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INITIATION OF ENVIRONMENTALLY-ASSISTED CRACKING IN LOW-ALLOY STEELS

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ABSTRACT

Environmentally-Assisted Cracking (EAC) in low alloy steels is activated by a critical level of sulfide ions at the crack tip, which is produced from dissolution of sulfide inclusions (MnS, FeS, etc.) in the steel following exposure by a growing crack (Scott, 1988). EAC of concern herein is the increase of fatigue crack growth rate of up to 40 to 100 times the rate in air that occurs at 240-300°C in high temperature LWR or boiler water environments. The initiation of EAC is the onset of the higher fatigue crack growth rates in fully developed cracks already presumed to be present due to fatigue, stress corrosion cracking, or induced by fabrication. Initiation of EAC is induced by a change in loading parameters causing the fatigue crack growth rate to increase from a small multiple (2-4) to 40-100 times the air rate. A steady state theory developed by Combrade, suggests that EAC will initiate only above a critical crack velocity and cease below this same velocity. However, more recent tests show that EAC can persist down to much lower velocities (100 times lower) in low oxygen water at slightly lower temperatures. A special set of experiments on high sulfur plate material demonstrate that EAC will not initiate from surface cracks with low sulfide inventories at low crack tip velocities. Transient diffusion calculations show that a finite crack extension at a high crack tip velocity is necessary to initiate EAC, providing a possible explanation for the lack of high crack growth observations reported in low alloy steels in structural applications involving low oxygen environments.

INTRODUCTION

Environmentally assisted cracking (EAC) in low alloy steels exposed to light water reactor coolants can increase fatigue crack growth rates up to 100 times. EAC of concern herein is the increase of fatigue crack growth rate of 40 to 100 times the rate in air that occurs at 240-300°C. EAC is generally believed to be activated by a critical level of sulfide ions in high temperature LWR or boiler water environments. The initiation of EAC in this paper refers to the onset of the higher fatigue crack growth rates in fully developed cracks already presumed to be present due to fatigue, stress corrosion cracking, etc., or induced by fabrication. The fundamental role of the sulfur content in the steel in causing this accelerated crack growth rate at 290°C, the kinetics of the growth rate, dependence on electrochemical potential, and micromechanisms of fracture have been extensively studied in laboratories around the world. Excellent reviews of fatigue crack growth and stress corrosion cracking in low alloy steels have been recently performed by Scott (1988) and James (1995a), and a detailed correlation of crack growth kinetics has been developed by Eason (1987). The fundamental role of sulfide ions in EAC at 290°C is to delay repassivation and consequently increase corrosion rates at the crack tip in low alloy steels, as discussed by Ford and Combrade (1985). Using EAC crack growth rates, fatigue crack growth can be conservatively assessed. For plants which operate mostly in a steady state mode, the crack growth predicted due to occasional transients may be acceptably small.

For applications where the calculated EAC crack growth is unacceptably high, less conservative crack growth rates are needed. EAC has been mitigated by high flow rates in laboratory tests, consistent with the concept of the sulfur being flushed from the crack tip. Alternately, if the sulfur content of the steels is known to be low and sulfide morphology is favorable, the likelihood of EAC may be considered to be remote in deaerated water.

The importance of the crack growth rate in describing EAC has been recognized for some

time. The crack tip strain rate is recognized as fundamental driving parameter for describing the oxide fracture at the crack tip during crack advance, but there are difficulties in calculating this parameter according to Scott (1988). Shoji, Takahashi, Suzuki, and Kondo (1981) successfully used the fatigue crack growth rate in air, which is proportional to the crack tip strain rate, to correlate EAC fatigue crack growth data. Gilman (1985) has more recently discussed this approach. Atkinson and Forrest (1985) qualitatively identified the role of crack tip velocity in the production rate of sulfide ions, and stated that a critical crack velocity was needed to cause EAC in several steels. This critical crack tip velocity depended on the sulfur content in the steels and diffusion in water.

The work by Combrade, Foucault, and Slama (1988) suggests a quantitative approach to describe EAC in high sulfur steel low oxygen and low flow conditions. In their model, the steady state sulfur concentration at the crack tip would be determined by a balance of production of sulfur determined by the advancing crack tip and losses due to diffusion. Under low oxygen conditions consistent with presence of deliberate hydrogen additions used in PWR, the corrosion potential will be the same at the crack mouth and crack tip, as dictated by the presence of the hydrogen. With low water flow conditions and cycling below 1 Hz, Combrade, et al identified diffusion as the dominant mass transport mechanism determining loss of sulfide ions from the crack. They theorized that a critical crack tip velocity of about 10^{-5} mm/s was necessary to produce the sulfur concentration for EAC to be sustained. They successfully correlated the occurrence or cessation of EAC with a critical crack tip velocity for tests at 288°C on several steels with sulfur levels of 0.013-0.025% S. Recent test data at lower temperatures of 243°C (James, 1994) and 204°C (Van Der Sluys, 1993) show that once EAC was turned on, the steady state crack tip velocities to sustain EAC could be as low as 5×10^{-8} mm/s, in contrast to the values observed at 288°C. These results seem to undermine the notion of a critical, safe velocity, below which EAC is of no concern. The concept of a critical velocity is restored by examining the transient conditions required to actually start EAC in a low alloy steel. It is shown that additional factors inhibit the startup of EAC in low oxygen

water, including delays due to the finite sulfide dissolution rates, minimum crack extension required to expose sulfides in sufficient quantity, loss of sulfide ions due to adsorption, and mass transport by diffusion during intermittent cycling.

The results show that for cracks due to, for example, thermal fatigue or from pre-existing austenitic cladding defects, EAC will not initiate in deaerated water unless crack velocities are above a minimum value of about 5×10^{-7} mm/s for high sulfur steel for an extended cycling period.

EXPERIMENTAL EVIDENCE FOR EAC INITIATION THRESHOLDS

Rapid increases in fatigue crack growth rates have been noted frequently, and in fact have been explicitly modeled by Eason (1987) as apparent thresholds. As pointed out by Eason et al (1987) many of these test results were not true thresholds, but represent changes in crack growth rate during testing due to startup transients or chemistry control problems. Determination of thresholds requires tests over a sequence of loading conditions to define the limiting condition causing the onset of EAC.

Two systematic studies of deliberate reductions in loading frequency to induce cessation of EAC and increases in frequency to re-establish EAC have been performed by Van Der Sluys et al. (1993) and Combrade, et al. (1988) at 288°C. The crack length versus loading cycles curve obtained by Van Der Sluys for a very long term test are shown in Figure 1. The tests were performed on a A533B plate material containing 0.013% S. Steady state high crack growth rates were established at a frequency of 0.0005 Hz, and then the frequency was reduced to 0.0001 Hz. The figure shows that high crack growth rates persisted for about 80 cycles after the frequency change, which at this very low frequency amounts to about 250 hours. Hence, even though the low frequency did not support EAC on a steady state basis, a very long transient period where EAC persisted did occur. It is believed this long transient represents the time for the crack tip to come to the reduced sulfide ion level required to turn off EAC.

After a long (about 300 cycles) period of steady state crack growth at low rates, the frequency was increased back to 0.0005 Hz. The low crack growth rate of 1.4×10^{-6}mm/s persisted for 500 cycles and a crack extension of 1.4mm, and a transient time of about 300 hours. After this the crack growth rate increased to a rate consistent with EAC. It is concluded that this velocity (1.4×10^{-6}mm/s) is close to minimum crack tip velocity V_{in} required to initiate EAC in this steel. The term crack velocity (V) as employed herein is defined as the average crack extension (Δa) per unit time, and is intended to describe general loading conditions which may occur in service including dwell times where loads are effectively constant. In this respect it differs from the time-based environmental crack growth rate $\mathring{a}_e$, which is defined as the crack extension (Δa) divided by the load rise-time for a continuous fatigue loading cycle in laboratory tests.

Both the long transient times where crack growth rates persisted at a rate corresponding to past frequency and the crack growth rate dependence on the past frequency prove that the presence and degree of EAC is history dependent. Combrade et al. (1988) did a series of tests to demonstrate this effect as illustrated in Figure 2. The tests were performed on an A508 Cl3 forging containing 0.013-.014% S. The Figure shows that the crack growth rate is really double valued, exhibiting either high EAC rates if loading went from high to low frequencies, and low non EAC rates if loading started from low frequencies where EAC was off. The authors described the transient times for the rate persisting at the prior frequency rate as "delayed transients", and these times ranged from 16 hours to 62 hours. Combrade, et al. suggested that these tests provided evidence for a critical velocity, below which EAC cannot be sustained due to low sulfur production rates. EAC could be turned on again by increasing the frequency, and therefore by increasing the crack tip velocity above 7×10^{-6} mm/s. Above this critical velocity, the rate of sulfur supply was sufficient to obtain a critical sulfide ion concentration to turn on EAC.

