Modeling the fatigue crack growth of X100 pipeline steel in gaseous hydrogen

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ABSTRACT

This work proposes a phenomenological fatigue crack propagation (FCP) model for API-5L X100 pipeline steel exposed to high-pressure gaseous hydrogen. The semi-empirical model is predicated upon the hypothesis that one of two mechanisms dominate the fatigue crack growth (FCG) response depending upon the crack extension per cycle (da/dN) and the material hydrogen concentration. For da/dN between approximately 1 × 10^-6 mm/cycle and 3 × 10^-6 mm/cycle, fatigue crack growth in hydrogen is markedly increased over that in laboratory air, resulting in a Paris exponent over two and a half times that of air and producing a predominately intergranular crack propagation surface. Fatigue crack growth in hydrogen at da/dN above approximately 3 × 10^-4 mm/cycle result in FCP rates over an order of magnitude higher than that of lab air. The Paris exponent in this regime approaches that of lab air and the crack morphology is predominately transgranular. Increasing the hydrogen test pressure from 1.7 MPa to 20.7 MPa increases the FCG rate by as much as two, depending upon the stress intensity factor. It is proposed that the FCG response in hydrogen at da/dN < 3 × 10^-4 mm/cycle is primarily affected by the hydrogen concentration within the fatigue process zone, resulting in a hydrogen-dominated mechanism, and that the FCG response in hydrogen at da/dN > 3 × 10^-4 mm/cycle results from fatigue-dominated mechanisms. The proposed model predicts fatigue crack propagation as a function of applied AK and hydrogen pressure. Results of fatigue crack growth tests in gaseous hydrogen as well as fracture morphology are presented in support of the proposed model. The model correlates well with test results and elucidates how the proposed mechanisms contribute to fatigue crack propagation in pipeline steel in environments similar to those found in service.

1. Introduction

Hydrogen will likely play a key role as a sustainable energy carrier in the future. In recent years the United States has supported a significant amount of research through initiatives such as the Department of Energy’s (DoE) Hydrogen Program, DoE Energy Efficiency & Renewable Energy program, joint government-industry projects such as the FreedomCAR and Fuel Partnership, as well as research at numerous national laboratories and universities. However, the majority of the research performed to date in the United States has focused not on hydrogen infrastructure and transportation, but rather on fuel cells and other end-use issues [1,2]. The DoE report “Basic Research Needs for the Hydrogen Economy” [3] details eleven “high-priority research directions,” ranging from hydrogen production and fuel-cell technology to hydrogen storage and distribution infrastructure. The DoE clearly states in its report that one of the two primary barriers to realizing the promise of hydrogen as a practical and sustainable alternative energy source is “…an infrastructure that provides seamless transitions from production to storage to use.”

Distribution is a required first step toward the development of hydrogen as an alternative energy source. Utilization of the existing natural gas infrastructure is the fastest and most cost effective solution to introduce hydrogen to the masses, while the infrastructure exclusively for hydrogen distribution is being funded and created [1,4]. However, extensive research needs to be performed before hydrogen can safely be transported in either the existing natural gas infrastructure or a future hydrogen-specific infrastructure.

The deleterious effects of hydrogen upon pipeline steels have been studied for some time. However, a full understanding of the effects that hydrogen has upon the initiation and propagation of fatigue cracks in service conditions is still lacking. General experimental observations of hydrogen’s effect upon material properties are compiled in Table 1.1.
Fundamental understanding of the mechanisms controlling hydrogen-assisted fatigue crack growth (HA FCG) will lead to comprehensive models based upon the underlying deformation physics. A considerable amount of research is still required to achieve this level of understanding. In the interim, mechanistic models based upon general understanding of the deformation modes present, empirical evidence from FCG tests in high-pressure hydrogen, and an eye towards established literature in the area of general environmental fatigue can bridge the gap between a non-existent hydrogen transport infrastructure and one designed based upon physics-based models. This approach was generally laid out in [17].

A theoretical framework for HA damage mechanisms generally falls into three categories: hydrogen enhanced decohesion (HEDE), hydrogen enhanced localized plasticity (HELP) and adsorption induced dislocation emission (AIDE). Although a review of these theories is outside of the scope of this work, interested readers are directed to [18]. A common theme to all three theories is the understanding that damage is in some way proportional to the amount of hydrogen present in the material, regardless of how the hydrogen came to be in the material and under what conditions the hydrogen degrades the material. Furthermore, a consensus is building around the notion that there exists a critical distance (\(X_{\text{crit}}\)) in front of the crack tip within the fatigue process zone (FPZ) where hydrogen damage nucleates/accumulates. Current estimates place this distance between 0.05 µm and 1 µm from the crack tip for hydrogen-environment assisted cracking (HEAC) [19–30].

