN increases with increasing f. This behavior is illustrated in Fig. 4 for a titanium alloy at low ∆K; in addition, note a crossover to time-dependent CF above 20 MPa√m and time-cycle-dependent CF at intermediate ∆K [43].

Figure 10 illustrates the minimal effect of loading frequency on CF crack formation and early growth for blunt notched steel specimens in aqueous chloride solution at free corrosion [46]. These data are notable for the rare combination of low f and high cyclic lives (175 days were required to obtain 3 × 10^6 cycles at 12 cpm), and for the lack of a frequency effect on the cycles required to produce 1 mm of CF cracking. This result indicates that one or more of the early

FIG. 9—The effect of loading frequency on CF propagation in API-2H and A710 steels, at the 625 to 750 MPa yield strength level, exposed to aqueous NaCl solution with CP to -1000 mV/CE at constant ∆K and R [51].

FIG. 11—The effect of environment on tensile and torsional high-cycle corrosion fatigue in the 7075/NaCl solution system [57].
stages of CF (cyclic plastic deformation, pitting, crack nucleation, and small crack growth) are frequency-insensitive, consistent with the \( f \)-independence of long crack CF at low \( \Delta K \) for many alloys including steels in NaCl [16,51]. Results of the sort shown in Fig. 10 are limited and this behavior has not been modeled.

**Other Mechanical Factors**

Applied load or strain waveform, stress ratio, load spectrum, and overloads can affect CF [16,22,23,54–56]. This chapter emphasizes uniaxial tensile loading of CF specimens because environmental effects on fatigue under torsional or multiaxial loading have not been studied. An exception is illustrated in Fig. 11, showing fatigue life data for smooth specimens of AA7075 in moist air and aqueous NaCl [57]. Note the strong environmental degradation of \( N_f \) for uniaxial loading represented by normal stress range (\( \Delta \sigma \)), but a reduced effect for torsion at a given applied shear stress range. Such results can be explained based on the deleterious role of triaxial tensile stresses, and the associated high hydrostatic (mean) tension, in CF propagation by HEE; this stress state is present for uniaxially loaded Mode I cracks, but not for torsional loading and Mode II or III cracks. Fatigue initiation may be similarly environment-enhanced for uniaxial tensile and torsional loading, explaining the modest reduction in \( N_f \) for torsion (Fig. 11).

**Electrochemical Variables**

**Electrode Potential**

Both anodic and cathodic polarization can affect CF, with different trends observed for crack initiation compared to propagation, and for steels compared to either aluminum or titanium alloys. For ferritic and martensitic steels in aqueous chloride solution, high-cycle CF occurs at electrode potentials near free corrosion for aerated solution (\( E_c \approx -650 \text{mV SCE} \)), but is often reduced in severity or eliminated by cathodic polarization to near –1000 mV SCE [58]. This behavior is illustrated in Figs. 6 and 12 for notched and smooth-uniaxial fatigue specimens, respectively [47,59]. CF of polished specimens of 1020 and 4140 steels, exposed to NaCl during high-frequency rotating bending, occurred only if a critical anodic current was exceeded [38,39]. In this study, CF was essentially eliminated by solution deaeration which reduced the steel corrosion rate current and free corrosion potential (Fig. 2). Applied cathodic polarization similarly reduced CF of polished specimens.

Understanding the effect of applied polarization on CF propagation requires a description of crack tip electrochemistry, particularly local pH and potential, as affecting the kinetics of passive film formation, dissolution, hydrogen production, and hydrogen entry. Occluded crack processes are complex, as are the observed dependencies of CF \( da/dN \) on electrode potential. For example, CF crack growth rates for steels in chloride increase with increasing cathodic polarization, with a modest minimum in \( da/dN \) at about 200 mV active to the free corrosion potential [16,20]. Figure 13 illustrates that the environmental enhancement of \( da/dN \) increases with the total rate of H production at the crack tip, raised to the \( \sim 4 \) power, for C-Mn steel in NaCl (\( E_c = -675 \text{mV SCE} \)), polarized between –750 and –1325 mVSCE [16]. Hydrogen production was calculated from a crack chemistry model [60]. For this system, solution deaeration does not affect CF \( da/dN \) when electrode potential is fixed potentiostatically [61]. The opposite effects of polarization on smooth specimen CF life and crack propagation in steel can be reconciled. Dissolution and pitting probably govern environment-enhanced fatigue crack initiation [14,38,39]; hydrogen plays a secondary role for the fast loading frequencies, near-threshold stress intensities, and uniaxial stress states typical of smooth specimen studies. Slow loading frequencies and crack tip hydrostatic tension promote crack growth by HEE. Here, important contributions to crack tip hydrogen production are from crack acidification near free corrosion and water reduction at cathodic potentials [16,60].

Cathodic polarization of aluminum and titanium alloys in chloride provides an interesting contrast to steels. Duquette
and others reported that the fatigue lives of smooth specimens of AA7075 and Al-Mg-Li in NaCl solution were maximum at potentials mildly active of free corrosion; both anodic and highly cathodic polarization degraded corrosion fatigue life \cite{15,57,58}. CF propagation occurs at the free corrosion potential, is exacerbated by either anodic polarization or extreme cathodic polarization, and is arrested by modest cathodic polarization. This trend was demonstrated for AA7079, AA7075 and AA2090 in NaCl and explained based on HEE \cite{19,62,63}. At negative potentials from cathodic polarization, crack tip hydrogen production may be reduced by the effect of alkaline occluded-crack solution on the overpotential and exchange current density for hydrogen production on strain-bared surfaces, and hydrogen uptake may be blocked by crack surface films.

