Title
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MECHANISTIC DISSIMILARITIES BETWEEN ENVIRONMENTALLY-INFLUENCED FATIGUE CRACK PROPAGATION AT NEAR-THRESHOLD AND HIGHER GROWTH RATES IN LOWER STRENGTH STEELS

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November 1981

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ABSTRACT

The role of hydrogen gas in influencing fatigue crack propagation is examined for several classes of lower strength pressure vessel and piping steels. Based on measurements over a wide range of growth rates from $10^{-8}$ to $10^{-2}$ mm/cycle, crack propagation rates are found to be significantly higher in dehumidified gaseous hydrogen compared to moist air in two distinct regimes of crack growth, namely i) at the intermediate range of growth typically above $\sim 10^{-5}$ mm/cycle, and ii) at the near-threshold region below $\sim 10^{-6}$ mm/cycle approaching lattice dimensions per cycle. Both effects are seen at maximum stress intensities ($K_{\text{max}}$) far below the sustained-load threshold stress intensity for hydrogen-assisted cracking ($K_{\text{Iscc}}$). Characteristics of environmentally-influenced fatigue crack growth in each regime are shown to be markedly different with regard to fractography and the effect of such variables as load ratio and frequency. It is concluded that the primary mechanisms responsible for the influence of the environment in each regime are distinctly different. Whereas corrosion fatigue behavior at intermediate growth rates can be attributed to hydrogen embrittlement processes, the primary role of moist environments at near-threshold levels is shown to involve a contribution from enhanced crack closure due to the formation of crack surface corrosion deposits at low load ratios.
INTRODUCTION

It is well known that hydrogen, either in gaseous form or internally charged or in "hydrogen-producing" environments, can result in severe deterioration of the resistance to fatigue crack growth in high strength steels (of yield strength exceeding ~1000 MPa), particularly when the maximum stress intensity of the fatigue cycle ($K_{\text{max}}$) exceeds $K_{\text{isc}}$, the threshold stress intensity for hydrogen-induced cracking under sustained loading. This phenomenon, which is often referred to as "stress-corrosion fatigue" (1) has been rationalized in terms of "superposition" (2) or "process-competition" (3) models, where environmentally-influenced crack growth is interpreted to result simply from sustained-load stress-corrosion cracking and pure mechanical fatigue components which are either additive or mutually competitive. Using such approaches, the role of load ratio, cyclic frequency and wave-form, for example, in influencing such hydrogen-assisted cracking has been readily explained for a wide range of high strength alloys (2-4).

Lower strength steels, on the other hand, with yield strength ($\sigma_y$) below ~1000 MPa, have until recently been considered to be relatively immune to such embrittlement in the presence of hydrogen gas. This notion has persisted mainly due to experimental evidence that conventionally-measured sustained-load $K_{\text{isc}}$ thresholds for such steels are found to be extremely high in gaseous hydrogen atmospheres, compared to those measured in high strength steels. Under cyclic loading, however, it has become clear that lower strength steels can be extremely susceptible to hydrogen-assisted cracking at stress intensities far below $K_{\text{isc}}$.

Walter and Chandler (5), for example, demonstrated that fatigue crack growth rates in high pressure hydrogen (103 MPa) were over an order of
magnitude higher than in non-corrosive environments for a ferritic ASME SA-105 steel (σ_y = 269 MPa). Similar behavior in the mid-range of growth rates (∼10^{-5} - 10^{-2} mm/cycle) has been observed in ferritic mild steels (σ_y = 207 MPa) (6), bainitic 2 NiCrMoV rotor steels (σ_y = 575 MPa) (7, 8) and martensitic pressure vessel steels (σ_y = 789 MPa) (9), tested in ambient pressure hydrogen gas. Such studies (6-10) further indicated that the enhancement in crack growth rates due to hydrogen increased with increasing pressure and decreasing cyclic frequency although, unlike stress-corrosion fatigue in high strength steels, no effects of wave-form were detected (7).

However, recent investigations (11-16) at very low growth rates below ∼10^{-6} mm/cycle, approaching the so-called threshold stress intensity range ΔK_0 below which cracks remain dormant or grow at experimentally undetectable rates, have revealed corrosion fatigue behavior distinctly different from reported data at higher growth rates. In several classes of lower strength alloy steels (σ_y < 800 MPa) (11-15), growth rates in dry gaseous hydrogen appear two orders of magnitude higher than in moist air, although the effect is only evident at low load ratios (R = K_{min}/K_{max}). At R = 0.75, for example, differences between crack propagation rates and the value of the threshold ΔK_0 in hydrogen and air are insignificant, indicating that the primary role of hydrogen in influencing near-threshold crack growth behavior may not necessarily be due to any embrittling effect of the gas.

The objective of the present work is to highlight the mechanistic dissimilarities between environmentally-influenced fatigue crack propagation behavior at intermediate (∼10^{-6} - 10^{-3} mm/cycle) and near-threshold growth rates (below ∼10^{-6} mm/cycle) in lower strength pressure vessel and piping steels in terms of fractography and sensitivity of growth rates to changes in load ratio, frequency and hydrogen fugacity. It is shown
that whereas hydrogen-induced accelerations in growth rates above typically $10^{-5}$ mm/cycle are associated with hydrogen embrittlement mechanisms, the significant differences in crack propagation rates between dry hydrogen and moist air at near-threshold levels are primarily due to crack closure effects promoted by the formation of crack surface corrosion deposits.