It has been shown empirically that fatigue crack growth rates (FCGRs) follow a multiplicative relationship between FCG driving force \(\Delta K\) and a deleterious diffusion process (potentially stress-assisted) in oxidizing environments [31–39], temperature-assisted viscoplastic deformation [40], as well as materials tested in hydrogen [17,41,42], such that

\[
da \frac{dN}{dN} = A \cdot \Delta K^n \cdot F(\text{env}),
\]

where \(A\) and \(n\) are material specific constants, and \(F(\text{env})\) is a term relating the diffusion kinetics to the deleterious environmental interaction. Models of similar functional form have been proposed for FCGR in hydrogen gas assuming hydrogen environment assisted cracking and are compiled in [43,44].

Two methods used in phenomenological modeling of multiple, concurrently occurring damage mechanisms will be employed here. First, the linear summation model [45,46] presumes that each increment of crack growth is a summation of the crack growth from independently occurring, non-interacting mechanisms. The model is as follows for FCG applications:

\[
da \frac{dN}{dN_{\text{Total}}} = \sum_i \frac{da}{dN_i},
\]

where the subscript \(i\) refers to any number of independent mechanisms. The second approach is the cumulative damage model, which presumes that multiple concurrent damage mechanisms “compete” with one another, such that any single mechanism may dominate total deformation, or the total deformation may result from an interaction of multiple mechanisms. The general framework for the cumulative damage model [47],

\[
D_{\text{Total}} = \sum_i D_i,
\]

states that the total damage from all competing mechanisms \(D_{\text{TOTAL}}\) is equal to the summation of each damage mechanism \(D_i\) as if they were occurring independently. Whereas the linear summation model treats the deformation mechanisms as if they occur in parallel, the cumulative damage model presumes that the independent deformation mechanisms occur in series, in which case the cumulative effect may incorporate damage mechanism interactions. When applied to life prediction, the cumulative damage model becomes

\[
N_t = \left( \frac{1}{N_{r1}} + \frac{1}{N_{r2}} \right)^{-1},
\]

where \(N_t\) is the number of cycles to failure and \(N_r1\) and \(N_r2\) are the number of cycles to failure for two isolated damage mechanisms. Underlying this model is the notion that material separation (failure) occurs at a total damage equal to one [48]. For fatigue crack growth composed of two competing crack growth mechanisms \(\frac{da}{dN_{r1}}\) and \(\frac{da}{dN_{r2}}\), the cumulative damage model becomes

\[
da \frac{dN_{\text{Total}}}{dN} = \left[ \left( \frac{da}{dN_{r1}} \right)^{-1} + \left( \frac{da}{dN_{r2}} \right)^{-1} \right]^{-1}.
\]

Competing damage mechanisms can lead to fatigue crack propagation behavior that deviates from Paris Law behavior. Fatigue crack growth of pipeline steels in gaseous hydrogen generally exhibits a bilinear trend in the Stage II FCG region. However, the bilinear trend observed in FCG in the presence of hydrogen is clearly in the long crack regime and beyond the region where crack propagation is affected by microstructural features (in air). Research has shown that the fatigue crack surface of specimens tested in hydrogen exhibit different morphologies depending on the region of FCG [49–52]. It has been shown that FCG may take the form of mixed-mode fracture, intergranular fracture with branching, intergranular fracture leading to dimple rupture, or intergranular stress corrosion fatigue [49].

In this paper, a single phenomenological FCGR model is proposed for API-5L X100 pipeline steel in air and high-pressure gaseous hydrogen. The functional form of the model approaches each of the two linear FCGR regimes produced during hydrogen-assisted FCG independently, then combines them in such a way as to allow interaction between the two presumed damage regimes. The model draws from the literature on general environmental-fatigue research to produce a functional engineering tool with excellent efficacy.

### 2. Material and experimental procedure

Fatigue crack growth experiments of API-5L X100 pipeline steel were conducted on compact tension (CT) specimens per ASTM E647-08 [53] in the transverse-longitudinal (T-L) orientation. The specimens were machined from new 1.3 m diameter by 20.6 mm thick commercially available pipe having been manufactured with thermomechanical controlled processing and were tested in the as-received condition. The specimens had length and width dimensions of \(W = 26.4\) mm and \(B = 10.96\) mm, respectively. The material’s chemical composition and microstructure are provided in Table 2-1 and Fig. 2-1, respectively. The as-tested monotonic mechanical properties for the material are provided in Table 2-2. The yield strength was determined using a 0.2% offset method and all stress values are engineering.

Fig. 2-1 shows the through-thickness microstructure of the as-tested alloy at the center of the pipe wall thickness. The pipe
rolling direction (collinear to the pipe length, as indicated in the figure) produces grain morphology and orientation anisotropy. The X100 microstructure consists primarily of bainite and acicular ferrite, although martensite, polygonal ferrite and retained austenite in lesser quantities are likely present.

Constant force (rising ΔK) fatigue crack growth tests were performed on a closed-loop 22 kip (100 kN) servo-hydraulic load frame per ASTM E647-08 [53]. The pertinent test variables are shown in Table 2-3. All tests were performed at room temperature.