Sulfur Ion Content

Sulfur ions in electrolytes exacerbate CF crack propagation in many alloys. Various forms of sulfur are important in sour oil or gas well and geothermal brine environments, and are also produced in unlikely ways. For example, the $\frac{d\sigma}{dN}$ versus $\Delta K$ data in Fig. 14 show the CF behavior of martensitic HY130 steel in sterile 3.5% NaCl solution with CP, an environment that enhances cracking by two- to eight-fold relative to moist air and more compared to FCP in vacuum. Note the strong environmental effect caused by a sulfate reducing bacteria (SRB; desulfovibrio vulgaris) cultured in Postgate C food-medium and with cathodic polarization \cite{64}. These, and similar data for both biologically active and abiotic gaseous H$_2$S saturated sterile chloride solutions, are interpreted based on sulfide-stimulated HEE \cite{64,65}. Bacteria metabolize the food-source and consume hydrogen to produce sulfide ions and other sulfur species. These anions poison recombinant hydrogen desorption to reduce H$_2$ production and increase hydrogen entry into the metal at the crack tip, similar to the deleterious effect of dissolved H$_2$S.

In a second example, CF is promoted by increased impurity-sulfur in ferritic steels subjected to low-frequency loading in pressurized pure water at 288°C (Fig. 15) \cite{22,23}. MnS inclusions, which intersect crack flank surfaces, dissolve to enrich the occluded crack solution in sulfide. These anions promote crack advance by increasing the anodic charge that is passed per film rupture event, or perhaps by the HEE mechanism. This effect of steel sulfur content is severe for a stagnant environment within the autoclave, and is eliminated by turbulent solution flow which reduces sulfide buildup within the crack \cite{66}.

Other Chemical Factors

Solution pH, ionic composition, conductivity, and temperature can affect CF \cite{14-17,22,23,43,58}.

Metallurgical Variables

Metallurgical factors can influence CF crack initiation and growth. Prominent in this regard are sensitization of grain boundaries in austenitic stainless steels \cite{22,23}, locally intense slip in aluminum alloys from dislocation interactions with shearable precipitates \cite{67}, and metalloid
impurities segregated to grain boundaries in steels [68]. CF crack initiation often occurs at surface intersecting inclusions that concentrate strain and may dissolve to produce a locally aggressive environment [69]. CF crack propagation in the ferritic steel/aqueous chloride system is apparently not affected by substantial changes in steel composition, microstructure, and yield strength [57]. In another case, aluminum alloy processing route, and the resulting degree of recrystallization and grain size, did not substantially affect aqueous environmental LCF life and FCP kinetics [35,44,70]. Increasing copper content in precipitation-hardened Al-Zn-Mg alloys reduced the environmental enhancement of $da/dN$, with the importance of the effect depending on aging condition [67].

**Relationship between CF and SCC**
Corrosion fatigue is related to, but uniquely distinct from, SCC [77]. Purely time-dependent CF crack propagation in SCC-prone alloys is governed by the integrated amount of time-based crack extension per fatigue load cycle. In such cases CF and SCC occur by the same mechanism and are affected by the same variables, as modeled by simple linear superposition [49,52,53]. SCC is discussed elsewhere in this manual.

Time-cycle- and cycle-dependent CF are more complex, involve unique mechanisms, and occur at stress intensities where SCC is insignificant. In these cases, the CF damage mechanism is unique for reasons traceable to cyclic loading, and including: (a) increased crack tip strain rate [22–24], (b) resharpening of the blunted crack geometry during unloading, particularly at high $\Delta K$, (c) altered crack chemistry by convective mixing [72], (d) evolution of persistent slip band, slip step, and dislocation cell structures into embryonic damage, often at low $\Delta$e or low $\Delta K$ [73,74], and (e) mobile dislocation transport of hydrogen in the crack tip process zone [18,50]. These additional factors must be considered when interpreting and modeling CF data [16].

**Literature Sources for CF Data and Mechanisms**
In addition to the examples presented in Figs. 1 through 15, extensive CF data have been published in several volumes [1,2,9–12,58,75–78].

**TESTING TECHNIQUES**

**Common Elements of a Corrosion Fatigue Experiment**
An experiment to characterize the CF properties of a metal involves cyclic straining of a precisely machined specimen in an electrolyte. (Precorrosion effects on fatigue are not considered.) Environment contamination about the specimen must guarantee constant solution purity and composition. Specimen potential should be monitored, often controlled potentiostatically, and not affected by galvanic coupling to the grips or test machine. The mechanical parameters that must be measured depend on the experiment, be it HCF, LCF, LEFM-crack propagation or notched, and are progressively more difficult to monitor from the HCF to notched cases. CF experiments follow directly from procedures for mechanical tests with benign environments; the latter are well-developed and standardized, while CF experiments are not. For example, ASTM Committee G-1 has published 14 standards or practices for SCC experiments (see Volume 03.02, Section 3 of the Annual Book of ASTM Standards), but none for corrosion fatigue.

