MECHANISMS OF ENVIRONMENTALLY-ASSISTED FATIGUE CRACK GROWTH
IN LOW STRENGTH STEELS

S. Suresh and R. O. Ritchie

Department of Mechanical Engineering Massachusetts Institute of Technology Cambridge, Mass., 02139, U.S.A.

## ABSTRACT

The role of gaseous environment on fatigue crack propagation in a bainitic  $2\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\mbox{$\$ 

# KEY WORDS

Fatigue crack propagation; corrosion fatigue, threshold stress intensity, hydrogen embrittlement, oxide-induced crack closure, pressure vessel steels.

## INTRODUCTION

It is well established that the presence of an aggressive gaseous environment such as hydrogen can cause considerable deterioration in fatigue crack growth resistance in high strength steels, particularly when maximum stress intensity  $(K_{\rm max})$  levels exceed  $K_{\rm ISCC}$ , the threshold for environmentally-induced cracking under sustained loads (e.g. McEvily and Wei, 1971). Lower strength steels (yield strength below 800 MPa), conversely, are often considered to be relatively immune to such "embrittlement" largely because of their relatively high  $K_{\rm ISCC}$  thresholds. Under cyclic loading, however, it is now clear that such steels become very susceptible to hydrogen-assisted fatigue crack growth, at  $K_{\rm max}$  values far below conventionally-measured  $K_{\rm ISCC}$  thresholds (Nelson, 1976; Brazill, Simmons and Wei, 1979; Ritchie, Suresh and Moss, 1980). Whereas most data have been obtained for growth rates in excess of  $10^{-5} \rm mm/cycle$  where mechanisms of hydrogen-assisted growth have been rationalized in terms of hydrogen embrittlement theories, recent observations have shown that the maximum enhancement due to hydrogen occurs at growth rates below

 $10^{-6}$ mm/cycle, approaching the so-called threshold stress intensity  $\Delta K_{\rm O}$  for no crack growth (Ritchie, Suresh, and Moss, 1980; Ritchie, 1980). Further, it is apparent that arguments based on hydrogen embrittlement models are not consistent with behavior patterns observed at such near-threshold levels (Ritchie, 1980).

In the present work, mechanisms of hydrogen-assisted fatigue crack growth are examined in a lower strength  $2\frac{1}{4}\mathrm{Cr-1Mo}$  pressure vessel steel tested over a wide range of growth rates from  $10^{-8}$  to  $10^{-3}\mathrm{mm/cycle}$  in environments of moist air and low pressure dehumidified hydrogen and helium gases as a function of load ratio (R =  $\mathrm{K_{min}/K_{max}}$ ) and frequency. It is shown that whereas hydrogen-assisted crack growth at higher propagation rates (typically >10^{-5}\mathrm{mm/cycle}) is consistent with hydrogen embrittlement concepts (although precise mechanisms in such low strength steels are unknown), at near-threshold levels differences in crack growth behavior in air and hydrogen may be ascribed to a new mechanism involving increased levels of crack closure promoted by excess oxide debris generated within near-threshold cracks propagating in moist environments (Stewart, 1980; Ritchie, Suresh and Moss, 1980; Ritchie, 1980). The implications of such "oxide-induced crack closure" with regard to the uniqueness and reproducibility of threshold stress intensity  $\Delta \mathrm{K}_0$  measurements are discussed.

# EXPERIMENTAL PROCEDURES

The  $2\frac{1}{4}$ Cr-1Mo pressure vessel steel examined was received in the form of a 175 mm thick plate, conforming to the ASTM A542 Class 3 standard (hereafter referred to as SA542-3). Prior heat treatment consisted of austenitizing at 950°C for 5 hrs, water-quenching, and tempering at 663°C for 7 hrs, before stress relieving at 593°C (15 hrs), 649°C (22 hrs) and 663°C (18 hrs). Microstructures and mechanical properties (Table 1) of this plate varied only marginally with through-thickness position, the structure being predominately upper bainite (grain size 60-70 $\mu$ m) with less than 3% polygonal ferrite at center thickness.