Tests performed in high-pressure hydrogen were conducted in a 20 kpsi (138 MPa) pressure vessel. Force feedback was provided via a 10,000 lbf (44 kN) proving ring located inside the pressure vessel capable of 5 lbf (0.02 kN) resolution. Hydrogen gas having 99.9999% purity was produced on-site with an electrolyzer from ultrapure water. Crack measurements for all tests were performed by the compliance method using a crack mouth opening displacement (CMOD) clip gage with a 3 mm range and 0.001 mm resolution. Crack growth rate (da/dN) was calculated using the incremental polynomial method and crack closure was found to have not occurred (post-test) following the procedures in Appendix X2 of ASTM E647.

3. Test results

Force-controlled (rising ΔK) FCG tests were performed on API 5L-X100 (X100) pipeline steel. Tests were performed in laboratory air, as well as 250 psi (1.72 MPa), 1000 psi (6.89 MPa), and 3000 psi (20.68 MPa) gaseous hydrogen. The vast majority of the tests were performed at R_m = 0.5 and frequency f = 1 Hz. Fatigue crack growth test results as a function of environment are provided in Fig. 3-1.

A single force-controlled FCG test of X100 pipeline steel was also conducted in 6.89 MPa gaseous hydrogen at R_m = 0.5 and a frequency of f = 0.1 Hz. Fatigue test results as a function of frequency are shown in Fig. 3-2.

The constant slope of the FCG results for the test performed in laboratory air indicates that the ΔK range tested falls within the region II or Paris regime of FCG; that is, the plastic zone ahead of the crack tip encompasses many grains. The FCG curves for X100 that were tested in high-pressure hydrogen all adhere to a similar trend regardless of hydrogen pressure, independent of the trend exhibited by FCGR of X100 in air. The HA FCG of the material tested appears to be primarily affected by hydrogen pressure and test frequency. The HA crack growth curves exhibit two distinct regimes of FCG as a function of ΔK, which are separated by a “knee point.” Particularly, for ΔK values less than approximately 13.0 MPa m¹/² (da/dN between 3 × 10⁻⁵ mm/cycle and 6 × 10⁻⁵ mm/cycle), the FCG exhibits a larger Paris-law exponent than that of the laboratory air test; however, for greater ΔK values, the rate of FCG decreases, tending toward a ΔK dependence similar to that of laboratory air. The transition regime between these two FCG regimes will be referred to as the transition driving force, ΔK_t ∼ 13.0 MPa m¹/², occurring at a transition crack extension per cycle da/dN_t. For this work the HA FCG results below ΔK_t will be referred to as “transient” HA FCG, as this accelerated FCG regime is assumed to be transitional. The results above ΔK_t will be referred to as “steady-state” HA FCG as this regime has a Paris-law exponent closely matching that of laboratory air tests and it is assumed that the FCG has reached a steady-state rate persisting until the onset of Region III crack growth.

The results presented in Fig. 3-1 indicate that, as ΔK is decreased, the HA FCGR curves would converge with those produced in air. This trend is indicative of what McEvily and Wei [56] describe as “stress-corrosion fatigue.” Suresh describes the point at which the HA FCGR curve departs from that of air as K_max, or the “effective threshold stress intensity in fatigue for gaseous

<table>
<thead>
<tr>
<th>Table 2-1</th>
<th>Nominal composition of API-5L X100 steel (wt.%).</th>
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<tbody>
<tr>
<td>N</td>
<td>0.003</td>
</tr>
<tr>
<td>Nb</td>
<td>0.017</td>
</tr>
<tr>
<td>Ni</td>
<td>0.47</td>
</tr>
<tr>
<td>P</td>
<td>0.009</td>
</tr>
<tr>
<td>Si</td>
<td>0.099</td>
</tr>
<tr>
<td>Ti</td>
<td>0.017</td>
</tr>
<tr>
<td>V</td>
<td>0.002</td>
</tr>
<tr>
<td>Al</td>
<td>0.012</td>
</tr>
<tr>
<td>C</td>
<td>0.064</td>
</tr>
<tr>
<td>Co</td>
<td>0.003</td>
</tr>
<tr>
<td>Cr</td>
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<tr>
<td>Cu</td>
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<tr>
<td>Fe</td>
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</tr>
<tr>
<td>Mn</td>
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</tr>
<tr>
<td>Mo</td>
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<tr>
<th>Table 2-2</th>
<th>Monotonic tensile properties collected per ASTM E8 [54].</th>
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<tr>
<td>Orientation</td>
<td>σ_y (MPa)</td>
</tr>
<tr>
<td>L</td>
<td>689</td>
</tr>
<tr>
<td>T</td>
<td>810</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Table 2-3</th>
<th>FCG test parameters.</th>
</tr>
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<tr>
<td>Environment</td>
<td>ΔP (kN)</td>
</tr>
<tr>
<td>Air</td>
<td>3.25</td>
</tr>
<tr>
<td>1.72 MPa H₂</td>
<td>2.375</td>
</tr>
<tr>
<td>6.89 MPa H₂</td>
<td>2.75</td>
</tr>
<tr>
<td>20.68 MPa H₂</td>
<td>3.25</td>
</tr>
</tbody>
</table>

Fig. 2-1. SEM micrograph of as-tested X100 steel, 2% nital etch.