EXPERIMENTAL DETAILS

Lower strength steels ranging in yield strength from 290 to 770 MPa were examined in this study, consisting of three classes of 2-1/4 Cr-1Mo pressure vessel steel and a pipeline steel. They were normalized and tempered ferritic-bainitic ASTM A387 Class 2 Grade 22, quenched and tempered bainitic ASTM A542 Class 3, quenched and tempered martensitic ASTM A542 Class 2, and normalized ferritic-pearlitic ASTM A516 Grade 70. These materials are hereafter referred to as SA387, SA542-3, SA542-2 and SA516-70, respectively. Heat-treatments for these alloys conform to the appropriate ASTM standards and are described elsewhere (11, 13, 15). Chemical composition and ambient temperature mechanical properties are listed in Tables 1 and 2 respectively.

Fatigue crack propagation tests were performed on 12.7 mm thick compact specimens (T-L orientation) using electro servo-hydraulic testing machines operating under load control. Cyclic frequencies between 0.5 and 50 Hz were examined with load ratios varying between 0.05 and 0.75. Crack lengths were continuously monitored using d.c. electrical potential methods. Growth rates above $\sim 10^{-6}$ mm/cycle were measured under constant load amplitude (increasing $\Delta K$) conditions, whereas at near-threshold levels, tests were performed under decreasing $\Delta K$ (load-shedding) conditions, with threshold $\Delta K_0$ values defined in terms of a maximum growth rate of $10^{-8}$ mm/cycle (17). Tests in gaseous environments were conducted using an O-ring sealed chamber,
locally clamped onto the test-piece, where gas purity was maintained by means of an extensive purification system involving molecular sieves, liquid nitrogen traps and heat-bakeable stainless steel lines. Ambient temperature (23°C) and pressure (138 kPa) environments of moist air (30% relative humidity) and purified and dehumidified gaseous hydrogen were utilized. Full experimental details are described elsewhere (10-14).

RESULTS

The variation in fatigue crack propagation rate (da/dN) with stress intensity range (ΔK) for the bainitic SA542-3 steel is shown in Figure 1 at a load ratio of R = 0.05 and at frequencies between 0.5 and 50 Hz, in environments of moist air and dry hydrogen gas. It is apparent that there are two regimes of growth rates where crack velocities are higher in hydrogen compared to air.

The major difference in crack growth behavior between hydrogen and air can be seen below \( \sim 10^{-6} \) mm/cycle, where near-threshold crack propagation rates are up to two orders of magnitude lower and threshold ΔK₀ values are almost 50% higher in air compared to hydrogen. Similar behavior has been observed in other lower strength alloys, such as martensitic SA542-2 (Fig. 2) and ferritic-bainitic SA387-2-22 (11, 12) pressure vessel steels, and ferritic-pearlitic SA516-70 (Fig. 3) and X-60 (18) pipeline steels. However, when such alloys are tested at R = 0.75 (Figs. 2-4), near-threshold crack growth rates and threshold ΔK₀ values for air and hydrogen environments are essentially similar. Thus, the apparent role of hydrogen near ΔK₀ is only evident at low load ratios. Fractographically, failure mechanisms in air and hydrogen are virtually indistinguishable (Figure 5) despite the large difference in growth rates at R = 0.05. Below \( \sim 10^{-6} \) mm/cycle, a fine-scale transgranular mode is observed for both environments.
with little evidence (<10%) of intergranular facets. Such a fracture morphology is very characteristic of steels tested at near-threshold levels (13).

With increasing growth rates above ΔK_0, the difference between behavior in air and hydrogen becomes progressively lessened, as clearly shown in Fig. 1. Around ~10^{-5} mm/cycle (for R < 0.5), however, an abrupt enhancement in growth rates due to hydrogen (up to twenty times), which is sensitive to frequency, load ratio and pressure, can be observed (Figs. 1-4). Although behavior in moist air in this regime is both independent of frequency (2-50Hz) and load ratio (R = 0.05-0.75) over the ranges studied (Figs. 1, 3 and 4), below a frequency of 2 Hz hydrogen gas results in the onset of considerably higher growth rates above a ΔK value of approximately 20 MPa√m. Similar behavior is seen for dry gaseous hydrogen and hydrogen sulfide (9) at 5 Hz in the higher strength SA542-3 steel (Fig. 2), and for high pressure (6.9 MPa) hydrogen gas (19) at 0.1 Hz in SA516-70 (Fig. 3). The effect of changing mean stress is shown for SA542-3 in Fig. 4, where it is clear that although load ratio has little influence on the overall ("plateau") (7) hydrogen-assisted growth rates, the onset of the acceleration is critically dependent upon R. Provided the frequency is below a critical value (dependent upon R), the onset of hydrogen-assisted fatigue crack propagation in the intermediate growth rate regime occurs at a critical maximum stress intensity, termed K_max^T, which is approximately 20 MPa√m in SA542-3 (Table 3), i.e., the acceleration occurs at lower ΔK levels with increasing R as shown in Fig. 4. Thus, although no embrittling effect of low pressure hydrogen is observed at 50 Hz for R = 0.05 (Fig. 1), increasing the load ratio to 0.3 or above (Fig. 4), or decreasing the frequency to 2 Hz or below (Figs. 1 and 4) or increasing the hydrogen pressure (Fig. 3) results in marked hydrogen-
assisted crack growth.