More recently, James (1994) has performed frequency decreasing tests at 243°C. The tests were performed on high sulfur (0.026-0.035%) A302B plate material in hydrogenated low oxygen water. In contrast to results at 288°C in low oxygen water, EAC rates persisted to very low crack tip velocities as shown in Figure 3. The lowest velocity obtained was 5×10^{-8}mm/s, over 100 times lower than observed by Combrade at 288°C for EAC to turn off. Unfortunately, EAC did not turn off even though the test was run over 40 days at this condition. The rate was still over 5 times that of the low sulfur or non-EAC line or ten times the rate in air. Van Der Sluys (1993) noted a similar behavior occurring in oxygenated BWR water with EAC turning off at 288°C but persisting at 204°C to the lowest velocity tested, 5×10^{-8}mm/s.

This behavior shows that EAC if started in high sulfur steels, could be maintained for long times at low frequencies or low velocities at 243°C and 204°C. However, it does not imply that EAC will initiate at these low velocities or frequencies.

EAC INITIATION TESTS

A special test series on high sulfur A302B was designed to verify whether EAC initiation was a threshold related phenomena at 243°C. The test conditions were low oxygen water containing 20-60 ml H_2/kg H_2O and room temperature pH 10.1 to 10.3, with quasi stagnant flow conditions. Fatigue loadings were applied using feedback-controlled servo-hydraulic systems. A "positive sawtooth" loading waveform was employed that maximized the rise time T_r for a given cyclic period: 85 percent of the cyclic period was utilized during the load rising phase, and 15 percent of the cyclic period was the load falling phase. Most experiments utilized 1T-CT specimen from high-sulfur heats of ASTM A302-B steel (Heats 21478-10 and 20869-2), with minimum sulfur level of 0.026 wt%. Use of this high sulfur plate material provided assurance of EAC susceptibility. The air pre-crack lengths were about 2.5mm, which exposed a sufficient sulfide inventory to cause EAC at the start of cycling in all previous tests. As pointed out by Combrade, the undissolved sulfides from a pre-crack can provide the critical sulfur level at the crack tip independent of cycling conditions and provide a false threshold indication. To avoid this, two methods of preparing clean sulfide free crack tips were used. For compact tension specimens, a soak at the test temperature of at least two weeks with the crack held open at 82% of the maximum fatigue load was employed,

while for surface crack specimens a special crack flushing apparatus constructed for other tests was employed. The surface crack specimen and crack flushing apparatus are described by James, et al. (1995b). The time-domain "base" crack growth rates ($\dot{a}_b$) for these tests covered a range from 2.5×10^{-8} mm/s to about 2.5×10^{-6}mm/s, in order to define a minimum velocity to initiate EAC.

An overall summary of tests run on high sulfur specimens which had cracks cleaned of sulfides prior to cycling is provided in Fig 4. The Figure shows that EAC initiated only above a rate of about $V_{in} = 5 \times 10^{-7}$mm/s. Below this rate, no EAC transition was observed to 2000 hours, the longest time tested. A total of 15000 hours test time was spent verifying no EAC at low velocity. The data show there is a critical velocity for EAC initiation for this steel and temperature.

A summary of the test conditions for EAC initiation from the present tests and those by Combrade and Van Der Sluys et al. is provided in Table 1. A recent test by Atkinson, et al (1995) is also included. It is seen that the present test results on high sulfur A302B steel plate (0.026% S) show about three times lower threshold velocities compared to the A533B plate (0.013% S) results developed by Van Der Sluys et al. The threshold velocity for the forging (0.013% S) studied by Combrade is five times higher than observed by Van Der Sluys at the same temperature on a plate steel with the same nominal sulfur level, suggesting that both the sulfur content and morphology can be important in the threshold velocity. These results are consistent with the concept of a threshold velocity required to turn on EAC when the inventory of sulfides from precracking has been soaked away. There is also a clear threshold at 149°C as reported by James (1994). It is recognized that the fundamental role of sulfur ions has not been established at the lower temperature of 149°C. Despite this fact, it is worthwhile to include the transitions at 149°C because from a phenomenological point of view, accelerated crack growth has occurred. The data show critical velocity transition, which is important for any practical applications at this lower temperature. The data at 243°C and 288°C show threshold velocities for EAC initiation, consistent with the Combrade concept.

Equally important, all the tests show that a finite crack extension greater than 0.3mm was required to turn on EAC, even when rates were above V_{in}. In other words, the initiation velocity must be operative for a sufficient crack extension to produce the critical crack tip sulfide concentration for EAC.

DIFFUSION ANALYSIS

Diffusion analyses were performed to relate the test data to fundamental theory of EAC, and establish a firmer foundation for application to more general loading conditions. The work by Combrade, Foucault, and Slama (1988) is the starting basis for this approach. In their model, the steady state sulfur concentration at the crack tip would be determined by a balance of these production of sulfur determined by the advancing crack tip and losses due to diffusion. The authors point out that diffusion is the dominant mass transfer in stagnant low oxygen pressurized water environments at frequencies below 1 Hz. Flow would decrease sulfur concentrations, so results here are conservative for non stagnant conditions. The symbols used in the analysis are listed in Table 2 for convenience.

The effects of segregation of sulfides observed by Bulloch and Atkinson (1994) are not explicitly modeled. It is recognized that such inclusion clusters can cause localized EAC on the fracture surfaces, and that inclusion clustering plays a role in making EAC more likely. Such inclusion clustering is quite common in the high sulfur (0.026%) A302B steels which were tested for EAC initiation in Figure 4, and the steels exhibit a clear transition to EAC with increasing crack tip velocity. Similar transitions to EAC occurred for the medium sulfur forging and lower sulfur plate listed in Table 1. The initiation velocities range from 5E-07mm/s on the A302B plate to 8E-06mm/s on the relatively low sulfur plate, a factor of 16. Hence, it is clear that for practical purposes, EAC initiation occurs in a wide range of steels, with a wide range of segregation expected. A continuum approach for sulfide morphology is used for simplicity. It will be demonstrated that such an approach describes the key features of sluggish sulfide dissolution rates and sulfur adsorption on EAC buildup to predict the actual time dependent behavior observed in the laboratory tests.

For a simple one dimensional steady state diffusion balance of sulfur production at a flux of F_o at the crack tip, and diffusion specified by the diffusion constant D to the crack mouth, the concentration C will decrease with distance x according to

$$F_o = -D \frac{dC}{dx} \qquad (1)$$

which for C=0 at a distance a from the source leads to

$$C = F_o a/D \text{ at the crack tip} \qquad (2)$$

Using the analysis by Combrade, the steady state sulfur supply rate or flux in a crack F_o is related to the crack growth rate å and the bulk sulfur level S in the steel by

$$F_o = (\rho_{steel}/\rho_w)(d_{eff}/d)S \text{ å } = H \text{ å} \qquad (3)$$

where ρ_{steel}, ρ_w are the densities of steel and water respectively, H represents the sulfide ion supply and d is the average crack opening. The distance d_{eff} is the "equivalent thickness of material" over which sulfides are exposed and is expected to be "significantly larger than the average size of the inclusions" due to non planar path caused by cracked inclusions ahead of the crack tip, according to Combrade, et al. (1988). In the steady state limit, Combrade et al. were able to rationalize a variety of laboratory test results at 288 °C showing the onset or cessation of EAC for crack tip velocities greater or less than a critical velocity å_{crit} which produces a critical sulfide ion concentration C_{crit} required for EAC. They assumed a critical sulfide ion concentration in water for EAC of 20 ppm. (The value of 3 ppm is considered a better estimate based on experiment by Van Der Sluys and Emanuelson, 1993 and is used elsewhere in this paper.) For a sulfur content in the steel of 0.02 wt % S and D = 2 x 10^{-4}cm²/s Combrade et al. were able to show consistency if they assumed values for d_{eff}/d of 2-20. The model explained the load history dependence, leading to the hysteresis effect shown in Figure 2.

The calculations will now be extended to dynamic conditions required to describe EAC initiation, and develop the basis for a critical crack extension observed in testing.

The diffusion based transport model can be directly extended to account for more sporadic loadings which occur in service, and to define the limits for EAC to be turned on in service. The physical case of interest is that of a clean crack of length a, which is subjected to cycling at time zero. If the solid were a continuous source of sulfides, as implied by the steady state equation above, this would lead instantly to a sulfur flux F_o, given by Equation 3. For a constant source flux F_o of sulfur ions starting at time = 0 at the crack tip, the time dependent sulfur concentration can be calculated exactly in the case of one dimensional diffusion flow. The results are available in Carslaw and Yaeger (1959)

$$C(x, t) = \frac{F_o(a-x)}{D} + \qquad (4)$$

$$\Sigma_n C_n \sin [m\pi(a-x)/2a)] \exp (-Dm^2\pi^2 t/4a^2)$$

where m = (2n + 1) and

$$C_n = \frac{-8 F_o a}{D\pi^2} \frac{(-1)^n}{m^2}$$

The time dependent concentration at the crack tip (x=0) is shown in Figure 5.