Fig. 3-1. Fatigue crack growth rate curves for X100 pipeline steel in various environments, R_m = 0.5 and f = 1 Hz.
hydrogen-induced cracking by (sustained-load) hydrogen-embrittlement mechanisms... [57]. Of note is that $K_{T_{\text{max}}}$ is typically equal to $K_{\text{ISSC}}$ in high-strength steels, but typically much lower than $K_{\text{ISSC}}$ in “lower” strength steels, as is the case here. Research has shown [57] that the value of $K_{T_{\text{max}}}$ is inversely proportional to pressure and directly proportional to test frequency. Extrapolation of the test results shown in Fig. 3-1 indicate that as the hydrogen pressure increases, $K_{T_{\text{max}}}$ also decreases. Furthermore, test results indicate that as the test frequency is decreased, so does $K_{T_{\text{max}}}$ (Fig. 3-2). Test results indicate that the HA FCGR is affected by changing hydrogen pressure at $\Delta K < 13 \text{ MPa} m^{1/2}$. The experimental FCGR curves appear to converge at higher stress intensity range values, indicating a decrease in hydrogen pressure dependence in this regime. These trends were also seen by [15,16]. While tests in hydrogen produced FCGRs up to an order of magnitude larger than those in air, the effect of changing hydrogen pressure from 1.72 MPa to 20.68 MPa only increases the HA FCGR by approximately two, depending upon the value of $D_K$. In general, FCGR results in gaseous hydrogen, as well as the FCGR results in air, are in excellent agreement with those presented in the literature [52,58,59].

4. Fractography

Micrographs of the fatigue crack propagation surface of X100 steel tested in hydrogen are shown in Figs. 4-1 and 4-2. The images were acquired in a scanning electron microscope (SEM) using a secondary electron detector.

The images in Figs. 4-1 and 4-2 indicate that the specimen’s fracture-surface morphology transitioned as a function of test environment and crack progression, when tested in hydrogen. The pre-crack FCG surface (tested in laboratory air) exhibits mixed intergranular–transgranular character. The HA FCG also exhibits a mixed intergranular–transgranular crack path, with the transient HA FCG regime being dominated by intergranular crack path morphology and the steady state HA FCG surface being dominated by transgranular crack growth. Although crack branching is evident throughout the entire FCG surface, the crack branching in the transient HA FCG regime is more dominant. These findings are consistent with previous results [52,57].

5. Analysis and model development

Based upon the experimental results, microscopy, and the literature regarding FCG in hydrogen, it is presumed that the transient HA-FCG occurs as a result of per-cycle crack extension occurring
within the FPZ most affected by the stress-assisted hydrogen concentration. A predominantly intergranular crack path results. Furthermore, it is presumed that the steady-state HA-FCG occurs due to the per-cycle crack extension exceeding the stress-assisted hydrogen concentration region by some amount. The size interactions of the crack extension and the FPZ are shown schematically in Fig. 5-1.

The transition between the two regimes is defined by a “knee point” occurring at da/dN of Xtr/cycle. Experimental results indicate that this transition occurs at a Xtr/cycle value of 0.31 μm/cycle, 0.36 μm/cycle, and 0.61 μm/cycle for hydrogen pressures of 1.72 MPa, 6.89 MPa, and 20.68 MPa, respectively. Furthermore, the results indicate that values of Xtr as a function of ΔK are fit by

\[ X_{tr} = 3.23 \cdot 10^{-2} \Delta K^2 \]

for the material tested. The results of Eq. (6) are proportional to (six times the size of) the plane strain cyclic plastic zone size estimate provided in [60]. Eq. (6) will be used to determine the transition between transient HA FCG and steady-state HA FCG for modeling purposes. That is, when the crack extension per cycle, for a given value of ΔK, exceeds the Xtr value for that ΔK, the fatigue crack growth response will have transitioned from transient to steady state fatigue crack growth. As was noted previously, the critical distance in front of the crack tip within the FPZ where hydrogen damage nucleates/accumulates (Xcrit) has an estimated range on the order of 0.05–1 μm [18]. As such, the experimental values of Xtr/cycle resulting from this work appear reasonable. Estimation of the region in front of the crack tip having the largest hydrogen concentration is performed using closed-form solutions. The equilibrium hydrogen concentration in metal is given by,

\[ [H]_{eq} = \theta \frac{[P]_0^{m}}{D} \exp(-Q/RT) \]

where \([H]_{eq}\) is the stress-free, equilibrium hydrogen concentration in the metal; \(\theta\) is the coefficient of hydrogen permeation; \(D\) is the coefficient of hydrogen diffusion; \(A\) is a constant; \([P]_0\) is the hydrogen pressure; \(Q\) is an activation energy; \(R\) the universal gas constant and \(T\) is the absolute temperature [61,62]. The stress-assisted hydrogen concentration has been shown to follow [63]

\[ [H]_{ia} = [H]_{eq} \exp((\sigma_a V)/RT) \]