CF experiments are hindered by several common factors. Aggressive environments are difficult to contain at a constant condition, and hinder precise measurements of specimen displacement, load, and crack size. CF is influenced by many interactive mechanical, chemical, and microstructural variables that must be factored into experimental design. It is often necessary to investigate slow-rate deformation and cracking phenomena in a realistic time; experiments must be conducted for one day to one year or more. CF damage is localized at surface slip structure and near the crack tip; high resolution observations are not generally available and behavior must be interpreted from indirect measurements.

**Smooth Specimen $\Delta$e-Life Method for High Cycle CF**

**Governing Standards**
Experiments to characterize high cycle CF life according to the Basquin Law (Eq 1) follow from ASTM standards for metals in moist air (see ASTM E 466, Practice for Conducting Constant Amplitude Fatigue Tests of Metallic Materials; and E 468, Practice for Presentation of Constant Amplitude Fatigue Test Results for Metallic Materials). Such methods were detailed for steels and aluminum alloys in aqueous chloride solutions [38,39,57–59,69,79,80]. Typical data are presented in Figs. 2, 11, and 12.

**Specimens and Loading**
High-cycle CF specimens focus failure in a carefully prepared reduced-uniform or mild-blend-radius gage section, often of circular cross-section and with ends for gripping in the fatigue machine. Typical specimen designs are shown elsewhere, including methods for low-damage gage machining and polishing (see ASTM E 466 and Ref 81). HCF specimens are loaded in uniaxial tension or bending (three-point, four-point, or cantilevered) with electromechanical, servohydraulic, or rotating wheel/mass machines, and grips of various designs (see ASTM E 466 and Ref 81). Elastic straining is load or displacement controlled; involves either negative, zero, or positive mean stress; and varies with time symmetrically in a sinusoidal or linear-ramp waveform. Since CF is dominated by electrochemical surface damage, $N_f$ could decrease and variability may increase with increasing surface area that is stressed.

High-cycle corrosion fatigue experiments are conducted for 105 to 109 cycles to failure, at a relatively high frequency of 25 to 100 Hz to conserve time. ($N_f$ of 106 cycles requires 5.5 h, while 109 cycles require 230 days of continuous loading at 50 Hz.) Multiple, reliable, and inexpensive rotating-bend machines are often dedicated to these experiments. Caution is required when extrapolating the results of relatively rapid frequency experiments, to lower $f$ and/or the very long life regime in excess of $10^9$ cycles.
Environmental Cell Design

The design of the environmental cell depends on electrolyte and temperature. A typical cell is illustrated in Fig. 16 for containing aqueous chloride solution at ambient temperature [79]. Glass, Flexiglas®, Teflon®, or other plastics are adequate cell materials. The specimen is gripped outside of the test solution to preclude galvanic effects, and the cell is sealed to the round or square/rectangular specimen with O-rings away from the high-stress gage section. Solution can be circulated from a large storage volume and at a constant flow rate. The cell should include reference and counter electrodes to enable specimen (working electrode) polarization with standard potentiostatic (or galvanostatic) procedures [38,39,59,79]. When fixing potential or current, care should be taken to correctly ground or isolate the test specimen, to uniformly polarize the gage surface, to account for IR effects when necessary, and to isolate counter-electrode reaction products. Provided that potential is controlled, there is probably no reason to control the oxygen content of the solution. Temperature is maintained between subzero and boiling levels with a heater or cooling coil, a specimen thermocouple, control electronics, and a condensation apparatus. Cells for more complex environments are detailed in ensuing subsections on Environmental Cell Design.

Parameter Measurement, Control, and Computer Automation

The maximum and minimum applied loads (or, alternately, displacements) are measured with a load cell (or remotely attached extensometer/LVDT) and controlled during a HCF experiment. \( \Delta \sigma \) is calculated from standard elastic solutions for bars under uniaxial tension, or beams subjected to bending. Elastic strain range is calculated from \( \Delta \varepsilon / E \) and gage displacement is not typically measured.

Crack Detection

Total load cycles to failure are measured, but crack initiation and growth are not monitored during an HCF experiment. Information on these stages of HCF is critical, but difficult to obtain. Methods for CF crack detection are discussed in the subsection on Small Crack CF Methods.

Data Analysis and Evaluation

High-cycle CF data are presented in a logarithmic plot of stress range versus cycles to failure according to the Basquin Law (Eq 1). Data are also plotted as stress amplitude (\( \Delta \sigma / 2 \)) versus reversals to failure (\( 2N_f \) for simple waveforms). The Basquin Law is based on the initial applied elastic stress range and does not consider the complicating effect of a growing crack on \( \Delta \sigma \). Material property constants \( \sigma_y, b \), and the endurance limit (or fatigue strength at a given number of cycles) are environment-sensitive. The mechanical information that should be reported with HCF data is standardized (see ASTM E 468), and electrochemical factors should be cited as discussed in this manual.

Design and alloy development studies require mean as well as minimum (lower bound) Basquin relationships and statistics on the distribution of \( \Delta \sigma \) versus \( N_f \) data. This distribution depends on the fatigue damage mechanism. Most CF studies have not provided such information, often because of time-intensive slow frequency experiments and the many important variables. A sense of the variability in CF data is portrayed by the extensive HCF results collected for C-Mn and alloy steels in marine environments [58]. The distribution of HCF lives at a given stress range was analyzed based on Weibull statistics applied to a data base of 30,000 points for steels in benign environments [82]. While instructive, these statistical results are not necessarily relevant to high-cycle CF where electrochemical reactions introduce additional variability.