The series converges very rapidly for all but small values of time because of the $(2n+1)^2$ dependence in the exponential terms, and the first term provides a good approximation for times as low as 0.1 of the diffusion time constant a^2/D. Using the value of D of 2×10^{-4} cm²/s cited by Combrade, and a crack length of 1cm, the concentration rises to 90% of its final value at the diffusion time constant which is 1.4 hour. This is much less than the experimentally observed times associated with the tests in Table 1, which range from a minimum of 16 to 350 hours. Furthermore, the calculated crack extension required would be extremely small for EAC initiation-e.g. only 1E-03mm for a crack velocity of 3E-07mm/s. Typical values of crack extension prior to initiation are 0.5mm. As a result, it is concluded that the idealized constant source of sulfur assumed above does not adequately describe the experimental observations. It is essential to look in more detail at the microscopic process of sulfide particle exposure

and dissolution to develop a more realistic descriptions of sulfur buildup.

The typical crack extension during a single fatigue cycle is very small compared to large sulfide spacing. This can be seen by noting that crack extension per cycle for a ΔK of 50 MPa$\sqrt{m}$ would be a few microns, in the absence of EAC. Conversely, sulfide densities are about 6000/cm^2 for the high sulfur plate material tested at Bettis, so that an average separation is about 125 microns. This means that many cycles will be required before a steady state is reached in such a steel.

If n is the number of particles per unit volume, a number $P = n(d_{eff})(B)da/dN$ of sulfides would be exposed during one cycle of crack extension da/dN, for a crack width B and begin producing sulfide ions at a finite rate proportional to P, i.e., Pq for a constant rate q. The cycling is assumed to be intermittent in a general situation, with an increasing stress period (rise time) of T_r, a decreasing stress period T_{drop} and a constant load portion between cycles (dwell time) of T_{dwell} (Fig. 6). New sulfides are exposed during the rising load portion of the load cycle. During the next cycle occurring after a time $T_c = T_r + T_{drop} + T_{dwell}$, a new set of sulfides would be uncovered, and begin producing sulfide ions, along with the set previously exposed. The exposure of new sulfides occurs during the rising load portion while dissolution and diffusion are occurring at all times.

The flux F at the crack tip from the particles dissolving after one cycle is

$$F = P*Rate/(Bd) = Rate(nd_{eff}\,da/dN)/d \qquad (5)$$

where the sulfide ion production rate is q for a constant dissolution rate and $Mk_1\exp(-k_1t)$ for an exponential dissolution rate defined by k_1.

For a constant production rate q after N cycles, the flux would be

$$F = (qnd_{eff}\,da/dN*N)/d = qnd_{eff}\,\Delta a/d \qquad (6)$$

where Δa is the total crack extension. This is valid as long as all particles formed are dissolving - $NT_c < \tau$, where τ is the particle lifetime. Noting that $M = q\tau$, and $nM = \rho_{steel}\,S$,

and dividing by ρ_w to normalize it is seen that the expression for the flux can be compared to the Combrade expression in Eqn. 3):

$$F = (\rho_{steel}/\rho_w)\,(d_{eff}/d)\,S\,\frac{\Delta a}{\tau},\ NT_c < \tau \qquad (7)$$

Here, $\Delta a/\tau$ has replaced the crack tip velocity in Eqn 3. For greater generality, this is written as

$$F = H\,\Delta a/\tau,\ \text{where} \qquad (8a)$$

$$H_s = (\rho_{steel}/\rho_w)\,(d_{eff}/d)S. \qquad (8b)$$

A slightly modified calculation for H which incorporates the sulfide area fraction AF and allows for sulfide cracking above the crack plane is obtained by substituting the quantity ρ_s AF for bulk sulfur ρ_{steel} S to yield

$$H_{AF} = (\rho_s/\rho_w)\,(d_{eff}/d)\,AF \qquad (8c)$$

The sulfide area fraction is a direct measure of sulfides exposed on a crack plane, and allows for the possibility of some sulfur remaining in solution in the metal.

For small crack extensions, Eqn. 7 shows the flux buildup is sensibly proportional to the crack extension, which shows that the flux would be expected to be very small for a few cycles of crack extension. This shows that EAC initiation would not be expected for a few cycles of crack extension as shown in the calculations for an infinite crack. The flux buildup will be linear in N until particles formed at the first cycle are dissolved away, i.e. until $t = \tau$, the particle dissolution time. Since $t = NT_c$, the flux reaches a maximum value of

$$F_{max} = \frac{Hda/dN}{T_c} = HV \qquad (9)$$

The flux buildup is shown in Figure 7. It is a simple linear ramp in time, with a slope t/τ and maximum value reached at $t = \tau$. Defining the average velocity at the crack tip as $V = da/dN/(T_c)$, $F = H\,V(t/\tau) = $ which is valid for $t < \tau$. This expression can be compared to that developed by Combrade (Eqn. 3). There are two essential differences; the first is that the flux value used by Combrade is a maximum steady state

value while the actual case for a buildup increases as t/τ, and the second is that the velocity to be used is an average value, including the effects of dwell times which occur between cycles in service. This simple expression suggests the reason that a finite time and crack extension is required to reach a critical flux to initiate EAC, even when the average velocity exceeds the critical velocity required for EAC.

Physically, it may be expected that a crack extension at least as great as the sulfide spacing would be required to fully develop the maximum sulfur flux. On this basis, for the high sulfur A302B, a crack extension of about 0.125mm (0.005 in) would be required as a minimum. Hence, this concept explains some of the crack extension observed. The adsorption of sulfur on the crack faces treated below will be shown to increase this calculated crack extension.

An exponential dissolution rate represents a more realistic rate of sulfide ion production as particles shrink with time, and the flux can be calculated similarly as above. For the simple case of uniform cycles separated by a constant time, the time dependent flux is given by summing over N cycles with q in Eqn. 6 replaced by $Mk_1 \exp(-k_1 T)$ using the value $(N-j) T_c$ for time in the jth cycle. For N cycles this leads to

$$F = H \,(da/dN)\,(k_1)X \qquad (10)$$
$$(1-\exp(-Nk_1 T_c)) \,/\, (\exp(k_1 T_c)-1)$$

where H is the same as above. There are two limits of interest, depending on the value of $k_1 T_c$, and $k_1 N T_c = k_1 t$. For $t = N T_c$ less than $1/k_1$, F is simply $H(\Delta a)(k_1)$. This is the same Eqn. 8a, identifying $k_1 = 1/\tau$. The second limit of interest is for t greater than $1/k_1$, but $k_1 T_c$ is still small, i.e. cycling has occurred for many cycles but particle lifetimes are long compared to one cycle, the flux is given by $F_{max} = HV$, the same as above. The flux buildup is shown in Figure 7.

The flux buildup obtained for an assumed distribution of particle sizes $f(r) = f_o \exp(-r/r_o)$ is also shown. The more gradual flux buildup represents the fact that the larger particles contribute much of the sulfur, as the volume of sulfur varies as r^3 and dissolve over a longer period of time. The rate of buildup is reduced by a factor of about three.

Calculation of crack velocity based on T_c is appropriate since EAC initiation is dependent on the process of dissolution of metallurgical sulfides, which occurs throughout the entire stress cycle. Because of the importance of the average velocity being reduced by dwell times (Figure 6), a special test was performed in 243°C deaerated water. The stress cycle consisted of a triangular loading profile with 25.5-second load-rise time and a 4.5-second load-drop time; a dwell period was also incorporated at minimum load.

Two phases of dwell time testing were completed: Phase I used a 536-second dwell while Phase II used a 200-second dwell. In the absence of the applied dwell period in the loading cycle, the parameters chosen would have produced a time-based air rate, $\mathring{a}_b$, of approximately 1.6×10^{-6}mm/s. This corresponded to a region of time domain that was previously shown to initiate EAC in 30 hours. However, because of the incorporation of the dwell period at minimum load, the air crack velocity, $V_{air} = (da/dN)_{air}/T_c$, was reduced to a region of the time domain where EAC was not expected. V_{air} was roughly 9.1×10^{-8}mm/s in the case of the 536-second dwell, and 2.3×10^{-7} mm/s in the case of the 200-second dwell.

The crack length versus load cycle count results of Figure 8 are shown with the expected mean air rate, mean non-EAC rate, and mean EAC rate for comparison. Test results show that EAC did not occur after 520 hours of Phase I testing using a dwell time of 536 seconds. The average crack tip velocity, $\nabla = (da/dN)_{env}/T_c$, was roughly 1.3×10^{-7}mm/s. Without the 536-second dwell time, EAC would have been expected in about 30 hours. Approximately 622 hours of Phase II testing using a dwell time of 200 seconds also did not produce EAC. ∇ was roughly 2.4×10^{-7} mm/s. Based on crack length measurements made from the post test fracture surface, the total crack growth sustained during Phase I and Phase II was about 0.8mm. This crack length exceeds the estimated critical crack growth increment (0.3mm) to turn on EAC in this type of material. As shown in Figure 8, the crack growth behavior observed is more consistent with crack growth predicted by the mean air rate than the mean non-EAC rate. The results obtained in this experiment verify the concept that incorporation

of a dwell time in the loading cycle increases the time for sulfide ion transport away from the crack tip and thus decreases the sulfide ion concentration below the critical level for EAC. As a final demonstration of the effect of dwell time, EAC was turned on in the specimen shortly after reduction of the dwell time to zero.