where \([H]_{ia}\) is the stress-assisted hydrogen concentration, \(\sigma_a\) is the hydrostatic stress, \(V = 2.0 \times 10^{-6} \text{ m}^3/\text{mol} [51.64-66]\) is the partial molar volume of hydrogen in the metal and all other constants are as defined above. The hydrostatic stress is provided by

\[ \sigma_a = \frac{1}{3} \sigma_{tr} \]

and the stress tensor is estimated using the Hutchinson, Rice, Rosenhagen (HRR) equation [67,68] for the stress distribution in front of a sharp crack of a strain-hardening material in polar coordinates \((\rho \text{ and } \theta)\). It is given by

\[ \sigma_\theta = \sigma_{tr} \left[ \frac{E J \rho^2}{2 \rho_{tr}^2 d} \right]^{1/\nu_{tr}} \sigma_{tr}(\rho, \theta), \]

where \(\sigma_{tr}\) is the material yield strength, \(E\) the modulus of elasticity, \(J\) the value of the J-contour integral, \(\nu\) a dimensionless constant, \(d\) the distance in front of the crack tip, \(n\) the work hardening exponent from the Ramberg–Osgood equation for fitting stress–strain data in uniaxial tests, \(\sigma_{tr}\) a dimensionless function of \(n\) and \(\theta\), and \(I_2\) an integration constant that depends upon \(n\) and \(\sigma_{tr}\). The J-integral may be replaced by \(K_{IC}^2/E\) for linear elastic Mode I loading [60], where \(K\) is the stress intensity factor. The maximum stress intensity, \(K_{max}\), is used here in place of \(K_I\) for cyclic loading. While the HRR crack tip stress solution was derived for monotonic loading conditions, the closed-form relationship provides a sufficient estimation of the cyclic crack-tip stress field for the purposes of this model. Previous work on API-5L X80 (X80) pipeline steel [64] used this methodology to estimate crack tip stresses in a fatigue specimen and determined the following parameter values, \(n = 6.6\) and \(\nu = 0.01\). A schematic of the normalized stress-assisted hydrogen concentration for a stress intensity range of 13 (as a function of distance) is shown in Fig. 5-2.

Hydrogen concentration within a material is very difficult to measure, especially within the highly stressed fatigue process zone. Closed-form solutions using diffusion coefficients from the literature are used here as a starting point for modeling of the crack tip hydrogen concentration interactions. Fig. 5-2 schematically shows the non-stressed far-field hydrogen concentration at \([H]_{eq}/[H]_0 = 1\) as predicted by Sievert’s law \(([H]_0 \propto [P]_0^{2/3})\) and the distribution of the stress-assisted near-field hydrogen concentration in front of the crack tip (Eq. (8)). The outer bound of the cyclic fatigue process zone estimate is indicated at 2r and the estimated transition crack extension per cycle (Xtr, defined in Eq. (6)) is indicated at 6r for the loading conditions analyzed. Fig. 5-2 provides a visual reference for the hypothesized crack-tip to hydrogen concentration interaction producing the bi-linear HA-FCG trends described here as transient and steady state FCG. Specifically, at \(da/\text{d}N < X_{tr}\), the crack extension per cycle occurs within the region having greater hydrogen concentration and therefore the FCGR is presumed to be dominated by the stress-assisted hydrogen concentration or dependent predominantly on \([P]_0\). Whereas for \(da/\text{d}N > X_{tr}\), the crack extension per cycle extends beyond the region having far less hydrogen concentration and the FCGR is affected by the

**Fig. 5-1.** Sketch depicting conditions in which (a) transient HA crack growth would occur, and (b) steady-state HA crack growth would occur. Transient HA FCG occurs when the crack extension per cycle is contained within the FPZ created by the previous cycle, whereas transient FCG occurs when the crack extension per cycle extends beyond the FPZ. The FPZ is shown as a shaded region. Sizes are exaggerated for clarity.
intermediate-field hydrogen concentration (beyond the peak value associated with the location of highest hydrostatic stress yet not the lattice concentration predicted by Sievert’s law occurring far-field) and is therefore presumed to be dominated primarily by $\Delta K$ and less so by the hydrogen pressure.

If one assumes that an incremental extension of the crack tip due to HA FCG is comprised of a fatigue-in-air component and an environmental-fatigue (HA) component, the FCGR relationship would then have the following functional form:

$$\frac{da}{dN_{\text{Total}}} = \frac{da}{dN_{\text{Fatigue}}} + \frac{da}{dN_{\text{Fatigue}}}$$

where the subscripts fatigue and $H$ designate contributions to the total crack advance due to fatigue-in-air and HA fatigue, respectively. The general framework of FCG superposition has been successfully employed to data on environmental-fatigue crack growth in oxidizing environments [33,39], corrosive environments [69], high-temperature environments inducing viscoplastic deformation [39,70], thermomechanical fatigue [32], and crack advance segregated by microstructural considerations [33], to name just a few. One should note that Eq. (11) is proposed to correlate Region II crack growth only, as it is believed that the data presented here fall within this regime. The first term of Eq. (11) is given by the traditional Paris relationship

$$\frac{da}{dN_{\text{Fatigue}}} = A\Delta K^{m},$$

where $\Delta K$ is the stress intensity range defined in ASTM E647 [53] and $A$ and $b$ are constants fitted to the experimental data. Eq. (12) accounts for the fatigue-in-air contribution of crack extension, regardless of test environment. As such, Eq. (11) must collapse to Eq. (12) for tests performed in air.