Unlike behavior at near-threshold levels, the marked growth rate differences in hydrogen and air are accompanied by a distinct change in fracture morphology in these steels (Fig. 6). Below $K_{\text{max}}^T$ in both environments, failures are predominately transgranular, whereas above $K_{\text{max}}^T$ hydrogen-assisted crack growth occurs by a predominately intergranular cracking mode.

A summary of the different characteristics of environmentally-influenced fatigue crack growth at intermediate (> $\sim 10^{-5}$ mm/cycle) and near-threshold (< $\sim 10^{-6}$ mm/cycle) crack velocities, deduced from the above results, is listed in Table 4.

DISCUSSION

Although many mechanisms have been proposed over the years for the hydrogen embrittlement* of steels, such as the Pfeil-Troiano-Oriani decohesion models(20) and the Zappfe pressure model(21), it is unlikely that a single theory can provide a complete understanding of the problem. For high strength steels, however, decohesion theories appear to provide at least a partial description of observed behavior, both for monotonic and cyclic loading in "hydrogen-producing" atmospheres, such as $H_2$ and $H_2S$. Such models propose that hydrogen is adsorbed from the gas phase, or evolved by electrochemical reaction(22), on freshly reactive surface at the crack tip, thereby entering the lattice and being transported, under the driving force of the stress gradient, to the region of maximum dilation ahead of the crack tip where some form of embrittlement takes place presumably by a

*Although precise mechanisms of hydrogen embrittlement are in most cases unknown, particularly in low strength steels, we imply here mechanisms by which hydrogen enters the lattice and promotes some degradation in resistance to fracture.
reduction in cohesion at interfaces (Fig. 8)*. The reduction in cohesive strength ($\Delta \sigma_H$) can be assumed to be proportional to the local concentration of hydrogen at this point ($c_H$), where

\[ c_H = c_0 \cdot \exp\left(\frac{\sigma \bar{V}}{R_0 T}\right). \] (1)

$c_0$ is the equilibrium concentration of hydrogen in the unstressed iron lattice, $\bar{V}$ the partial molar volume of hydrogen in iron, $\sigma$ the hydrostatic tension, $R_0$ the gas constant, and $T$ the absolute temperature. Such models are consistent with an increasing susceptibility to hydrogen embrittlement with increasing material strength, since hydrogen enrichment factors ($c_H/c_0$) are an exponential function of the hydrostatic tension.

The mechanistic aspects of hydrogen-induced cracking in lower strength steels, on the other hand, are still unclear. Classical decohesion models (20, 23) pose a problem since they predict only marginal enrichment factors due to the small magnitude of the hydrostatic tension in lower strength materials. Accordingly, Beachem has proposed that hydrogen assists deformation in some unspecified manner and thereby promotes fracture, which is consistent with observations of reduced flow stress after charging (24). However, the precise interaction between hydrogen atoms and dislocations, although clearly of importance to the embrittlement of iron alloys, remains undefined at this time. Recent metallographic studies (26, 27) have indicated that hydrogen may enhance the nucleation and growth of microvoids at internal surface in low strength steels, but it is not known whether such "micro-decohesive" mechanisms are important during fatigue, where a complete

*Unlike behavior ahead of a blunt notch, the point of maximum dilation ahead of a sharp crack may be very close to the crack tip, i.e., of order of twice the crack tip opening displacement. Accordingly, in the latter case, the critical event involved in the embrittlement process may rather occur at some microstructurally-significant characteristic distance ahead of the crack tip.
mechanistic basis for crack growth, even in the absence of environmental
effects, is still lacking.

In light of the current work, however, the role of hydrogen gas appears
to have contrasting effects in different growth rate regimes. These are
now examined in detail.

1. Intermediate Growth Rate Regime ($> \sim 10^{-5}$ mm/cycle):

Hydrogen-assisted fatigue crack propagation in this regime is charac-
terized by a marked load ratio/frequency dependence, is often coincident
with a fracture mode change from predominately transgranular to intergranu-
lar cracking, and occurs above a critical $K_{\text{max}}$ value, $K_{\text{max}}^T$, which is small
compared to $K_{\text{ISCC}}$ (Tables 2 and 3).

Many authors have observed similar hydrogen-assisted cracking in high
strength steels, with identical load ratio/frequency dependence, when $K_{\text{max}}$
exceeds $K_{\text{ISCC}}$ (1-4). The phenomenon, referred to as "stress-corrosion
fatigue" (Fig. 9b)(1), has been interpreted in terms of a superposition(2)
or process-competition(3) of sustained-load hydrogen-induced cracking and
pure mechanical fatigue components. Reaction kinetic studies(9, 22) indicate
that such environmentally-induced cracking can be attributed to a mechanism
of hydrogen embrittlement, rate-limited by surface reactions at the crack
tip. Specifically, it appears that in gaseous hydrogen atmospheres this
rate-limiting step involves chemisorption of hydrogen atoms, whereas in
water environments, crack growth is limited by the oxidation of freshly
exposed iron surface at the crack tip(9, 22, 28). At higher frequencies,
other processes such as gas phase transport may be limiting(28).