CONCENTRATION CALCULATIONS FOR TIME DEPENDENT FLUX

The sulfur ion flux at the crack tip has been shown to be time dependent following exposure of a fresh crack to solution. Part of the time dependence is due to time dependent exposure of metallic sulfides due to crack extension, which itself can be intermittent. Another part is due to the dissolution rate of the sulfides following exposure. The combined effects of dissolution time and exposure to sulfides can be incorporated in the time dependent flux calculation, as shown above. At the same time, diffusion in finite boundaries is time dependent with its own time constant a^2/D, where "a" is a characteristic length, in this case the crack length. The following calculation illustrates how the concentration is affected by the combined time dependence of diffusion and flux buildup for the case of most interest, which is the linear ramp to reach the maximum flux. The flux is described by

$$F = F_o(kt), \text{ for } 0 < t < 1/k \text{ and} \tag{11}$$
$$F = F_o \text{ for } t \geq 1/k$$

Solutions to the diffusion equation with time dependent boundary conditions in general would require extensive numerical calculations. However, one particular case of interest can be solved directly by using series solution in Eqn. 4. This is the solution for sulfur concentration for a constant flux F_o starting at time equal to zero. The solution for the time dependent case can be built up from this formulation by breaking the time dependent flux into small increments F_o/N which start at time $t = j/(kN)$, for $j = 0$ to N. Here, N is an arbitrary integer, and k is the slope of the flux buildup with time.

The summation over j can be performed to revert to a single series, leading to the normalized concentrations at $x = 0$

$$\frac{DC}{F_o a} = kt \left[1 - \frac{8}{\pi^2} \sum_n \frac{[\exp(-m^2 k_2 t)][\exp(+m^2 k_2 t) - 1]}{m^4 k_2 t} \right] \tag{12}$$
$$m = 2n + 1 \qquad\qquad \text{for } kt \leq 1 \text{ and}$$

$$\frac{DC}{F_o a} = 1 - \frac{8}{\pi^2} \sum_n \frac{[\exp(-m^2 k_2 t)(\exp(m^2 k_2/k) - 1)]}{m^4 k_2/k} \tag{13}$$
$$\text{for } kt \geq 1$$

where $k_2 = D\pi^2/4a^2$ is essentially the reciprocal of the characteristic diffusion time a^2/D for the system, and can be thought of as a diffusion rate.

Plots of the buildup in the normalized concentration are given in Figure 9 for a series of values of k_2/k. The limit of $k_2/k << 1$ corresponds to fast dissolution compared to the diffusion times, and which physically could represent the case where particles are small or are relatively highly soluble. In this case, the simple case described in Eqn. 4 for the flux instantaneously reaching its maximum value is recovered.

As k_2/k increases, or dissolution times become significant compared to diffusion times, the buildup of the sulfur ion concentration is slowed, and longer times are required to reach the same fraction of the maximum concentration. For example, at $k_2/k = 1$, the sulfur concentration reaches 70% of the maximum value at $k_2 t = 1.5$, compared to $k_2 t = 1.0$ for high dissolution rates. At $k_2/k = 2$, the same level of sulfur ion is reached only at $k_2 t = 2$. For $k_2/k = 10$, it is seen that the level is less than 10% at $k_2 t = 1.5$.

Following Swann and Chapman (1990) and using values obtained from the literature of $D = 2E\text{-}04 cm^2/s$ at 288°C and a particle dissolution time of ten hours for a large sulfide of diameter 30 microns leads to a ratio $k_2/k = 17.8$, for a crack length of 1 cm. Such large particle diameters have been found, especially in high

sulfur plate material. For these particle dissolution times, the buildup in crack tip concentration would be delayed to $k_2 t = 18$, i.e., about a factor of 20 greater time than expected from diffusion. For a more nominal particle size of 10 microns, and assuming as Swann and Chapman that the dissolution time varies as the square of the radius of the initial particle, the time for dissolution would be 1.1 hour, corresponding to $k_2/k = 1.8$, or a delay in sulfur buildup of about a factor of two. The diameter of 10 microns represents the maximum observed by Bettis in medium sulfur forgings, $S = 0.010 - 0.015\%$. For low sulfur forgings, maximum diameters of 2 microns have been observed, leading to k_2/k of less than 0.1. In this limit, the sulfur buildup to the maximum level would be expected to be very rapid, and the diffusion rates would be limiting for sulfur buildup. However, the small particle size is associated with low amounts of sulfur in real steels, and EAC would be unlikely.

SEM exams of A302B specimens show that sulfide particles survive more than two days in A302B at 243°C, suggesting $k_2/k >> 1$. Qualitatively, this result verifies the significance of dissolution time noted above in the flux calculations. This is qualitatively consistent with the delay times for transitions to EAC, which show times of typically 10-30 hours delay to the start of EAC at high cycling rates.

Sulfur is known to be absorbed on crack flank sulfides, as shown by Hanninen, Vulli, and Cullen (1988). The authors identified both FeS and FeS_2 in the oxide film of test specimen crack surfaces. The atomic concentration of sulfur was as high as 0.32 of the iron level (or about 13 atomic %) on the top of the oxide layers at the crack tip for a plate specimen exhibiting EAC, and about half this level at the middle of the crack. Sulfur was present at significant depths in the oxide film, up to 100nm, indicating that it had become a part of the oxide itself, rather than just a surface layer. This was true, even for specimens which did not show EAC, indicating that chemical reaction with sulfur occurs even at lower sulfur concentrations in the crack solution.

The effect of adsorption is rather simple to model, as shown by Crank (1975). If the sulfur is adsorbed on the crack flanks at a concentration given by $R_a C$, where R_a is assumed to be greater

than one, the one dimensional diffusion equation becomes

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} - \frac{R_a dC}{dt} \quad \text{which becomes} \quad (14)$$

$$\frac{dC}{dt} = \frac{D}{(R_a+1)} \frac{d^2C}{dx^2} \quad (15)$$

which shows that the effect of adsorption is to reduce the diffusion constant by $1/(R_a+1)$. Hence, adsorption merely slows down the diffusion process, which will lead to longer times for buildup to the maximum fluxes. No new calculations are needed, as the existing solutions can be applied by substituting using the reduced values for the diffusion constant in the time constants. The maximum steady state values for $C = F_o a/D$ do not require a changed value of D because this level is set by the applied flux at the crack tip. The effect of adsorption is then to reduce the effective diffusion rate k_2 by $1/(R_a+1)$, and hence the ratio of diffusion rate to dissolution rates k_2/k. This is shown in Figure 10. The time and crack extension to reach EAC are increased by a factor (R_a+1). This result identifies another cause for the observed longer times to initiate EAC than would be anticipated from the diffusion time constant a^2/D.

Side Leakage

It is necessary to assess whether the diffusion out the sides of compact tension specimens leads to a significant correction on calculated sulfur concentrations at the crack tip. The one dimensional calculations in the text assume an infinite sample width, i.e., the concentration is uniform in the y direction. The effects of finite width can be calculated using the methods illustrated in Carslaw and Yaeger (1959), page 146 for heat transfer. The equation for steady state diffusion and steady state temperature are identical - i.e.,

$$\frac{\partial^2 C}{dx^2} + \frac{\partial^2 C}{dy^2} = 0 \quad (16)$$

The boundary conditions for a compact tension specimen of thickness B, and crack length a immersed in sulfur free water are that the sulfur

concentration is zero at the sides and the crack mouth, i.e., that is

$C = 0$ at $x=a$, for $0<y<B$ crack mouth   (17)

$C = 0$ at $y=0$, and $y=B$ for $0<x<a$, crack sides

$-\dfrac{\partial C}{\partial x} = F_o/D$, at $x=0$, for $0<y<B$,
a constant sulfur flux at the crack tip

Applying the same methods in Carslaw and Jaeger (1959), to these particular boundary conditions leads to

$$\frac{DC}{F_o a} = \frac{4B}{a\pi^2}\sum_{n=0}^{\infty} \frac{\sin[m\pi y/B]}{m^2}\frac{\sinh[m(a-x)\pi/B]}{\cosh[m\pi a/B]} \quad (18)$$

where $m = 2n + 1$

Plots of this function are shown in Figure 11, for $a/B=0$ to 0.5 for $y=0$ to B. It is seen that the concentrations at the crack tip are only slightly reduced with a/B less than 0.1, with only a 13% reduction within 10% of the specimen edge, and for a/B less than 0.3, less than a factor of two reduction within 10% of the specimen edge. The EAC tests performed used had crack extensions of $a/B < 0.2$, so were not affected by side leakage. However, it appears that compact tension specimens for $a/B=0.5$ or more would have concentrations reduced below the maximum value of unity even in the center of the specimen. Hence, caution should be used in correcting any critical concentration assessments in deeply cracked compact tension specimens.