Based upon the presumed segregation of deformation modes producing the bilinear HA-FCG results and the previous work performed on the kinetics of environmental fatigue [31,33,34,37–40,71,72], one might expect that the functional form for a HA FCGR relationship would follow

$$\frac{da}{dN_{\text{Fat}}} = F(F[a\Delta K^{m}H] = F[a\Delta K^{m}p_{m}^m \exp((-Q + \sigma_{1}v)/(RT)\tau)]$$,

where $F$ indicates “a function of” and all parameters are defined above. Inherent to the functional form of Eq. (13) is the presumption that an increased hydrogen concentration within the material would enhance FCG. Though one may readily accept this notion due to the experimental results presented in the literature, the multiplicative nature of this interaction as proposed in Eq. (13) is purely empirical, as a thorough understanding of the specific interactions between the hydrogen concentration, stresses, and inelastic strains at the crack tip occurring during HA FCG are yet to be determined. The term $p_{m}^m$ incorporates the ambient hydrogen pressure and accounts for the steady-state concentration, $[H]$, of hydrogen within the steel. The coupled exponential-time term, $\exp((-Q + \sigma_{1}v)/(RT)\tau)$, accounts for the kinetics of hydrogen transport via an Arrhenius-like relationship, which includes the contribution of lattice dilatation due to the hydrostatic stress, and the time, $t$, that the material has been exposed to high-pressure hydrogen. In the absence of materials-specific hydrogen diffusion data, the time term, $\tau$, will be dropped from the final relationship. This omission is appropriate for very long time periods of hydrogen exposure (on the order of 150 h [73]) as hydrogen saturation in the lattice will have been achieved. As the dissociative dissolution of hydrogen in metals typically follows Sievert’s law, one might expect the pressure exponent to be $m = 1/2$ under equilibrium conditions and zero applied stress. In order to determine a first order estimate of the pressure exponent, $m$, experimental $da/dN$ values from each of the hydrogen pressure data sets were collected for a single $\Delta K$ and plotted versus hydrogen pressure. Power-law fits then provided the power-law pressure dependence for the material at that particular value of $\Delta K$. This process was repeated for all values of $\Delta K$ for which there was data in all three hydrogen pressures tested. The results of the exercise are shown in Fig. 5-3.

The results in Fig. 5-3 indicate that the FCGR’s hydrogen pressure dependence is highly dependent upon $\Delta K$ within the transient region of HA FCG. The pressure dependence of the FCGR in the steady-state regime, on the other hand, is far less dependent upon the $\Delta K$. The dependence of hydrogen pressure upon $\Delta K$ changes drastically at $\Delta K_{t}$, or $\Delta K = 13$ MPa-m$^{1/2}$. Inclusion of the term for hydrostatic stress in the $[H]$ relationship does not minimize the dependence of the pressure exponent upon stress, as might have been expected. These results may indicate an interaction between the hydrogen uptake at the crack tip (hydrogen pressure dependence other than a power of $m = 1/2$) and the hydrogen diffusion kinetics within the material ($m = 1/2$). Furthermore, the results likely indicate that Eq. (13) may not sufficiently capture the hydrogen–$\Delta K$ interactions occurring. Research on this is ongoing.

6. Proposed FCG model

Based upon the understanding that two competing mechanisms produce the HA FCG response of this material, a relationship similar to that of linear damage summation is proposed. Specifically, it is assumed that FCG driven by the hydrogen pressure occurs in

![Fig. 5-2. Schematic showing the normalized stress-assisted hydrogen concentration and fatigue process zone relative length scales.](image-url)
series with ΔK-dominated FCG, thereby setting up a competition between the two mechanisms. Following the derivation of Eq. (4), the HA FCGR is given by

$$
\frac{dA}{dN_{\text{fatigue}}} = \left( \frac{dA}{dN_{\text{ph}}} \right)^{-1} + \left( \frac{dA}{dN_{\text{sk}}} \right)^{-1}^{-1},
$$

where \( \frac{dA}{dN_{\text{fatigue}}} \) is the total HA FCGR comprising FCG dominated by the hydrogen–stress field interactions at the crack tip, \( \frac{dA}{dN_{\text{ph}}} \), and intermediate-field HA FCGR \( \frac{dA}{dN_{\text{sk}}} \) dominated by ΔK. Given that there will be a pressure dependence in the denominator of Eq. (14), and that the FCGR relationship is intended to be valid for pipeline operating conditions ranging from air (laboratory air in this case) and 20.7 MPa hydrogen, the following modification must be made to Eq. (11):

$$
\frac{dA}{dN_{\text{total}}} = \frac{dA}{dN_{\text{fatigue}}} + \delta(P_h - P_{h0}) \frac{dA}{dN_{h}},
$$

where \( \delta \) is the Heaviside step function and \( P_{h0} \) is a threshold hydrogen pressure below which HA FCG does not occur. This value is assumed to be below \( P_{h0} < 0.02 \) MPa [12], and a value of 0.02 MPa will be used here due to lack of experimental results at lower pressures. Combining Eqs. (14) and (15) yields,

$$
\frac{dA}{dN_{\text{total}}} = \frac{dA}{dN_{\text{fatigue}}} + \delta(P_h - 0.02) \left( \frac{dA}{dN_{h}} \right)^{-1} \left( \frac{dA}{dN_{\text{sk}}} \right)^{-1},
$$