Future work must address two areas to provide the foundation for statistically based analyses of high-cycle CF (as well as environmental LCF and FCP). For simple laboratory conditions, the Weibull analysis of mechanical HCF failure probability [82] must be extended to include CF. Second, variable load, temperature, and environment chemistry histories are likely to be complex in applications and significantly affect CF life. Such history effects have not been studied. The scaling of Basquin relationship data to predict the life of a structure is qualitative and uncertain. Either the local strain approach to CF crack formation/early growth life or the fracture mechanics analysis of CF propagation provide a better foundation for life prediction and failure analysis.

Smooth Specimen \( \Delta \varepsilon_p(N) \) Method for Low-Cycle CF

Governing Standards

Experiments to characterize low-cycle CF life according to the Coffin-Manson relationship (Eq 2) follow from an ASTM standard for LCF of metals in air, and a classic ASTM manual on laboratory methods (see Ref. 37 and ASTM E 606, Practice for Strain-Controlled Fatigue
Testing). Low-cycle CF experiments are detailed elsewhere [33–36, 74,83], and typical data are presented in Figs. 3 and 7.

Specimens and Loading

Uniform-gage or mild-radius (hourglass) round specimens are subjected to uniaxial tensile loading with rigid gripping and a test machine that provides for either tension-compression or tension-tension strain cycling. Square or rectangular specimens have also been successfully employed. Specimen alignment is critical for this rigid gripping system [81]. Total axial displacement is generally controlled, with regard to maximum and minimum limits as well as time-dependence, while load is measured, often with a computer-automated servoelectric or servohydraulic closed-loop test machine. Such machines provide a variety of strain-time profiles. Loading frequencies are typically less than those employed for HCF experiments because failure occurs in less than 104 cycles. Low-cycle CF experiments differ from the HCF case in that gage displacement must be measured with sufficient resolution to apply $\Delta \varepsilon_P$ between $10^{-4}$ and $10^{-1}$.

Environmental Cell Design

Cells for environment containment and control are identical for LCF and HCF (see previous subsection with this title). LCF cells are, however, more complicated because of the requirement to measure specimen gage displacement, as illustrated in Fig. 17 [33,36]. For simple aqueous environments, diametral or axial displacement is measured by a contacting (but galvanically insulated) extensometer, perhaps employing pointed glass or ceramic arms extending from a body located outside of the solution. A hermetically sealed extensometer or LVDT can be submerged in many electrolytes over a range of temperatures and pressures. Alternately, the specimen can be gripped in a horizontally mounted test machine, and half-submerged in the electrolyte, with the extensometer contacting the dry side of the gage (Fig. 17a) [33]. For both simple and aggressive environments, grip displacement can be measured external to the cell-contained solution, as shown in Fig. 17b for high-temperature water in a pressurized autoclave [34,36]. It is necessary to conduct LCF experiments in air (at temperature), with an extensometer mounted directly on the specimen gage, to relate grip displacement and specimen strain.

Parameter Measurement, Control, and Computer Automation

Applied load and gage displacement are measured throughout an LCF experiment. From these data, it is possible to calculate true $\Delta \sigma$, $\Delta \varepsilon_T$, and $\Delta \varepsilon_P$, where axial plastic strain range equals $(\Delta \varepsilon_T - \Delta \sigma/E)$. For the hourglass specimen, true total diametral strain can be measured at any time, and converted to axial strain according to [37]

$$
\varepsilon = (\sigma/E)(1 - 2\nu) - 2\varepsilon_d
$$

(4)

If $\Delta \varepsilon_T$ or $\Delta \varepsilon_d$ is maintained constant by the test machine, then $\Delta \sigma$ increases and $\Delta \varepsilon_P$ decreases until the hysteresis loop stabilizes at a constant form for a cyclically hardening material, and vice-versa for a softening alloy [7,37]. The stabilized-loop value of axial $\Delta \varepsilon_P$ is used in the Coffin-Manson Law to correlate $N_f$. When substantial crack growth occurs, these stress and strain range calculations are not accurate. Experiments are often terminated and failure is defined for a percent decline in $\Delta \sigma$. Total strain rate, average plastic strain rate, or the frequency of displacement cycling should be maintained constant during the low-cycle corrosion fatigue experiment.

Personal computer programs are available to control the closed-loop test machine during an LCF experiment and to analyze load-displacement-time data.

Crack Detection, Data Analysis, and Evaluation

These procedures are identical for LCF and HCF, as discussed in the previous subsections, Crack Detection and Data Analysis and Evaluation.

Fracture Mechanics Methods for Corrosion Fatigue Crack Propagation

Governing Standards

Experiments to characterize CF crack propagation kinetics, in terms of LEFM Paris relationships (Eq 3) and near-$\Delta K_{TH}$
data, are guided by an ASTM standard for metals in air (ASTM E 647, Test Method for Measurement of Fatigue Crack Growth Rates), a compilation of laboratory experience with this standard [84], and a review of inert environment FCP testing [85]. The ASTM standard contains an appendix specific to CF crack growth in marine environments (ASTM E 647 and Ref 86). Procedures for CF in other environments are not standardized; however, methods have evolved for specific technologies [2,4]. CF da/dN data are presented in Figs. 4, 5, 8, 9, and 13 to 15.