DISCUSSION

The time to buildup depends on both diffusion rates of sulfide ions in water and the dissolution rates of metallurgical sulfide particles. The actual buildup time will be limited by the slower of the two processes, and can be estimated roughly as $t = 1/k+1/k_2$. As noted previously, diffusion is effectively slowed by adsorption, increasing the diffusion time to R_a/k_2. Also, the buildup rate due to dissolution is skewed to longer times by the decreasing rates with dissolution time and in plates and forgings where particle sizes cover a wide range, the larger particles with longer dissolution times tend to dominate. SEM of test specimens show that sulfides in A302B survive up to 58 hours. The delay in sulfide dissolution explains the observed minimum thirty hour time observed prior to the observation of EAC in high sulfur Alloy 302B at a high crack velocity. While the diffusion time for the diffusion constant $D=2 \times 10^{-4}$ cm^2/s suggested by the literature leads to a time of less than an hour, an adsorption ratio of ten would increase this to 7 hours. Actual times to change the crack tip chemistry are always longer than expected on the basis of diffusion alone because of adsorption and slow sulfide dissolution.

The times of 300 hours observed by Van Der Sluys (1993) et al. for the start of EAC in the A533B plate at a factor of ten lower crack tip velocity are much longer than the dissolution times even for large particles. Similar times for EAC initiation have been observed at low crack velocities in Bettis tests. This supports the concept that a finite crack extension is required to turn on EAC and that sulfur adsorption on crack flanks increases the required crack extension. The minimum cycling time to EAC would increase as $\Delta a/(velocity)$, which is consistent with factor of ten increase in time.

The model predictions are qualitatively consistent with the data in Table 1. However, the bulk sulfur is reduced by only two compared to A302B, yet V_{in} is over ten times larger for the forging tested by Combrade. The area fractions observed for forgings of this type are about a factor of five smaller (James and Poskie 1993), which would lead to a factor of five higher velocity required for EAC initiation in forgings based on Eqn 8c, which is more consistent with the higher velocity observed by Combrade. Hence, it appears that the area fraction correlates better with EAC initiation velocities than the bulk sulfur content. The area fraction can also explain the fact that EAC has not been observed for medium sulfur forgings at 243°C. The EAC rates are very similar to non-EAC rates at the velocity of 2.5×10^{-6}mm/s, where EAC should turn on based on area fraction calculations (see Figure 3). At 288°C where EAC rates are far higher than non EAC rates, EAC would be expected.

Data supporting this is shown in Figure 12. A medium sulfur forging, heat 5610, showed EAC at 288°C (Liaw, et al, 1989) for air crack growth

rates around and above 2.5×10^{-6} mm/s, but did not show EAC when tested at 243°C for air crack growth rates less than 2.5×10^{-6} mm/s James (1994). Hence, by using the concept of a critical concentration of sulfur required for EAC initiation, and using the area fraction of sulfides available, it is seen that EAC susceptibility is really a function of the crack velocity times the sulfide area fraction, and is not a property tied to a specific heat of steel.

Using the relationship $V_{in} = DC/Ha$, from combining Equations 2 and 3 a quantitative comparison can be made with the observed critical velocities. For A302B the initial crack lengths were 0.3 cm in initiation tests, and the quantity H_{AF} Equation 8c is 0.0024 (d_{eff}/d) using the average area fraction 0.0012. Using the critical sulfur concentration of 3 ppm based on Van der Sluys tests, it is seen that a d_{eff}/d of 20 would be required to agree with the minimum value of V_{in} of 5E-07mm/s. This suggests that far more sulfides than exposed on a perfect crack plane are active in the process. However, the value V_{in} used (5E-07mm/s) is a minimum value for all tests, which should correspond to a maximum sulfide area fraction. In fact, EAC was not initiated at this velocity in two out of three experiments. If the average velocity 1.9 E-6 mm/s prior to EAC initiation is used, then d_{eff}/d calculated is 5.2. Equations 8a and 2 can be used to predict the minimum crack extension required for EAC initiation. Using 2.4 days observed for sulfide survival and d_{eff}/d of 5.2 leads to Δa predicted of 0.4mm, which is in agreement with experiment.

The fact that the initiation velocities vary only slightly with temperature for A302B is consistent with the model, which contains only one parameter which varies with temperature, the diffusion constant. For an activation energy of 4kcal/mole, only a 25% decrease would be predicted as the temperature decreases from 288°C to 243°C.

SUMMARY AND CONCLUSIONS

A steady state theory by Combrade, et al. based on a balance between sulfide supply rate due to sulfide exposure by an advancing crack and mass transport by diffusion successfully correlated EAC data at 288°C in terms of a critical crack tip velocity, above which EAC could be activated and below which EAC would cease. This velocity was relatively high, about 10^{-5} mm/s. Practically speaking, this would mean that only applications that produced crack growths of greater than 320mm per year using air crack growth rates would be subject to the 40-100 times increase in crack growth due to EAC. Components using low alloy steels would typically be designed to last 50 years, so that crack growth rates would be of order 100 times lower, far below the value which turns on EAC. However, more recent data at 243°C in low oxygen water and past data at 204°C in BWR water showed EAC was still occurring down to velocities as 5×10^{-8} mm/s, the lowest velocities tested. A special series of tests on high sulfur plane with initially clean, low sulfide inventories was performed, demonstrating that the concept of a critical velocity for initiation of EAC was still valid, and providing a minimum value of 5×10^{-7} mm/s for this velocity and a crack length of 2.5mm. In addition, a critical crack extension of order 0.5 mm is required at rates above the critical velocity before EAC is activated.

Transient diffusion analysis was performed in an attempt to relate the minimum crack extension and observed times to EAC initiation to fundamental EAC theory. The finite crack extension required is a direct consequence of the fact that a significant area of sulfides exposed is required to provide the diffusion flux needed to obtain the critical sulfide ion concentration to turn on EAC. While diffusion transient times are only of order 1-2 hours, the sluggish dissolution times of two days observed for the high sulfur steels were successfully modeled to reproduce the minimum times of 30 hours for EAC to turn on.

The theory also predicted that dwell times would directly reduce the sulfide ion flux, meaning that service loading of intermittent nature would produce a much reduced sulfide density. This was successfully demonstrated experimentally.

The critical velocity for EAC in different steels was shown to correlate better with the sulfide area fraction than the bulk sulfur level, explaining the surprising fact that forgings of 0.013%S appear to have a ten times higher critical velocity than plates of the same or only two times higher sulfur levels.

The results of this analysis offer an explanation for the fact that observations of EAC fatigue crack growth are very rare or perhaps nonexistent in service under low oxygen conditions (Scott, 1988). The successful experience in vessels around the world cannot be considered definitive because crack extension measurement have not always been made at the beginning of life and periodically through service. However, experience from around the world has shown excessive crack growth is rare in low alloy steels in service and when it occurs it appears to be associated with large initial flaws, high cycle loads not considered in design, or the presence of high oxygen, copper or sulfur contamination.

The transient diffusion performed herein provides an explanation for the differences between service experience and laboratory data in low oxygen environments. The average crack tip velocity in service for almost all components will typically be below the critical velocity to start EAC as the sulfide supply rate is low and diffusion will hold the sulfur ion concentration below a critical level, as shown by Combrade. Surface cracks are the most limiting starting defects. Surface flaws are realistically assumed to come from either weld defects in austenitic cladding or from pits or fatigue initiation in unclad components. Such defects would be small and have no significant MnS inventory so that EAC will not be initially on. The finite crack extension at crack tip velocities greater than V_{in} evidently does not occur for almost all large components in low oxygen water. However, EAC would be predicted to occur for deeper cracks in high sulfur steels, which reduces the critical velocity to rates which may be more limiting-for example, a 30mm crack leads to V_{in} = 1.6 mm/year.