Correlating the FCG data of X100 tested in laboratory air yields the following values for the constants in Eq. (12): \( A = 9.86689 \times 10^{-9} \text{m}^2/(\text{cycle MPa m}^{1/2}) \) and \( b = 2.82727 \) where \( b \) is unitless. The transient HA FCG is given by

$$
\frac{dA}{dN_{\text{trans}}}(i) = \sigma_{01} \Delta K_{01} \left( P_{h0}^{2} \exp \left\{ -\frac{Q}{RT} \right\} \right)^{d_{1}} ,
$$

and the steady-state HA FCG is given by

$$
\frac{dA}{dN_{\text{sk}}}(i) = \sigma_{02} \Delta K_{02} \left( P_{h0}^{2} \exp \left\{ -\frac{Q}{RT} \right\} \right)^{d_{2}},
$$

where \( \sigma_{0i} \) is determined using Eqs. (9) and (10), and the \( ai's \) and \( Bi's \) are fitting constants. The distance, \( d \), at which the hydrostatic stress is calculated (by use of Eq. (10)) is set to \( d = X_{0i} \) for Eq. (17) and \( d = da/dN_{i-1} \) for Eq. (18), where \( i \) indicates the previous cycle. The activation energy for lattice hydrogen concentration is taken as \( Q = 27.1 \text{kJ/mol K} \) [61] for both relationships (Eqs. (16) and (17)). Material-specific parameters used in the stress solution (Eq. (10)) were determined as \( \sigma_{0} = 0.89, n = 18.4, \sigma_{30} = 696 \text{ MPa for longitudinal and} \sigma_{03} = 807 \text{ MPa for transverse orientation} \) via monotonic test results conducted in air and hydrogen (data taken from [55]). The hydrogen concentration relationship currently does not account for trapping resulting from plasticity at the crack tip. The J-integral may be replaced with \( J = K_{\text{IC}}^2/E \) [60], however given that the loading here is cyclic, the following relationship will be used \( J = K_{\text{IC}}^2/E \). The remainder of the constants in the HRR relationship are \( \Omega_{0} = 3.2, \Omega_{11} = 0.6, \Omega_{21} = 1.2 \) [60] and \( \Omega_{31} = 0 \) (all from Eq. (10)). All other parameters were fit to the experimental data shown in Fig. 3-1. The parameter \( B1 \) was set equal to the average value for the transient ΔK dependence, \( B1 = 7.96 \). Based upon the relationship shown in Fig. 5-3, \( m1 = 0.75/d1 \) was used within the transient regime. In this way, the hydrogen pressure was raised to a constant 0.75 for \( da/dN < da/dN_{i} \). The final fitting parameter values for transient HA FCG were determined to be \( d_{1} = 1.5 \times 10^{-4}, d_{1} = 3 \). Following a similar methodology, \( B2 = 3.17 \) and \( m2 = 0.22/d2 \) were used. The fitting parameters for steady-state HA FCG were determined as \( d_{2} = 1.3 \times 10^{-4} \) and \( d_{2} = 1 \). Eqs. (12), (17), and (18) are graphed independent of each other in Fig. 6-1(a), and Eq. (12) along with (16) are graphed in Fig. 6-1(b). Fig. 6-1 graphically demonstrates the utility of combining Eqs. (17) and (18) in series as is done in Eq. (16).

Fig. 6-1 indicates that Eq. (17) dominates at smaller values of ΔK and Eq. (18) dominates at larger ΔK values, as would be expected by the argument on the segregation of the two mechanisms producing the bilinear HA FCG results.

In order to demonstrate the effectiveness of the model, the experimental FCGR results are graphed versus the correlated FCGR values (using Eq. (16)) and are shown in Fig. 6-2.

Eq. (16) does an excellent job of correlating FCGR data for X100 steel tested in air and high-pressure hydrogen, with 93% of all data correlations falling within a factor of 2X and 80% falling within a factor of 1.5X. Curves of experimental and correlated FCGR versus ΔK are provided on the same axis in Fig. 6-3.

The correlated FCGR curves in Fig. 6-3 were all produced with an identical ΔK range, specifically \( 6 \leq \Delta K \leq 30 \). This was done regardless of the ΔK range for each experimental data set in order to capture the trends produced by Eq. (16). In general, model predictions indicate that as hydrogen pressure increases, so does \( da/dN \) for a given ΔK. The model also indicates that the converse is true, i.e. there is an inverse relationship between hydrogen pressure and ΔK for a given \( da/dN \).