Specimens and Loading

CF crack propagation data are obtained with a variety of notched and precracked specimen geometries that are well-characterized in terms of stress intensity and compliance functions [85,87]. The Mode I compact tension, single-edge crack, three- or four-point bend, and center-cracked tension specimens are used commonly, and are prepared based on standardized procedures (ASTM E 647). Specimen in-plane dimensions are selected to guarantee elastic deformation with limited small-scale crack tip plasticity. Specimen thickness, and the plane stress or plane strain deformation state, is a variable. Closed-loop servohydraulic test machines are most effective for CF propagation experiments, with the control parameter being load. (Load-line displacement or crack mouth opening displacement control are sometimes used.) Such machines provide a range of load or displacement waveforms (sinusoidally time-dependent is typical) and frequencies (10−4 to 100 Hz are typical values).

Environmental Cell Design

Cells for CF crack propagation experiments are designed to control solution composition and specimen electrochemistry analogous to HCF and LCF (see previous subsections with this title), while allowing for measurements of applied load, crack opening displacement, and crack length. A variety of approaches is reviewed elsewhere, including electrochemical details for several environments [4]. Two cells for ambient temperature electrolytes are shown in Fig. 18. If the test machine and loading axis are mounted in a horizontal plane (90° to the normal orientation), then the compact tension crack tip can be dipped into solution which is exposed to air without complex sealing (Fig. 18a). The alternate approach in Fig. 18b employs a vertical loading axis with a segmented Plexiglas or Teflon cell, sealed to the faces of the compact tension specimen with O-rings and including a short segment in the notch mouth. Solution flow is through the notch, parallel to the crack front. Small cells clamped to specimen surfaces (Fig. 18b) are equally effective for center-through-cracked plate specimens. Specimens with surface cracks or single-edge cracks are effectively contained in environmental cells that are large and sealed to the round or flat ends inboard from the gripping points [88]. Compact tension and surface crack specimens have been contained in pressurized metal autoclaves with electrolytes or steam at elevated temperature (Fig. 19) [89]. In this particular study, a yoke was employed to simultaneously test two specimens in one autoclave and load frame.

Reference and counter electrodes are readily employed in the various cells (e.g., Fig. 18b), perhaps with salt bridges to remote containers and including high pressure and temperature compensation capabilities. Procedures to eliminate galvanic couples and to maintain solution purity and composition are identical to those employed in HCF and LCF experiments. Crack opening displacement is measured with a remote or immersed extensometer or LVDT. The cell must not interfere with specimen loading or displacement. For example, in Fig. 18b, the shaded midportion is a flexible membrane designed so that cell clamping forces do not alter specimen compliance. This is important for accurate measurements of crack closure.

Typically, metal-bellows/gasket sealed HIGH VACUUM chambers are utilized for environmental fatigue experiments in inert or deleterious gaseous environments [4]. Such an apparatus is outside the scope of this review.
Crack Length Measurement

CF propagation experiments are unique in the need to monitor crack length, often over a long time. Much has been written on two widely employed methods, direct or alternating current electrical potential difference and compliance (see ASTM E 647, and Refs 84,90,91), as well as on less-tried methods such as eddy current, acoustic wave, optical, or crack surface marking [92]. Compliance and EPD are broadly calibrated and well-suited for precision (±25 µm or better), long-term-stable monitoring of crack length in many common fracture mechanics specimens and aggressive CF environments. These methods can be computer-automated for test machine and stress intensity control (see following subsection). The principles and instrumentation for each method are detailed elsewhere (ASTM E 647 and Ref 84).

Several points are pertinent to CF. First, compliance allows monitoring of both crack length and crack closure [93]. The advantage of the EPD method is simplicity; it is not necessary to immerse a displacement gage in the electrolyte. (The compliance scheme illustrated in Fig. 18b avoids this complication.) The EPD method is best-suited for monitoring the growth of surface fatigue cracks. Second, there is no evidence that the 1 to 50 A direct or alternating current used in the potential difference method affects CF kinetics. Presumably, the resistance to current flow through the metal is orders of magnitude lower compared to that of the most conductive solutions in an occluded crack. Voltage differences along a crack surface, and due to this current distribution in the metal, are small (less than 1 mV) and probably unimportant. Nonetheless, prudence dictates that the influence of applied current be tested by employing an independent monitor of crack length in limited qualification and calibration experiments. Third, the electrical potential signal often increases with increasing load in the fatigue cycle because electrically conductive crack surfaces are increasingly parted. Accordingly, potential should be measured at maximum load, and errors in crack length due to residual “crack surface-shorting contact” should be corrected based on post-test crack length measurements [94]. Finally, solution flow or temperature changes can upset the stability of the electrical potential signal due to thermally-induced voltages and material resistance changes.

Ground-loops between potentiostat and electrical potential crack monitoring electronics degrade the quality of polarization as well as CF crack length and growth rate measurements. A successful approach to this problem is based on a specimen (working electrode) that is grounded commonly with the test machine, constant-current power supply and EPD amplifier, coupled with a potentiostat that uses a grounded working electrode. In this case the specimen should not be grounded virtually through an operational amplifier. With this procedure, and the several-ohm (or larger) alternate current path through the typical loading system and test machine, it is not necessary to electrically isolate the CF specimen from the grips. As a test of ground-loop integrity in CF, guarantee that specimen electrochemical current does not change, at fixed electrode potential, upon reversing the polarity of the crack monitoring current.