Similar kinetic studies(9) in lower strength 2-1/4 Cr-1Mo steels (SA542-2)
have shown that hydrogen-assisted cracking in this regime (i.e., above $K_{\text{max}}^T$)
is also rate-limited by chemisorption for crack growth in gaseous hydrogen,
and the acceleration in growth rates has been attributed to hydrogen embrittle-
ment mechanisms (although the precise nature of these mechanisms for lower
strength steels are uncertain). In view of the presence of a predominantly intergranular fracture for hydrogen-assisted cracking in the present steels (Fig. 6), however, it is reasonable to presume that the embrittlement mechanism involves hydrogen-induced decohesion at grain boundaries, similar to that observed in high strength steels\(^{(20)}\).

In terms of macroscopic growth rate behavior, the data in Figs. 1-4 indicate that an effect analogous to stress-corrosion fatigue takes place in the mid-range of growth rates (above \(\sim 10^{-5}\) mm/cycle) in lower strength steels, with the very notable exception that it occurs at stress intensities well below \(K_{\text{Iscc}}\), i.e. at \(K_{\text{max}} < K_{\text{Iscc}}\) where no such hydrogen embrittlement would normally result under purely sustained loading. This suggests some synergistic interaction (rather than additive or mutually-competitive interactions) between environmental and mechanical fatigue contributions to crack growth. However, rather than occurring through some basic change in embrittlement mechanism, it is felt that the role of cyclic loading is simply to maintain a sharpened crack tip, thus continuously providing freshly exposed metal surface there for hydrogen to adsorb.

We are now faced with a terminology problem since the nature of the hydrogen-assisted growth observed, with its characteristic fracture mode and frequency/load ratio dependence, conforms to stress-corrosion fatigue (c.f. Fig. 1 with Fig. 9b), yet in lower strength steels, the effect clearly occurs "below \(K_{\text{Iscc}}\)". Conventionally, such environmentally-assisted fatigue behavior below \(K_{\text{Iscc}}\) has been termed "true-corrosion fatigue"\(^{(1, 29, 30)}\), as shown in Fig. 9a, yet the characteristics of the present effect clearly differ from those depicted in this figure. It is apparent that the commonly used "above the below \(K_{\text{Iscc}}\)" terminology\(^{(1, 29, 30)}\) for corrosion fatigue, whilst perhaps providing a simple and useful classification for strain-rate-insensitive high strength steels, can be misleading for lower strength materials. This follows from the fact that in such ductile alloys, the stress intensities necessary
for the onset of such hydrogen-induced cracking (from hydrogen embrittlement) are different under sustained and cyclic loading (i.e., $K_{\text{iscc}} \neq K_{\text{max}}^T$). Two reasons can be advanced for this. First, as pointed out by Ford (31) and Dawson and Pelloux (32) for aqueous corrosion fatigue, lower strength steels are more strain-rate-sensitive than high strength steels such that $K_{\text{iscc}}$ environmental thresholds should not be taken as material constants for a particular alloy/environmental system, and can be expected to be reduced under dynamic (i.e. cyclic) straining conditions. Second, since $K_{\text{iscc}}$ measurements are often performed on test-pieces previously pre-cracked in air, and stressed under fixed-load or rising-load conditions, the critical event for determining the $K_{\text{iscc}}$ threshold may often simply involve hydrogen permeation through, or fracture of, the protective oxide scale previously formed at the crack tip. In fact, by pre-cracking in the actual hydrogen environment under test and employing fixed displacement conditions on side-grooved specimens, Shaw and Johnson (33) have recently demonstrated that significantly lower $K_{\text{iscc}}$ values, approaching $K_{\text{max}}^T$ values, can be measured in lower-strength steels including 2-1/4 Cr-1Mo alloys.

Thus, we can regard the value of $K_{\text{max}}^T$ as an effective threshold stress intensity in fatigue for gaseous hydrogen-induced cracking by (sustained load) hydrogen embrittlement mechanisms*, which is nominally equal to the sustained-load $K_{\text{iscc}}$ threshold in strain-rate-insensitive high strength steels (1), yet is considerably less than $K_{\text{iscc}}$ in the present lower strength steels.