7. Discussion

In its current form, the model has six constants that are fit to experimental results: \( a1, m1, d1, a2, m2, \) and \( d2 \). While fitting of a scalar prefactor (both \( ai \) is trivial, the exponents acting upon the hydrogen concentration terms (\( mi \) and \( di \)) should be determined from first-order material-specific, stress-free, and

![Fig. 6-1](image-url)

Fig. 6-1. Model correlations: (a) Eqs. (17) and (18) plotted independently, and (b) model in final predictive form (Eq. (16)).
stress-assisted experiments. Realistically these experiments would be very difficult to execute, and would need to be performed for every alloy and microstructural variation. First-principle, stress-assisted, hydrogen diffusion and concentration tests in which the stress and strain tensors are known in full are required in order to determine values for the pressure exponents $m_i$, given that it has been shown that $m_i$ may be in some way related to the driving force for crack extension (Fig. 5-3). Furthermore, material-specific experiments are required to determine the effective activation energy for hydrogen diffusion with each new material, as ferrite-pearlite microstructures have different hydrogen diffusivities and solubilities than bainite or martensite [74]. As an engineering tool, however, the use of existing data for the activation energy and fitting of the $m_i$ and $d_i$ variables is likely sufficient.

Moreover, it is believed that the Paris-type relationship in the HA FCG terms does not fully capture the effects of deformation at the crack tip. Rather, the stress intensity factor range ($\Delta K$) should likely be replaced with a term that accounts for the accumulated inelastic (shear) strain. In this way, the crack tip deformation as well as the shear-driven hydrogen concentration may be addressed. A constitutive model that couples deformation and hydrogen diffusion may provide insight into these issues. The proposed model is likely to be used as an engineering tool only until such time as the hydrogen concentration of pipeline steels can be determined with relative ease.

As tests in high-pressure gaseous hydrogen were performed at only two frequencies, $f = 0.1$ Hz and $f = 1$ Hz, the FCGR dependence upon frequency could not be determined here. However, assuming a frequency dependence resulting from hydrogen diffusion from the crack tip to the FPZ as the rate limiting step, the HA FCGR with respect to cyclic frequency would then be [44].

$$\frac{da}{dn_{Total}} \propto f^{-1/2}$$

(19)

However, the minimal results here indicate a frequency dependence of $f^{-2}$, as shown in Fig. 7-1. Of note, the model predicts that increasing the hydrogen pressure from 6.89 MPa to 18.00 MPa has the same effect as decreasing the frequency from 1 Hz to 0.1 Hz, as shown in Fig. 7-2.

Although the model presented here is purely phenomenological, its utility is twofold. First, is as an engineering tool to predict the HA FCG of API pipeline steels. The full derivation of the tool here for API 5L X100 steel is supported by the implementation of the model for other API pipeline steels with minimal upfront calibration tests, presented elsewhere [75]. The model has proved to perform well for multiple API pipeline steels. Second, the functional form of the proposed model separates the HA-FCG based upon the bi-linear experimental results. The separation of these two FCG regimes is supported by the microscopy indicating a difference in fatigue crack path morphology. It is hypothesized here
that two separate mechanisms dominate the HA FCG response. It is thought that the independent mechanisms are triggered based upon the length of crack extension per cycle and hydrogen concentration interactions, among other things. Certainly, more research is required to ascertain the underlying deformation physics occurring, but the concept of competing damage mechanisms producing the bilinear HA FCG response is worth continued research. This paper intends to pave the way for that research.

8. Conclusions

The following conclusions can be drawn from this work:

1. The FCG response of API X100 pipeline steel is highly affected by gaseous hydrogen, with FCGRs increasing by over an order of magnitude in certain ranges of ∆K.

2. Increasing the hydrogen pressure from 1.72 MPa to 20.68 MPa can increase the FCGR by as much as twofold.

3. The HA FCG of X100 exhibits a bilinear da/dn vs. ∆K response. Each "leg" of the bilinear response is separated by “knee point”, designated as da/dn_k. The transition coincides with a crack extension per cycle equal to six times the estimate of the fatigue process zone size.

4. At lower values of ∆K and crack extension (da/dn < da/dn_k), the HA FCG exhibits a Paris exponent on the order of eight and the fatigue crack surface exhibits primarily intergranular morphology. At higher values of ∆K and crack extension (da/dn > da/dn_k), the Paris exponent approaches that of air and the fatigue crack surface is primarily transgranular.

5. A single relationship is proposed to correlate fatigue crack growth of X100 steel in both air and high-pressure hydrogen. The relationship

\[
\frac{da}{dN} = AAK^a + D \left( \frac{P_n}{C_0} \right)^{1-a}
\]

presumes that: (a) each increment of HA crack extension comprises a superposition of fatigue-in-air and an environmentally-fatigue compo-
nent, and (b) the environmentally-fatigue interaction has two domi-
nant HA damage processes occurring in series. The model performs well at correlating the data presented here, with 93% of the model correlations falling within a factor of two. Furthermore, the model has been implemented for other API pipeline steels with similar efficacy [7,5,6].

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