Given the success of the direct-EPD method, with current applied through the bulk of the CF specimen, there is generally no need to employ an indirect method based on a foil gage bonded to the specimen surface and solely carrying the applied current. This latter method eliminates the effect of applied current on crack electrochemistry (if such an effect exists); however, long-term crevice and galvanic corrosion associated with the attached foil may be important. CF crack growth in the midregion of a specimen is reasonably indicated by compliance or direct EPD, but not by the surface-mounted foil gage method.

Parameter Measurement, Control, and Computer Automation

Applied load and crack length from electrical potential or compliance are measured as a function of load cycles during a CF experiment. Apart from simple constant load range (increasing ∆K) loading, modern FCP and CF experiments are computer-automated to control the ∆K-history, with the mode selection based on the goal of the work, be it mechanism- or application-based. Load is computer-varied, in real time and at frequencies between 10–4 and 50 Hz, to maintain the crack length dependence of stress intensity range according to (ASTM E 647)

$$\Delta K = \Delta K_0 \exp\left[C(a-a_0)\right]$$

R-value is typically maintained constant as ∆K changes. A programmed C of 0 yields a constant ∆K experiment, which
is useful for establishing transient and steady state CF growth rates for mechanistic research. Negative C-values provide for a ΔK-decreasing experiment for measuring near-ΔK_TH CF. Positive C gives a ΔK-increasing experiment that yields data in a reasonable time and confirms stress intensity governed cracking when used in conjunction with a negative C experiment. Guidance on those values of C that minimize the effect of prior load history is standardized (see ASTM E 647).4

Data Analysis and Evaluation

Applied stress intensity range and CF crack growth rate are calculated at regular crack length intervals, based on standardized analytical procedures (ASTM E 647). For continuously increasing or decreasing ΔK experiments, da/dN is calculated by either a point-to-point difference (secant) or incremental polynomial method. For constant ΔK, da/dN is determined by linear regression of cyclic crack length data. The simple secant calculation amplifies da/dN variability, while polynomial methods average the growth kinetics over seven (typically) a versus N points. Growth rate variations depend on the size of the crack growth interval. It is particularly challenging to establish physically meaningful variations from an average growth rate law.

FCP variability was considered in conjunction with an interlaboratory test program that measured da/dN versus ΔK for a well-behaved high-strength steel in moist air [95]. For this best case and 14 laboratories, da/dN variability from replicate standardized experiments within a single laboratory equaled between ±13% and ±50% (±2 residual standard deviations about the mean regression curve) at fixed ΔK. Variability in CF experiments has not been addressed quantitatively; however, the results from the moist air FCP program provide a lower bound. The increased complexity and prolonged test times typical of CF experiments, as well as the FCP behavior of more complex alloys, should lead to increased variability and uncertainty.

Two complications are notable for CF experimentation. CF da/dN versus applied ΔK data may be affected by a crack closure mechanism that depends on aqueous environment exposure (see subsection, Mechanical Variables) [6,45]; such CF growth kinetics are defined as an extrinsic property that may be test method-specific. As a diagnostic, if CF da/dN depends strongly on R, if the environmental ΔK_TH value is high and increases with decreasing loading frequency, or if crack arrest occurs during CF propagation at constant applied ΔK, then environment-sensitive crack closure should be suspected. A bilinear specimen compliance trace (of applied load versus crack mouth or load line displacement) confirms the presence of crack closure.

Closure is characterized and eliminated approximately for a given da/dN by reducing the applied ΔK to ΔK_eff, the difference between K_max and K_cl rather than K_max and K_min. K_cl is determined by a global compliance method that is nearing standardization [96]. CF da/dN versus ΔK_eff data, as well as results obtained at high constant R (above about 0.7) or high constant K_max (see Fig. 5 and subsection, Programmed Stress Intensity Experimentation), are reasonably closure-free and are an intrinsic property for a given material-environment system [62]. Closure-free CF data are necessary for basic studies of crack tip process zone damage mechanisms, while crack closure phenomena may be important to applications. As an example, corrosion fatigue cracks in steels exposed to seawater at low R are arrested by cathodic polarization, because calcareous corrosion products precipitate within the growing crack and cause crack surface closure contact at K levels well above zero [20,97]. ΔK_eff is substantially less than both the applied ΔK and the intrinsic ΔK_TH. Rough intergranular CF crack surfaces, coupled with local Mode II displacements, may also promote crack closure. Closure benefits may, however, be limited to simply loaded laboratory specimens. For example, compression elements of a complex load history can crush corrosion debris and crack surface roughness asperities, and can thus reduce crack closure.