Similar arguments (31, 32) have been proposed for corrosion fatigue crack growth in aqueous environments for a number of alloy systems, where the environmental contribution to cracking involves active path corrosion

*The separate role of hydrogen in influencing fatigue crack growth at near-threshold levels is considered to be primarily independent of conventional hydrogen embrittlement mechanisms, (11, 13, 16) as discussed below.
in addition to, or in place of, hydrogen embrittlement mechanisms. Dawson and Pelloux (32), in fact, refer to their environmental threshold as $\Delta K_{SCC}$ for aqueous corrosion fatigue in titanium alloys. However, since the onset of the environmentally-assisted crack growth occurs above a constant maximum stress intensity ($K_{max}^T$) (independent of $R$) for the present case of gaseous hydrogen environments (Table 3), it is preferable to define the environmental threshold in terms of a $K_{max}$ value, rather than a particular alternating stress intensity. It is perhaps worth noting here that certain authors (6, 10, 19, 34, 35), who have examined fatigue crack propagation behavior over a limited range of growth rates, have mistakenly interpreted this environmental threshold as the $\Delta K_0$ threshold for no fatigue crack growth. As shown by the data in Fig. 1-4, this is clearly erroneous, since $\Delta K_0$ thresholds are generally an order of magnitude smaller.

Finally, the question arises as to the reason for the existence of an environmental threshold stress intensity ($K_{max}^T$) for a hydrogen embrittlement contribution to fatigue crack growth. From the present data, the value of $K_{max}^T$ appears dependent upon frequency (Figs. 1 and 2) and hydrogen pressure (Fig. 3), and independent of load ratio (Table 3). Such observations are consistent with modelling studies (20, 23) which equate the critical stress intensity, above which hydrogen embrittlement is predominant, with a critical solubility of hydrogen ahead of the crack tip. From Eq. (1), this critical hydrogen concentration ($c_H$) is dependent upon the hydrostatic stress (i.e. flow stress and stress state), and the hydrogen concentration in the lattice (i.e. gaseous hydrogen pressure and temperature). Thus, by increasing the hydrogen pressure an earlier onset of hydrogen-assisted growth is to be expected (Fig. 3), whereas the similar effect observed with decreasing frequency (Fig. 1) is at least qualitatively consistent with the kinetic aspects of there being sufficient time for the critical step in the hydrogen embrittlement process to occur. This critical step can be considered in terms of a
competition between several processes (Fig. 8), principally involving the rate of hydrogen adsorption at the crack tip, its transport into the lattice and the rate of formation of fresh surface as the crack grows. Of these, hydrogen transport can be quickly dismissed as a rate-limiting step simply from hydrogen diffusion data. Using the electrochemical permeation technique of Devanathan and Stachurski(36), our measurements on unstressed samples of the three classes of 2-1/4 Cr-1Mo steels yielded an average diffusion coefficient for hydrogen permeation (D) of roughly $5 \times 10^{-7}$ cm$^2$/sec. Using the simple relation for the distance $x$ for hydrogen diffusion into the lattice in time $t$, namely

$$x \sim 4 \sqrt{Dt},$$

implies that hydrogen will permeate through the lattice by distances of roughly 4 and 40 μm during one cycle, for frequencies of 50 and 0.5 Hz respectively. Since this is several times larger than the crack advance per cycle, without even allowing for dislocation-aided transport(25), hydrogen transport can clearly be dismissed as rate-limiting over the frequency range studied. However, as noted above, more detailed kinetic studies by Wei and co-workers(9, 22, 28) equate the rate-limiting step to chemisorption of hydrogen at the crack tip for gaseous hydrogen atmospheres. Related arguments have been advanced for the analogous effect of an environmental threshold for corrosion fatigue in aqueous environments, where now the frequency dependence on $k_{max}^{T}$ is assumed to be a function of the interaction between the rate of oxide rupture at the crack tip, the rate of passivation and the rate of metal dissolution or hydrogen production at the bared surface(31, 32, 39).