ACKNOWLEDGEMENTS

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Table 1

EAC INITIATION THRESHOLD TEST SUMMARY

MATERIAL	SULFUR %	TEMP °C	V_{in} (min) mm/s	CRACK EXTENSION* mm
A533B	0.013	288	1.4×10^{-6}	1.4
A508CL3	0.013	288	7.1×10^{-6}	0.4-.8
A302B	0.026	243	5.1×10^{-7}	0.3-.8
A533B	0.007	290	8×10^{-6}	NA
A302B	0.026	149	1.0×10^{-6}	1.0

*CRACK EXTENSION OBSERVED PRIOR TO EAC

|	
a	crack distance to diffusion sink in pure water
$\mathring{a}$	environmentally affected fatigue crack growth rate
$\mathring{a}_b$	fatigue crack growth rate in air environment
$\mathring{a}_e$	fatigue crack growth rate in water with EAC on
d	average crack opening
d_{eff}	equivalent thickness for sulfides exposure due to nonplanar crack growth
k	flux buildup rate
k_1	metallic sulfide dissolution rate constant
$k_2 = \pi^2 D / 4a^2$	diffusion rate constant
m	volume of sulfides per unit length of crack
n	number of sulfide particles per unit volume in steel
q	sulfide production rate for single particle
r	particle radius
t	time from start of cycling in diffusion calculations
AF	area fraction of sulfides exposed
B	crack width or specimen thickness for compact tension
C (x, t)	instantaneous sulfide ion concentration in liquid at position x, time t
C_{cnat}	minimum sulfide ion concentration to sustain EAC
D	sulfide ion diffusion constant in water
F	sulfide ion diffusion flux at crack tip, F_o steady state value
H_s	amount of metallic sulfides exposed per unit crack volume, using bulk sulfur.
H_{AF}	amount of metallic sulfides exposed using sulfide area fraction.
K	stress intensity
M	sulfide particle volume
N	number of fatigue cycles
R_a	sulfur adsorption ratio
S	sulfur concentration in metal
T_{dwell}	dwell time between cycles where loads are constant
T_r	load rise time lending to crack extension
T_{drop}	load decreasing portion of cycle
T_c	average cycle period including hold time = $T_r + T_{drop} + T_{dwell}$
V_{in}	threshold crack tip velocity for EAC initiation
X	distance measured from the crack tip toward the crack mouth
τ	dissolution time for the particles
ρ_s	manganese sulfide density
ρ_w	water density
ρ_{steel}	steel density
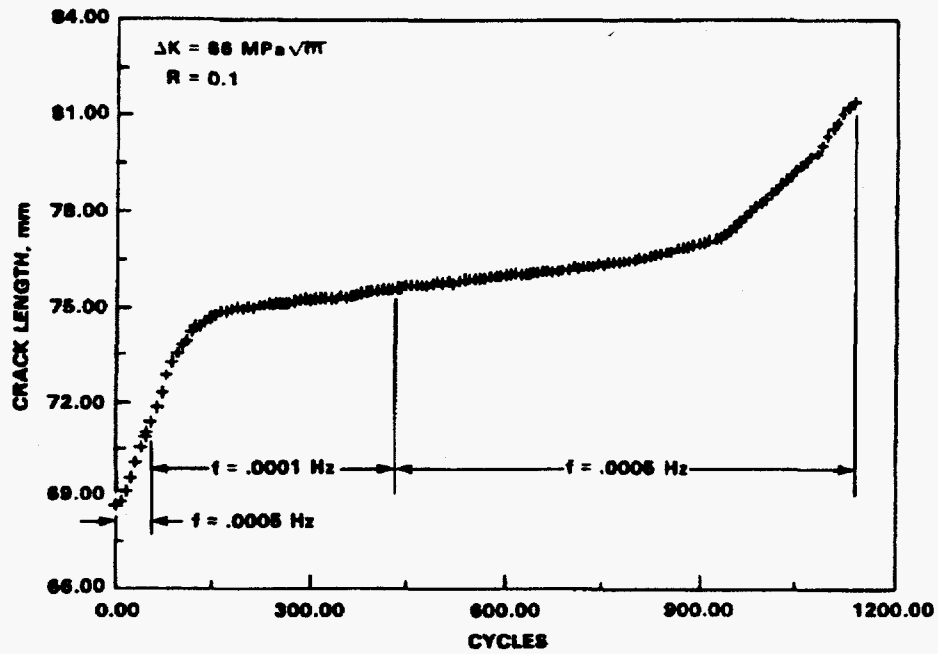
FIGURE 1. EAC SWITCHING ON AND OFF DUE TO FREQUENCY CHANGES (VAN DER SLUYS, 1993).
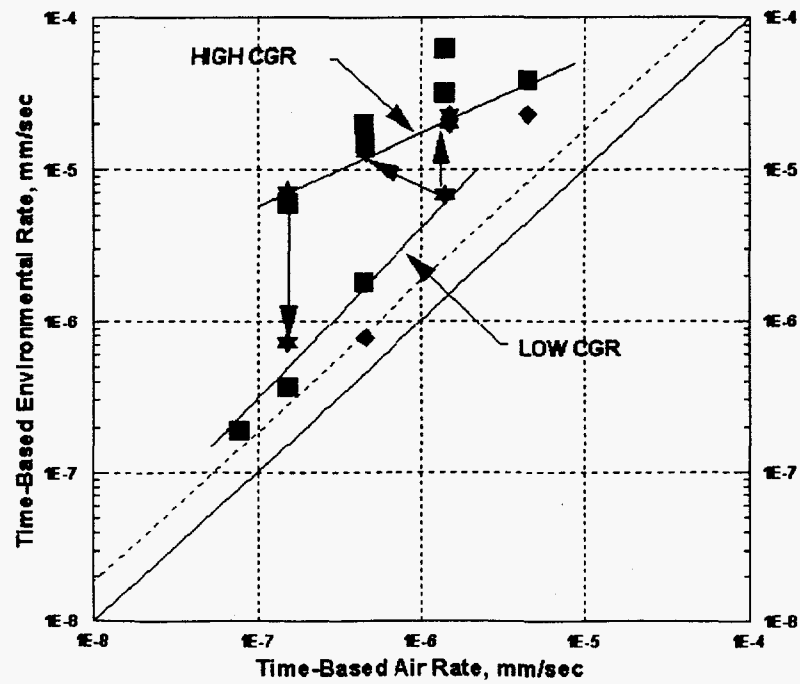

FIGURE 2. EAC SWITCHING ON AND OFF DUE TO FREQUENCY CHANGES (COMBRADE, 1988). AT CRITICAL VELOCITY, EAC TURNS ON OR OFF (ARROWS).
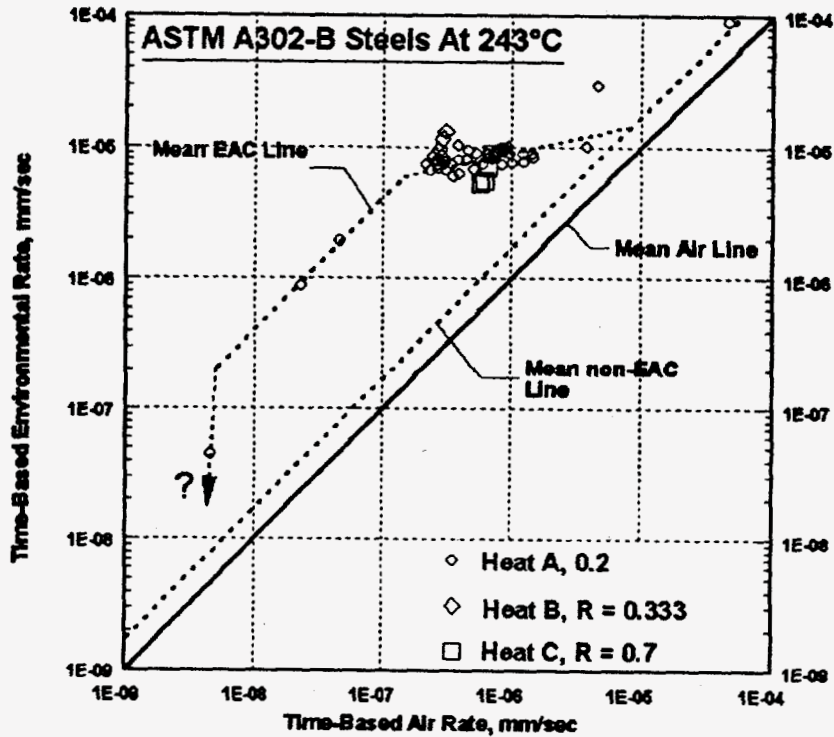
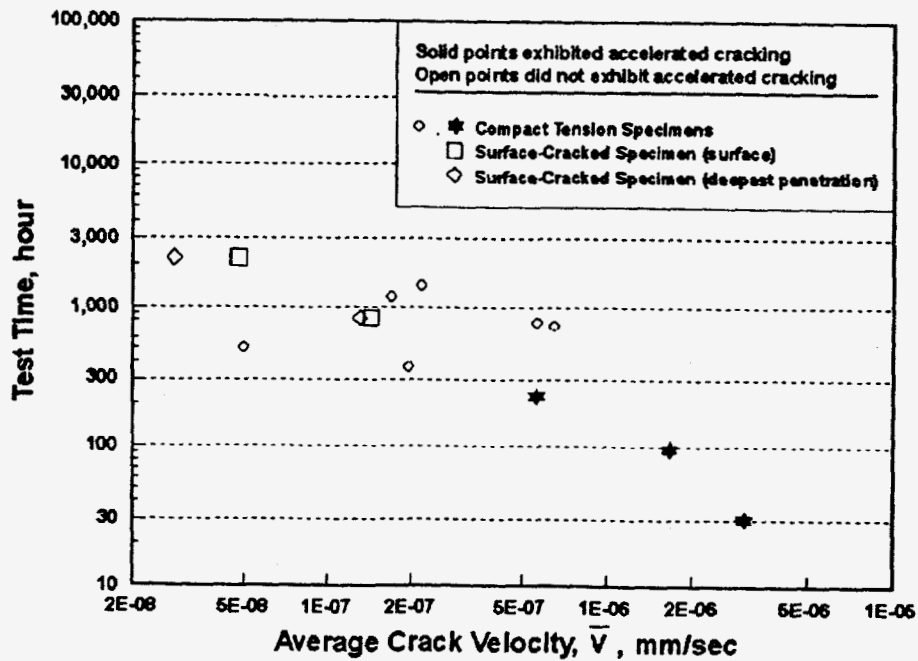FIGURE 3. PERSISTENCE OF EAC TO LOW CRACK VELOCITIES AT 243°C.