As a second complication, crack tip stress, strain, and strain rate within the process zone are more fundamental than ΔK or ΔK_eff, and govern CF crack growth kinetics. It is not presently possible to unambiguously calculate the stress intensity dependence of these more fundamental parameters [16,22–24]. Shoji and coworkers argue that the time-based rate of mechanical FCP (da/dt) in an inert environment is proportional to the rate of dislocation emission from the crack tip, or equivalently, to the crack tip strain rate [98]. The value of da/dt, for FCP in vacuum, or more typically moist air, is therefore an indirect crack tip driving force parameter for correlating CF da/dN data which are also often stated with respect to a time-rate. In this approach, da/dt is the product of da/dN and f. An example of this correlation is shown in Fig. 20 which represents the CF enhancement in da/dN relative to the air case for three

During fatigue and CF crack propagation, a sudden large decrease or increase in the maximum stress intensity level of the load cycle produces a strong reduction in subsequent growth rates, or so-called delay retardation. These growth rates are important, but are not steady-state and not simply governed according to Eq 3 [6–8]. Most CF experiments are designed and conducted to avoid such overload effects.

FIG. 20—Time-based CF propagation rate for several heats of A302B steel in high-temperature water versus mechanical da/dt for the same alloy in moist air and at several R values [99].
The cyclic-mechanical depassivation method involves measurement of transient electrochemical current during cyclic plastic straining of a smooth specimen in an electrolyte at fixed potential [34,101]. A three-electrode cell, coupled with a fast-response potentiostat and the mechanical LCF procedures described in the subsection on the Smooth Specimen Method, are employed in this regard. Data include time-dependent applied plastic strain, stress, and anodic current density. The phase difference between the mechanical and electrochemical parameters, the strain dependence of the current density during repeated repassivation repair of ruptured surface films, the anodic charge passed per fatigue cycle, and the charge accumulation with increasing cycles and time are interpreted to probe CF damage mechanisms. For example, peak anodic current density and the cycle-cumulative charge increased with increasing strain rate for LCF of a ferritic stainless steel in NaCl, consistent with the film rupture model [34]. (This current reflects metal oxidation to produce cations in solution and in formation of the passive film, or, collectively, metal removal.) Additionally, the time dependence of repassivation and the magnitude of current transients depended on the sign of the plastic strain, and the repassivation characteristics for this system varied with cycle count, demonstrating the complexity of CF. This method was employed to rank the susceptibility of alloys to CF, based on the stability of surface passive films [101].

Small Crack CF Methods

An important goal of CF experimentation and modeling is to quantitatively couple smooth specimen and fracture mechanics approaches to understand the total life of components with microscopic defects. Studies of the so-called “small crack problem” have contributed in this regard [6]. Small crack size can be a particularly important variable that affects CF propagation rates [102,103]. For example, CF cracks sized between 100 and 1000 µm grew up to 1000-fold faster than predicted compared to long crack compact tension specimen da/dN data at fixed ∆K, for the case of a high-strength martensitic steel in NaCl [104]. Such crack geometry effects are traced to differences in crack solution mass transport and crack surface electrochemical reactions that govern HEE and film rupture processes [16,102,103].

Both electrical potential and high magnification optical methods have been developed to monitor the formation and growth of CF cracks smaller than 500 µm [105,106]. Each method is capable of micron-level resolution. The electrical potential approach monitors average short crack growth into the specimen bulk, while microscopic methods focus on surface crack interactions with specific microstructural features including inclusions and corrosion pits. The data presented in Fig. 21 were obtained from in situ monitoring of AA2024 in aqueous chloride solution with a long focal length (15 to 40 cm) and high magnification (500× with 1 µm resolution) optical microscope interfaced with a servohydraulic test machine and video system [106]. Microstructurally small CF cracks initiated at constituent particles and grew at rates that were equal to values obtained with the standard LEFM method discussed in the subsection on Fracture Mechanics Methods. While the
chemically small crack effect is not observed for the system in Fig. 21 [106], data of this type are important and lacking for a range of materials and environments [102–105].

The use of short crack specimens provides an important benefit for corrosion fatigue experimentation. Since high-resolution crack monitoring is employed, crack growth rates are quantitatively defined with small crack extensions and the associated reduced $N$. It is possible to obtain accurate low growth rate CF data at low loading frequencies. For example, a short crack specimen was employed to measure a $da/dN$ value of 0.5 $\mu$m/cycle at constant $\Delta K$ and $f$ of 0.0 Hz during a CF test time of 10 days [16,105]. A 10- to 20-fold longer test time is required to obtain this measurement with a standard long crack method.

**Measurement of CF Crack Solution pH and Potential**

It is important to measure occluded crack pH, potential, and solution composition because these factors govern CF by either HEE or film rupture mechanisms. Several experimental approaches have succeeded in this regard for simple ambient temperature and complex high-temperature pressurized water electrolytes [107,108]. Reference and pH electrodes were located in small holes drilled in the compact tension specimen to intersect the CF crack plane growing from the notch, as shown in Fig. 22 [108]. This method provides information on the crack size and position dependence of local pH and potential, as well as on the effects of $\Delta K$, $R$, and $f$. Additionally, crack solution can be sampled from crack-intersecting holes for composition analysis by ion chromatography and capillary electrophoresis [109]. Important data were obtained to test models of crack chemistry [72,108] and to understand solution-dissolved oxygen and metal sulfide effects on CF [22,23,109]. Given the very small volume of a typical CF crack, solution extraction methods are likely to upset crack electrochemistry and alter $da/dN$.