TABLE 1 Ambient Temperature Mechanical Properties of SA542-3 Steel

0.2% Proof Stress	U.T.S.	Redn.in Area	Charpy Impact Energy	K <sub>Ic</sub>	K <sub>Iscc</sub>
(MPa)	(MPa)	(%)	(J)	(MPa√m)	(MPa√m)
496 ± 7	610 ± 17	77	197 ± 18	295	>85

Fatigue crack growth experiments were performed using 12.7 mm thick compact-tension specimens (T-L orientation), in environments of ambient temperature moist air (30% relative humidity) and dehumidified and purified hydrogen and helium gases (138 kPa pressure) over a range of frequencies (0.5 to 50 Hz sine wave) and load ratios (0.05 to 0.75). Ultra-low growth rates (below  $10^{-6}$ mm/cycle)were obtained using a load-shedding (decreasing K) technique, whereas higher growth rate data were obtained at constant load amplitude, the electrical potential method being utilized to monitor crack lengths. Thresholds  $^{\Delta}$ K values were defined at a maximum growth rate of  $10^{-8}$ mm/cycle. Experimental techniques are described in detail elsewhere (Ritchie, 1977; Ritchie, Suresh and Moss, 1980).

#### RESULTS

A comparison of fatigue crack propagation in moist air and dry hydrogen for SA542-3 steel is shown as a function of varying frequency at R=0.05 in Fig. 1, and as a function of load ratio at 50 Hz in Fig. 2. Clearly two distinct growth rate

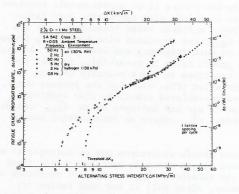


Fig. 1: Influence of cyclic frequency on fatigue crack growth in quenched and tempered 2½Cr-IMo steel (SA 542 Class 3), tested at R = 0.05 in moist air and dry hydrogen (courteay of S. Suresh).

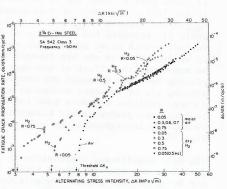


Fig. 2: Influence of load ratio R on fatigue crack growth in 2%Cr-lHo steel (SA542 Class 3), tested at 50 llz in moist air and dry hydrogen (courtesy of S. Suresh).

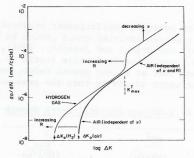


Fig. 3 : Schematic diagram showing regimes of hydrogen-assisted growth for lower strength steel

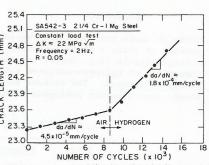


Fig. 4: Fatigue crack growth in 2 1/4 Cr-1Mo steel tested at 2Hz at a constant stress intensity of AK-22 MPa/a showing effect of introduction of hydrogen gas.

regimes are apparent where hydrogen markedly enhances propagation rates, namely at near-threshold levels below  $10^{-6} \, \mathrm{mm/cycle}$  and at higher growth rates typically above  $10^{-5} \, \mathrm{mm/cycle}$  (Fig. 3).

Above growth rates of typically  $10^{-5}$  mm/cycle (at R<0.5), an abrupt acceleration in crack growth rates (up to 20 times) can be observed in the presence of hydrogen (Figs. 1-3). The onset of this acceleration occurs at an approximately constant K<sub>max</sub> value, termed K<sub>max</sub>, i.e. at lower  $\Delta$ K levels with increasing load ratio (Table 2), provided the frequency is below a critical value (dependent upon R). Further growth rates in hydrogen above K<sub>max</sub> are increased with decreasing frequency whilst rates in air are insensitive to both frequency and load ratio. As might be expected, the effect of hydrogen on growth rates is reversible, in that replacing hydrogen by moist air causes a reduction in crack velocity whereas replacing air by hydrogen causes an acceleration (Fig. 4). For the present steel, a characteristic fracture mode for hydrogen-assisted growth is also observed; failures are predominately transgranular in air and hydrogen below K<sub>max</sub> and predominately intergranular in hydrogen above  $K_{max}^{T}$  where an acceleration occurs (Fig. 5).

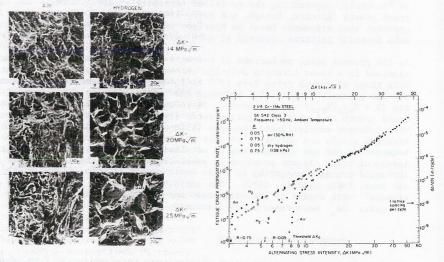
The most significant degradation in crack growth resistance due to hydrogen is apparent in the near-threshold regime where growth rates in hydrogen exceed those in air by up to two orders of magnitude, and threshold  $\Delta K_{\rm O}$  values are decreased by up to 30% (Fig. 6). Such effects, however, occur only at low load ratios (at R=0.75 behavior is virtually identical in air and hydrogen (Fig. 6)) and appear independent of frequency (Fig. 1). Further, despite the large accelerating influence of hydrogen, there is no significant difference in fracture mode between air and hydrogen below  $10^{-6} {\rm mm/cycle}$ , failures being predominately transgranular with sporadic intergranular facets. Moreover, unlike behavior at higher growth rates, effects of hydrogen on near-threshold growth rates appear non-reversible. By changing environment from dry hydrogen to moist air, a deceleration in crack velocity is observed (Fig. 7a), as would be expected from constant environment data (Fig. 6). However, replacing moist air by dry hydrogen at stress intensities close to  $\Delta K_{\rm O}$  produces no corresponding acceleration in crack velocity (Fig. 7b).