FIGURE 4. EAC INITIATION TEST RESULTS FOR HIGH-SULFUR A302B STEEL. EAC DID NOT OCCUR BELOW A CRACK TIP VELOCITY OF 5X10^{-7} mm/S.
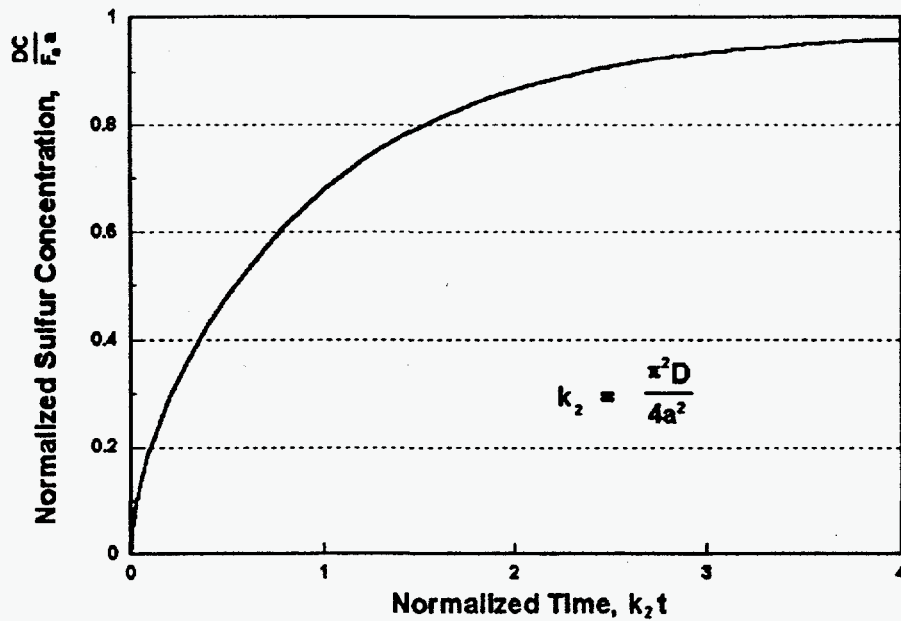
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FIGURE 5. CRACK TIP SULFUR CONCENTRATION FOR ASSUMED SULFUR ION
FLUX F_o STARTING AT TIME=0.
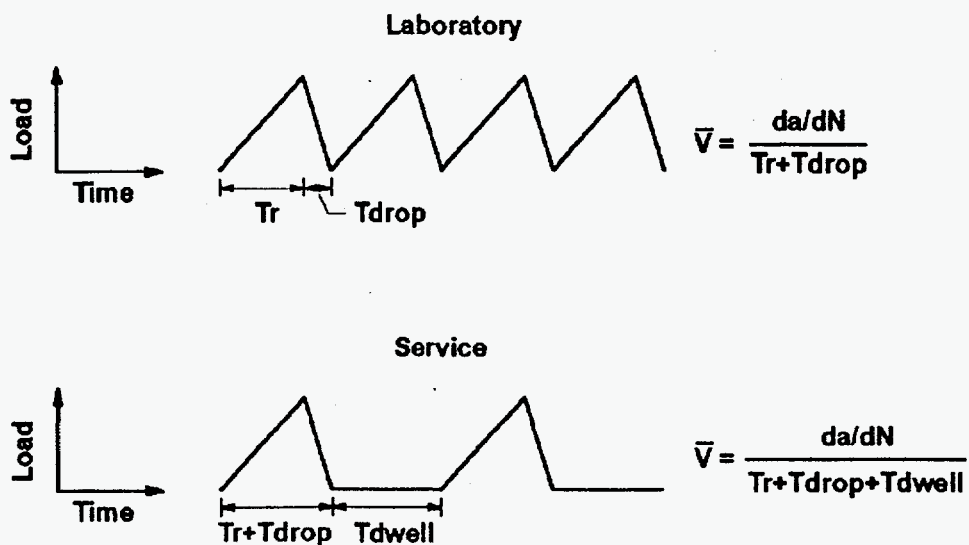
FIGURE 6. SCHEMATIC OF TYPICAL FATIGUE CYCLE IN LABORATORY AND IN
SERVICE. THE AVERAGE VELOCITY IS REDUCED BY PERIODS OF CONSTANT
STRESS, Tdwell.
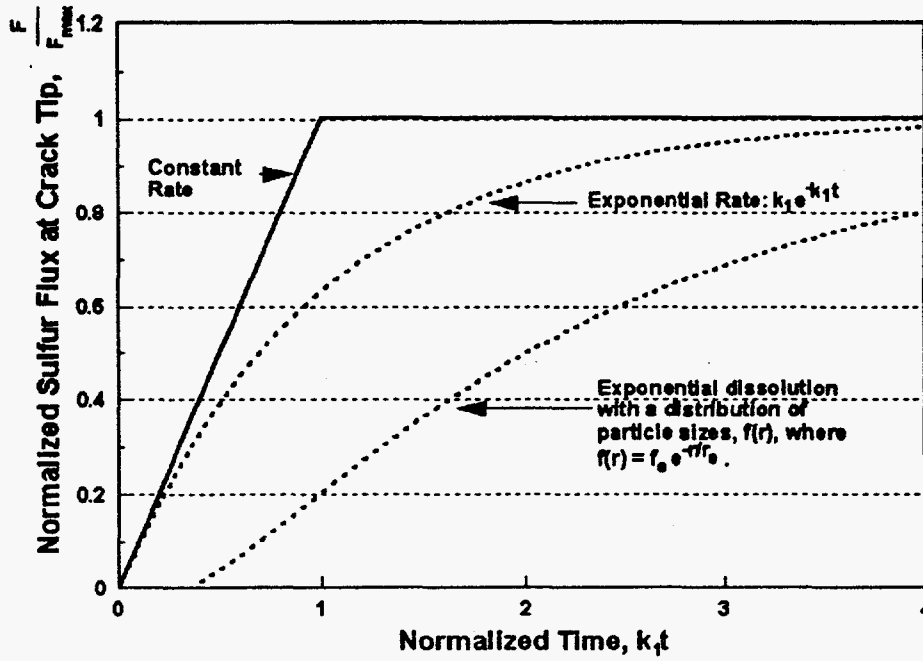
FIGURE 7. SULFUR ION FLUX FOR VARIOUS DISSOLUTION RATES. THE FLUX BUILDUP IS SLOWER WITH A DISTRIBUTION OF PARTICLE SIZES.
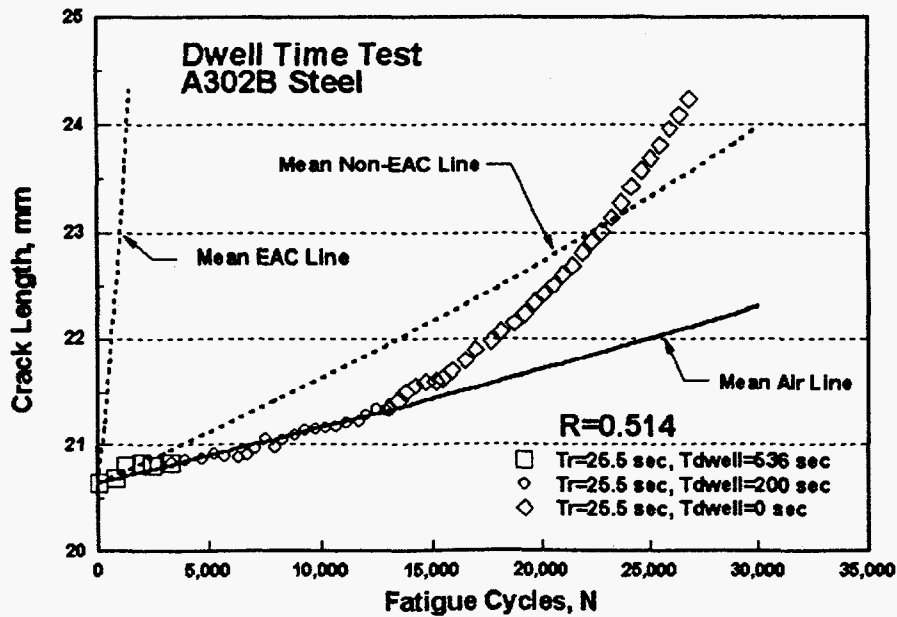
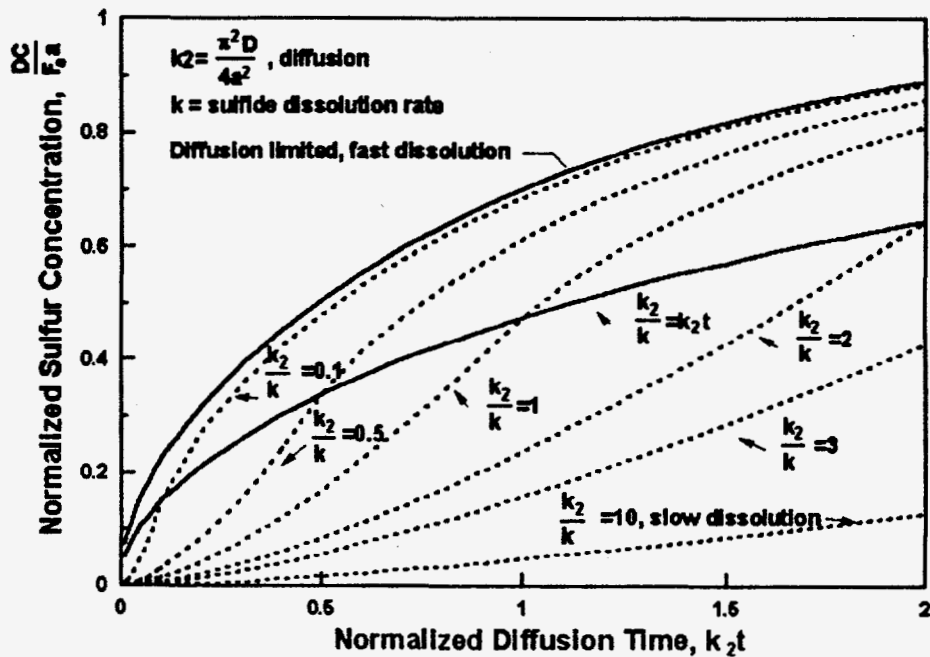FIGURE 8. EFFECT OF DWELL TIME ON EAC INITIATION.