**APPLICATIONS OF CORROSION FATIGUE TEST RESULTS**

**Modern Approach to CF Life Prediction**

A cardinal principle is to design the CF experiment to isolate and characterize quantitatively any one of the four stages of fatigue damage defined in the Definition subsection of this chapter. The choice of stage depends on the problem, be it pitting-based crack nucleation in a polished and rigorously inspected medical implant or steam turbine blade, or macrocrack propagation from a weld defect in a large offshore marine structure. If a CF experiment measures total life, without quantifying the four damage stages, then basic understanding and component life prediction are compromised. This is the situation for standardized high- and low-cycle fatigue experiments that measure total $N_f$ of a small laboratory specimen. The CF material properties embodied in the Basquin and Coffin-Manson relationships (Eqs 1 and 2) are not directly scalable to predict the lives of components of alternate geometries and perhaps containing preexisting flaws. These data cannot be used to test models of CF because $N_f$ embodies cyclic deformation, microcrack nucleation and coalescence, small/short crack growth, and long crack propagation.

Implementing the correct method for CF life prediction and CF-resistant alloy development is often controversial, as existing approaches (often based on smooth specimen HCF data) are challenged by more modern approaches. A consensus is perhaps developing; an effective method couples the local strain approach to CF crack formation and early growth to a given detection threshold with the LEFM approach to propagation in order to calculate the summed total component life. The recommendation is that the Coffin-Manson approach be employed, but that the number of cycles to form a (reasonably) resolvable crack size (perhaps 0.1 to 1 mm) be measured in place of total cycles to failure. Equation 2 then describes the CF crack formation resistance of a given alloy-environment system, with the size of the initiated crack defined operationally. These material-environment property data are coupled with Neuber’s method or finite element calculations of local plastic strain range in a component to define service initiation life [7].

The fracture mechanics approach should be employed to characterize CF crack propagation kinetics, with emphasis on both the microstructurally small, physically short, and conventional long crack regimes [6,8]. The Paris relationship (Eq 3), or more complex formulations, are employed with stress intensity similitude and an analysis of the stress and stress intensity conditions of the component to predict CF propagation life, integrated from the size of the crack formed in the initiation stage [41]. A variety of desktop computer programs have been developed for the LEFM portion of the fatigue life prediction problem [110]. If nondestructive testing so indicates, then the LCF initiation portion of the problem can be equated to zero, and the fracture mechanics integration started at the appropriate existing flaw size.

The output of an integrated CF prediction method is plots of total cyclic life as a function of applied stress range, or
crack length versus load cycles at constant applied \( \Delta \sigma \), for specific material, time, and environment chemistry variables. Coffin-Manson and Paris Fatigue law depend on the variables cited in the section, Factors Controlling Corrosion Fatigue. Since a legion of variables is important, and since prolonged CF test times are often required, mechanistic modeling of the nucleation and crack propagation processes is a critical tool to develop algorithms for extrapolating the results of limited laboratory experiments [111].

Examples of Component Service Life Prediction with Laboratory CF Data

Corrosion fatigue problems have been attacked aggressively in several technologies over the past decade. The coupled local strain-formation and LEFM-propagation approach has not, however, been broadly employed. Early codified design predictions, using elastic smooth-specimen fatigue data (HCF-SN) adjusted empirically for deleterious time-dependent environmental effects, are being replaced by LEFM predictions of crack propagation from an inspection-based or estimated initial crack size [111]. Examples of this procedure were reported for CF in welded offshore structures in the marine environment [1,3,58,111–113], in-core and out-of-core components in commercial light water nuclear reactors [2,22,111,113], oil and gas pipelines [114], and aircraft [115,116]. Emphases focused on the conflicting effect of cathodic polarization on CF crack formation and growth (marine structures), the unifying role of crack tip strain rate (nuclear reactors), the deleterious effect of sulfur contaminants (nuclear reactor systems and pipelines), and the CF kinetics of small multiple fatigue cracks (aircraft). Tens of man-years are typically required to address a complex CF problem, and large databases for SCC and CF resulted from these efforts [58,117].

Future Research Needs in CF Experimentation

Environmental effects have not been rigorously incorporated in fatigue life prediction procedures [110]. The time dependence of CF, the many important interacting variables, and several uncertainties confound the problem. From the experimental perspective, LCF and LEFM-based laboratory CF methods must be improved to address the following uncertainties:

1. Methods must be further developed to probe the growth of single small CF cracks sized below 500 \( \mu \)m, and the interaction and coalescence of multiple small cracks must be characterized. Both LCF and LEFM approaches must be modified in this regard.
2. Near-threshold CF crack formation and propagation, and environment-dependent crack closure, must be characterized including the important effect of low loading frequency [118].
3. Load- and environment-spectrum history effects on CF crack formation and propagation must be characterized.
4. The statistical distribution of CF initiation/early growth and crack propagation properties must be defined.
5. High-resolution probes must be developed to measure occluded crack chemistry, transient crack surface electrochemical reactions, crack tip process zone damage processes, and microcrack advance.

6. Fractographic analyses of CF must be improved, including quantitative measurement of crack surface crystallography [119], and computerized image analysis methods to characterize and reconstruct the CF process [120].

7. For mechanistic modeling, CF results must be coupled with transient electrochemical reaction kinetics, hydrogen permeation, and hydrogen trapping analyses described elsewhere in this manual.

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In addition, the emerging body of literature on the effect of pre corrosion on fatigue life, particularly of aerospace alloys, is important. These include the following:


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