## DISCUSSION

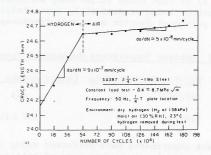
Although there have been many mechanisms for hydrogen embrittlement proposed which provide at least a partial description of hydrogen-assisted crack growth in higher strength steels (e.g. Zappfe and Sims, 1941; and Oriani and Josephic, 1974), the phenomenon of hydrogen-assisted failure in lower strength ductile steels is still poorly understood. The current studies show that at higher growth rates, such steels show behavior analogous to higher strength steels in that the presence of

TABLE 2 Conditions for Onset of Hydrogen-Assisted Crack Growth

Load Ratio	Frequency (Hz)	$\frac{\Delta K^{T}}{(MPa\sqrt{m})}$	K <sup>T</sup> max (MPa m)	
0.05	50	no effect		
0.05	5	no ei	ffect	
0.05	2	21.8	22.9	
0.05	0.5	21.2	22.3	
0.30	50	15.3	21.9	
0.30	5	14.4	20.6	
0.50	50	11.8	23.6	
0.75	50	4.7	18.8	







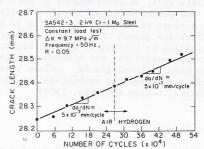


Fig. 7: Near-threshold fatigue crack growth in 2 1/4 Cr-1Mo steel at 50 Hz (Re0.03) showing non-reversible effects of changing enviorment, a) bydropen cas to moist air, and h) moist air to bydropen cas.

hydrogen results in a sudden acceleration in growth rates above a critical  $K_{\text{max}}$ value  $(K_{max}^T)$ . This phenomenon, which is sometimes referred to as "stress-corrosion fatigue", occurs in high strength steels when  $K_{max}$  exceeds  $K_{TSCC}$ , and has been rationalized in terms of "superposition" (Wei and Landes, 1969) or "processcompetition" (Austen and McIntyre, 1979) models, where the environmentally-assisted crack growth is considered to result from sustained-load stress-corrosion cracking and mechanical fatigue components which are either additive or mutually competitive. Reaction kinetic studies have indicated that such environmentally-enhanced cracking in both 4340 and 2½Cr-lMo steels can be attributed to hydrogen embrittlement mechanisms, rate limited by surface reactions at the crack tip, i.e. chemisorption of hydrogen in gaseous hydrogen or the oxidation of iron in water environments (Brazill, Simmons, and Wei, 1979). It is clear that in lower strength steels like 2½Cr-1Mo, such hydrogen-assisted growth occurs at stress intensities far be- $\ensuremath{\textit{low}}$   $\ensuremath{K_{\mathrm{Iscc}}}$  , reflecting the fact that cyclic loading maintains a sharp crack tip and thus continuously provides freshly exposed metal surface there for hydrogen to be adsorbed.

The most pronounced influence of gaseous hydrogen in  $24\mathrm{Cr}$ -1Mo steels, however, is seen at near-threshold levels, although somewhat surprisingly only at low load ratios (Fig. 6) and without change in fracture mechanism. Further, related studies in ultrahigh strength steels, which are very prone to hydrogen embrittlement, indicate a very small but decelerating influence of hydrogen at near-threshold levels (Ritchie, 1980). In addition, measurements in inert gas environments have revealed  $\Delta K_0$  values below those measured in air (Ritchie, 1980; Stewart, 1980). Such observations are clearly at variance with hydrogen embrittlement mechanisms for environmentally-assisted near-threshold crack growth. Very recently, an alternative explanation has been proposed based on the concept of "oxide-induced crack closure" (Stewart, 1980; Ritchie, 1980; Ritchie, Suresh and Moss, 1980). According to this model, near-threshold growth rates are accelerated in hydrogen simply because the dry, oxygen-free environment restricts the formation of oxide films within the crack tip. In moist atmospheres, such as air, at low load ratios, oxide debris is generated and thickened by fretting oxidation mechanisms (Benoit,