2. Near-Threshold Regime ($< \sim 10^{-6}$ mm/cycle)

Since it is established that hydrogen-assisted fatigue crack growth in the intermediate range of growth rates above $\sim 10^{-5}$ mm/cycle is associated
with hydrogen embrittlement mechanisms for lower strength steels tested in
gaseous hydrogen (9, 12, 22), and that the value of $K_{\text{max}}$ represents an
effective environmental threshold for such sustained-load embrittlement
under cyclic stresses, the question immediately arises as to the
nature and origin of the even larger differences in growth rates between
hydrogen and air at near-threshold growth rates at stress intensities below
$K_{\text{max}}$. As shown in the current work (Figs. 1-4), the apparent enhancement
of growth rates in hydrogen, as crack velocities are reduced towards $\Delta K_0$,
is only evident at low load ratios and involves no apparent change in
fracture mechanism. Based on detailed studies reported elsewhere (11-16, 18),
it is our belief that this effect in lower strength steels is primarily
controlled by mechanisms other than classical hydrogen embrittlement.
First, the paucity of appreciable differences in crack growth behavior in
air and hydrogen at high load ratios (Figs. 2-4) is inconsistent with such
embrittlement mechanisms since, from Eqn. (1), any increase in $K_{\text{max}}$ relative
to $\Delta K$ would tend to raise the local hydrogen concentration ($c_H$) ahead of
the crack tip. Second, related studies (14, 15) using moist hydrogen gas in
SA542-3 show near-threshold growth rates and the value of $\Delta K_0$ to be essentially
similar to results shown for room air in Fig. 1. In distilled water growth
rates are again comparable with room air data, and if anything marginally
slower (13-15). Third, when SA542-2 and SA542-3 steels are tested in dehumidified
helium gas, near-threshold fatigue crack growth rates are virtually identical
to behavior in dry hydrogen gas (13-15). Growth rates in the inert gas,
whilst showing the expected slower crack velocities at intermediate growth
rates, are two orders of magnitude faster than in moist air at near-threshold
levels at $R = 0.05$. Similar to behavior in hydrogen, though, this "apparent
acceleration" in helium is only evident at low load ratios (13-15, 18).
As described in detail elsewhere (11-16, 18), such anomalous behavior with regard to environmental effects at near-threshold growth rates can be explained in terms of the role of excess corrosion deposits formed within the crack in promoting crack closure in moist environments. According to this model, termed oxide-induced crack closure, near-threshold growth rates in lower strength steels are apparently enhanced in dehumidified environments (such as hydrogen and helium) principally because of an absence of moisture compared to air (and moist hydrogen). Moist atmospheres result in the formation of readily observable oxide films on the crack flanks (11-18, 38), which are thickened at low load ratios by "fretting oxidation" (38), i.e., a continual breaking and reforming of oxide scale behind the crack tip to create new zones of fresh surface due to a "smashing" together of crack surfaces as a result of plasticity-induced crack closure (34) and large Mode II displacements (41) characteristic of near-threshold growth. This oxide debris, which is far less predominant in dry, oxygen-free atmosphere or at high load ratios (where closure effects in general are minimal), provides a mechanism for increased crack closure in the form of a higher stress intensity to open the crack. The effect can be enhanced with irregular fracture morphologies, where due to the Mode II displacements associated with near-threshold crack advance, the crack can be wedged-open at discrete contact points along its length (termed "roughness-induced closure") (41-44). Such closure mechanisms, however, are specific only to near-threshold levels where the size-scales of the oxide debris and fracture surface roughness are comparable to the crack tip opening displacements.

Thus, interpretations of corrosion fatigue behavior in steels at near-threshold levels must include a contribution from the wedging action of corrosion deposits within the crack. Whilst conventional corrosion fatigue mechanisms, such as hydrogen embrittlement or active path corrosion, may
still play a role\(^{(14, 45)}\), at the frequencies generally utilized for near-threshold studies (i.e., in the range 20 to 200 Hz), the effect of oxide-induced crack closure can clearly dominate behavior, particularly in lower strength alloys, to an extent that environmentally-influenced fatigue crack propagation results appear markedly different from those normally observed at higher growth rates.

CONCLUSIONS

Based on a study of effects of gaseous hydrogen on ambient temperature fatigue crack propagation over a wide range of growth rates ($10^{-8}$ to $10^{-2}$ mm/cycle), in several classes of lower strength pressure vessel and piping steels ($\sigma_y = 290 - 770$ MPa), the following conclusions can be made:

1. Two distinct growth rate regimes exist where moist air environment leads to significantly slower crack growth rates than in dry gaseous hydrogen. Both regimes exist for stress intensities well below $K_{I_{sc}}$, the sustained-load environmental threshold for hydrogen-induced cracking.

2. In the mid-range of growth rates typically exceeding $10^{-5}$ mm/cycle, growth rates in hydrogen are enhanced by up to 20 times compared to air, coincident with a fracture mode change from predominately transgranular to predominantly intergranular cracking. Behavior in this regime is sensitive to load ratio ($R = 0.05 - 0.75$), cyclic frequency (0.5 - 50 Hz), and hydrogen pressure (0.14 - 6.9 MPa), and is analogous to so-called "stress-corrosion fatigue" in high strength steels, with the exception that it occurs above a critical maximum stress intensity $K_{T_{max}}$ (independent of R), which is considerably less than $K_{I_{sc}}$.

3. At ultralow, near-threshold growth rates (typically $10^{-6}$ to $10^{-8}$
mm/cycle) below $k_{\text{max}}^T$, crack propagation rates in moist air are progressively slower than in dry hydrogen (by up to 2 orders of magnitude) as the fatigue threshold $\Delta K_0$ is approached. The effect, which occurs without any apparent change in fracture mechanism, is only evident at low load ratios; little difference between the effects of the two environments is seen at $R = 0.75$.

4. In this near-threshold regime, growth rate behavior in dry helium gas is virtually identical to behavior in dry hydrogen, whereas behavior in moist hydrogen gas and distilled water is essentially similar to that in room air.

5. Primary mechanisms for environmentally-influenced crack growth in the two regimes are reasoned to be entirely different. Whereas behavior above $k_{\text{max}}^T$ in the mid-growth regime is attributed to hydrogen embrittlement, the role of hydrogen (and helium) at near-threshold levels is principally one of a dry, oxygen-free environment which minimizes the decelerating effect of oxide-induced crack closure.