FIGURE 9. CRACK TIP SULFUR CONCENTRATION FOR VARIOUS RATES OF SULFIDE DISSOLUTION. BUILDUP OF SULFUR ION CONCENTRATION OCCURS OVER MUCH LONGER TIMES THAN ANTICIPATED FROM DIFFUSION WHEN $k_2/k >> 1$.
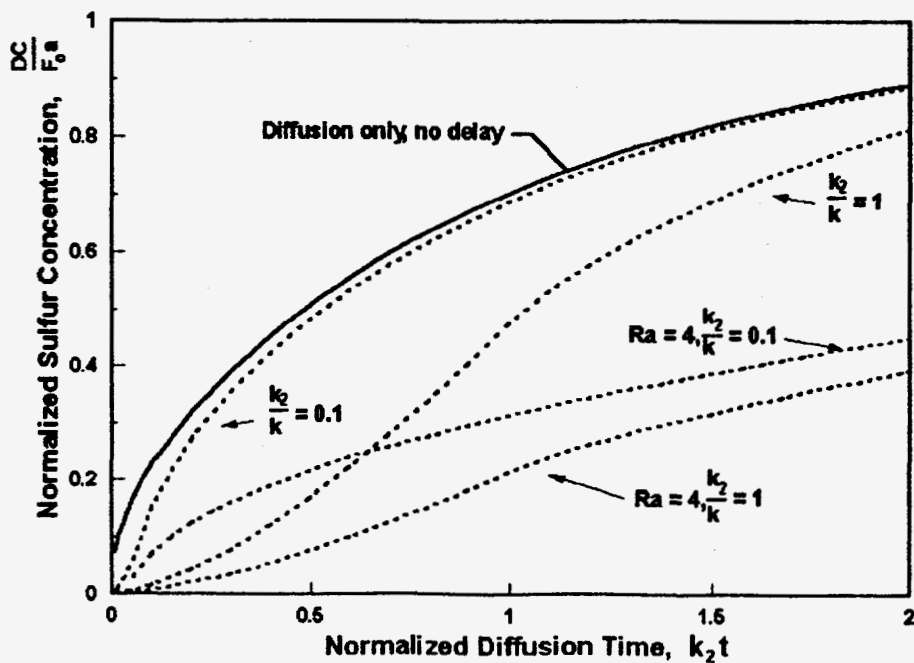

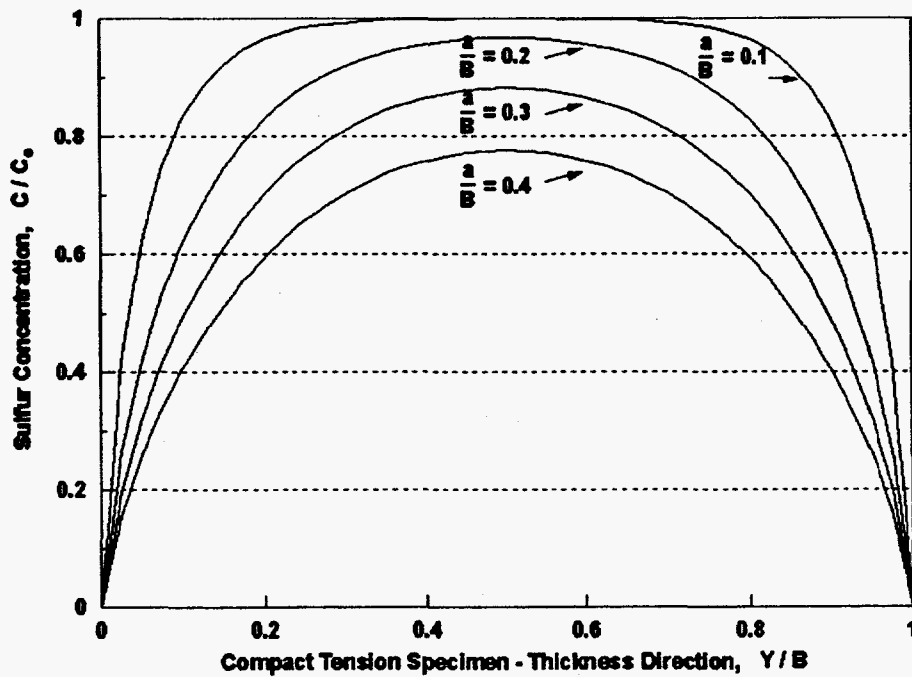FIGURE 10. EFFECT OF CHEMICAL ADSORPTION ON SULFUR CONCENTRATION AT THE CRACK TIP.

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FIGURE 11. CONCENTRATION PROFILES IN COMPACT TENSION SPECIMENS.
PEAK CONCENTRATIONS ARE NOT SIGNIFICANTLY AFFECTED AS LONG AS
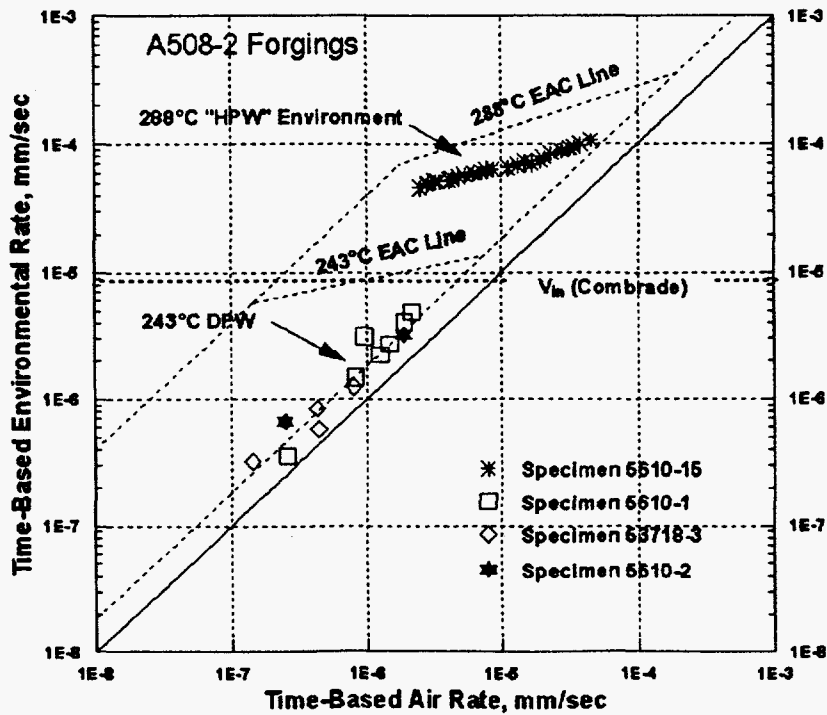CRACK EXTENSIONS ARE SMALL - a/B LESS THAN 0.2.

FIGURE 12. EAC OCCURRENCE AT 288°C AND ABSENCE AT 243°C FOR
FORGINGS WITH SULFUR CONTENT 0.011 - 0.013%. V_{th} IS AT THE LIMIT OF THE
243°C EAC RANGE.