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REFERENCES


15. S. Suresh, D. M. Parks and R. O. Ritchie, ibid.


### TABLE 1
Chemical Composition in wt. % of Steels Investigated

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA387</td>
<td>0.12</td>
<td>0.42</td>
<td>0.25</td>
<td>0.14</td>
<td>2.48</td>
<td>1.06</td>
<td>0.16</td>
<td>0.013</td>
<td>0.020</td>
</tr>
<tr>
<td>SA516-70</td>
<td>0.23</td>
<td>1.20</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.006</td>
<td>0.019</td>
</tr>
<tr>
<td>SA542-3</td>
<td>0.12</td>
<td>0.45</td>
<td>0.21</td>
<td>0.11</td>
<td>2.28</td>
<td>1.05</td>
<td>0.12</td>
<td>0.014</td>
<td>0.015</td>
</tr>
<tr>
<td>SA542-2</td>
<td>0.14</td>
<td>0.44</td>
<td>0.22</td>
<td>0.61</td>
<td>2.28</td>
<td>0.92</td>
<td>-</td>
<td>0.010</td>
<td>0.020</td>
</tr>
</tbody>
</table>

### TABLE 2
Ambient Temperature Mechanical Properties of Steels Investigated

<table>
<thead>
<tr>
<th></th>
<th>Yield Strength (MPa)</th>
<th>UTS (MPa)</th>
<th>Redn.Area(%)</th>
<th>$K_{ic}$ (MPa(\sqrt{m}))</th>
<th>$K_{iscc}$ (MPa(\sqrt{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Monotonic)</td>
<td>(Cyclic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA387</td>
<td>290</td>
<td>-</td>
<td>500</td>
<td>76</td>
<td>286 (H(_2) gas) &gt; 80</td>
</tr>
<tr>
<td>SA516-70</td>
<td>327</td>
<td>-</td>
<td>496</td>
<td>-</td>
<td>233 (H(_2) gas) &gt; 80</td>
</tr>
<tr>
<td>SA542-3</td>
<td>500</td>
<td>400</td>
<td>610</td>
<td>77</td>
<td>295 (H(_2) gas) 85</td>
</tr>
<tr>
<td>SA542-2</td>
<td>770</td>
<td>568</td>
<td>820</td>
<td>56</td>
<td>- (H(_2) gas) 80</td>
</tr>
</tbody>
</table>

### TABLE 3
Conditions for Onset of Hydrogen-Assisted Fatigue Crack Growth in SA542-3

<table>
<thead>
<tr>
<th>R</th>
<th>Frequency (Hz)</th>
<th>$\Delta K_T$ (*) (MPa(\sqrt{m}))</th>
<th>$K_{max}$ (*) (MPa(\sqrt{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>50</td>
<td>no effect</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>5</td>
<td>no effect</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>2</td>
<td>21.8</td>
<td>22.9</td>
</tr>
<tr>
<td>0.05</td>
<td>0.5</td>
<td>21.2</td>
<td>22.3</td>
</tr>
<tr>
<td>0.30</td>
<td>50</td>
<td>15.3</td>
<td>21.9</td>
</tr>
<tr>
<td>0.30</td>
<td>5</td>
<td>14.4</td>
<td>20.6</td>
</tr>
<tr>
<td>0.50</td>
<td>50</td>
<td>11.8</td>
<td>23.6</td>
</tr>
</tbody>
</table>

$\Delta K_T$ and $K_{max}$ are the values of the alternating and maximum stress intensities above which growth rates are sharply accelerated in hydrogen gas, with respect to air, in the mid-range of growth rates.
TABLE 4

CHARACTERISTICS OF ENVIRONMENTALLY-INFLUENCED CRACK GROWTH IN INTERMEDIATE AND NEAR-THRESHOLD GROWTH RATE REGIONS IN LOWER STRENGTH STEELS

<table>
<thead>
<tr>
<th>VARIABLE</th>
<th>INTERMEDIATE GROWTH RATES</th>
<th>NEAR-THRESHOLD GROWTH RATES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Range of Growth Rates</td>
<td>( \Delta a \geq 10^{-3} \text{ mm/cycle} )</td>
<td>( \Delta a \leq 10^{-9} \text{ mm/cycle} )</td>
</tr>
<tr>
<td>Influence of <strong>dry inert</strong> environment</td>
<td>growth rates <strong>smaller</strong> compared to moist environments</td>
<td>growth rates <strong>larger</strong> compared to moist environments</td>
</tr>
<tr>
<td>Influence of <strong>dry</strong> hydrogen gas</td>
<td>growth rates <strong>larger</strong> than in moist air</td>
<td>growth rates <strong>larger</strong> than in moist air</td>
</tr>
<tr>
<td>Influence of distilled water/aqueous media</td>
<td>growth rates <strong>larger</strong> than in moist air</td>
<td>growth rates marginally <strong>smaller</strong> than in moist air</td>
</tr>
<tr>
<td>Species responsible for differences in growth rates (between dry ( \text{H}_2 ) and moist air)</td>
<td><strong>HYDROGEN</strong> in gaseous form or internally charged or in “hydrogen-producing” media</td>
<td><strong>MOISTURE</strong></td>
</tr>
<tr>
<td>Magnitude of variations in growth rates caused by the above species</td>
<td>up to 20 times (over range studied)</td>
<td>up to 100 times (over range studied)</td>
</tr>
<tr>
<td>Fractographic feature characteristic of cracking in hydrogen</td>
<td>predominantly intergranular</td>
<td>predominantly transgranular</td>
</tr>
<tr>
<td>Magnitude of driving force</td>
<td>( K_{\text{mat}} (= \text{constant}) &lt; K_{1\text{sec}} )</td>
<td>( K_{\text{mat,0}} \ll K_{1\text{sec}} )</td>
</tr>
<tr>
<td>Influence of mechanical factors on corrosion fatigue</td>
<td>strongly dependent on load ratio and frequency (below a critical frequency)</td>
<td>environmental effects observed <strong>principally</strong> at low load ratios</td>
</tr>
<tr>
<td>Mechanistic process (responsible for environmental influences)</td>
<td><strong>Hydrogen Embrittlement</strong></td>
<td><strong>principally</strong> Crack Closure</td>
</tr>
</tbody>
</table>

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LIST OF FIGURE CAPTIONS

Figure 1. Influence of cyclic frequency on fatigue crack propagation in bainitic 2-1/4 Cr-1Mo steel (SA542-3) tested at R = 0.05 in moist air and dry hydrogen, showing two distinct regimes of environmentally-influenced crack growth.

Figure 2. Fatigue crack propagation in martensitic 2-1/4 Cr-1Mo steel (SA542-2), at R = 0.05 - 0.75 in air, hydrogen and hydrogen sulfide. (5 Hz data after ref. 9).

Figure 3. Fatigue crack propagation in ferritic-pearlitic SA516-70 steel at R = 0.15 - 0.75 in moist air and hydrogen gas, showing influence of high pressure (6.9 MPa) hydrogen. (Closed symbols refer to data from ref. 19).

Figure 4. Influence of load ratio on fatigue crack propagation in SA542-3 steel tested in moist air and dry hydrogen gas.

Figure 5. Predominately transgranular fracture morphology of near-threshold fatigue crack growth in 2-1/4 Cr-1Mo steel at 50 Hz, a) in moist air at ΔK = 7.3 MPa√m, and b) in dry hydrogen at ΔK = 4.8 MPa√m. Note absence of characteristic hydrogen fracture mode.

Figure 6. Fractography of fatigue crack growth in the mid-growth rate regime for bainitic 2-1/4 Cr-1Mo steel, tested at R = 0.30 at 50 Hz. Whereas failure remains predominately transgranular in air, note the fracture mode change in hydrogen to predominately intergranular fracture above ΔK = 14 MPa√m (K_{max} = 20 MPa√m), i.e. at K_T

Figure 7. Schematic diagram of the effect of dry gaseous hydrogen on fatigue crack growth in lower strength steels. R denotes load ratio, v frequency, T predominately transgranular fracture, and IG predominately intergranular fracture.

Figure 8. Schematic illustration of the possible steps involved in the embrittlement of steels by gaseous hydrogen atmospheres. \( \sigma_{yy} \) is the maximum principal stress as a function of distance x ahead of the crack tip (after ref. 28).

Figure 9. Basic types of corrosion fatigue crack growth behavior defined by McEvily and Wei (ref. 1); a) true-corrosion fatigue, b) stress-corrosion fatigue, and c) mixed behavior.
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XBL 8112-12990
Fig. 2. Fatigue crack propagation in martensitic $2\frac{1}{4}$Cr-1Mo steel (SA542-2), at $R = 0.05 - 0.75$ in air, hydrogen and hydrogen sulfide. (5 Hz data after ref. 9).
SA 516 Grade 70 Pipeline Steel

Ambient temperature

<table>
<thead>
<tr>
<th>R</th>
<th>Environment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>moist air (30% RH)</td>
<td>present study (50 Hz)</td>
</tr>
<tr>
<td>0.15</td>
<td>dry hydrogen (0.14 MPa)</td>
<td>present study (50 Hz)</td>
</tr>
<tr>
<td>0.15</td>
<td>laboratory air</td>
<td>Wachob and Nelson</td>
</tr>
<tr>
<td>0.15</td>
<td>dry hydrogen (6.9 MPa)</td>
<td>(0.1-10 Hz)</td>
</tr>
</tbody>
</table>

Fig. 3  Fatigue crack propagation in ferritic-pearlitic SA516-70 steel at R = 0.15 - 0.75 in moist air and hydrogen gas, showing influence of high pressure (6.9 MPa) hydrogen. (Closed symbols refer to data from ref. 19).
Fig. 4 Influence of load ratio on fatigue crack propagation in SA542-3 steel tested in moist air and dry hydrogen gas.

XBL 8112-12993
Fig. 5  Predominately transgranular fracture morphology of near-threshold fatigue crack growth in 2%Cr-1Mo steel at 50 Hz, a) in moist air at $\Delta K = 7.3$ MPa$\sqrt{m}$, and b) in dry hydrogen at $\Delta K = 4.8$ MPa$\sqrt{m}$. Note absence of characteristic hydrogen fracture mode.
Mechanisms of fatigue crack growth in the mid-growth rate regime for bainitic 2%Cr-1Mo steel, tested at $R = 0.30$ at 50 Hz. Whereas failure remains predominately transgranular in air, note the fracture mode change in hydrogen to predominately intergranular fracture above $\Delta K = 14 \text{ MPa}\sqrt{\text{m}} (K_{\text{max}} = 20 \text{ MPa}\sqrt{\text{m}})$, i.e. at $K_{\text{max}}^T$. 

Fig. 6
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