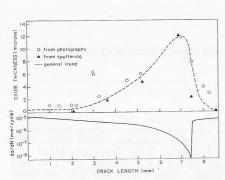


Fig. 3: Thickness of oxide scale as a function of crack length and crack growth rat for 25G-180 steel (58 My2-1), texted at 8 - 0.05 in noist atr. Oxide deposits measured from netallographic sections through near-threshold cracks and using Ar\* sputtering of fracture surfaces with Auger electron spectro-

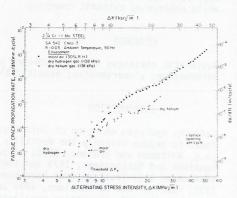


Fig. 9: Fatigue crack propagation in 2 1/4 Cr-1 No steel (SA 542 class 3) tested at 2-0.05 (SO No) in moist air, dry purified hydrogen and dry purified helium.

Namdar-Tixier and Tixier, 1980) resulting from plasticity-induced closure of the fracture surfaces. Such enlarged oxide debris in low strength steels is comparable in size with crack tip opening displacements at near-threshold levels, and correspondingly results in increased crack closure thereby reducing effective AK levels at the crack tip. Ar+ sputtering analysis using Auger spectroscopy by White (1980) has shown oxide layers near  $\Delta K_0$  to be almost 30 times thicker than at higher growth rates for the present SA542-3 steel tested in air at R=0.05 (Fig. 8). The major implication of this model is that hydrogen per se does not "accelerate" near-threshold growth compared to air, but rather prevents the deceleration due to crack closure from enlarged corrosion debris. The consequence of this is that near-threshold crack propagation in any dry (or oxygen-free) environment should exceed growth rates in air. This is verified in Fig. 9 where below  $10^{-6}$ mm/cycle, crack growth rates in dehumidified purified helium gas are accelerated with respect to air, with threshold values approaching those measured in hydrogen. Similar results have been reported for other 24Cr-1Mo steels, namely normalized SA387 tested in argon, and higher strength martensitic SA542-2 tested in helium (Ritchie, 1980). At higher load ratios, however, behavior in air, hydrogen and inert gas is identical since little oxide debris will be created where there is no plasticity-induced closure to promote fretting oxidation.

Observations of non-reversible effects of hydrogen on near-threshold crack growth rates from tests where environments were changed during crack growth (Fig. 7) are also capable of explanation in terms of oxide-induced closure. The result, where a crack, previously grown to near-threshold levels at R=0.05 in moist air, is abruptly flooded with hydrogen gas and yet shows no immediate acceleration in growth rate (Fig. 7b), follows from the fact that a distribution of oxide deposits has already been generated within the crack during prior near-threshold growth in air. The introduction of gaseous hydrogen under these circumstances will have little effect until the crack has grown a sufficient distance from the oxide deposits. This experiment raises important questions about the uniqueness of threshold measurements, since the value of  $\Delta K_{\rm O}$  determined may depend upon the amount of oxide debris created, which in turn may depend upon the route and time taken to reduce growth rates to near-threshold levels. Recently we have found evidence that various hold times at stress intensities above and below the conventionallymeasured  $\Delta K_{o}$  value can lead to premature crack arrest (an "apparent" threshold) due to the build-up of excess oxide during the hold periods. Clearly, from the point of view of the application of near-threshold fatigue data in design, further work on the question of the reproducibility of  $\Delta K_0$  measurements is warranted.

Finally, evidence to support oxide-induced closure concepts may be readily found in the literature. For example, results for pressure vessel and rotor steels show somewhat higher  $\Delta K_{\rm O}$  values in water compared to air (Paris and co-workers, 1972; Stewart, 1980). In addition, both Tu and Seth (1978) and Nordmark and Fricke (1978) report premature crack arrest for near-threshold crack growth in certain steels and aluminum alloys tested in aggressive environments due to the progressive build-up of corrosion products on the crack surfaces. In fact, observation of corrosion debris has traditionally provided a means to detect and monitor the growth of incipient flaws under service conditions (i.e. in aircraft components).

#### SUMMARY AND CONCLUSIONS

The role of gaseous environment on influencing fatigue crack propagation in a bainitic  $2 \frac{1}{4} \text{Cr-1Mo}$  pressure vessel steel has been examined for atmospheres of moist air, dry hydrogen and dry helium gases. It is apparent that whereas hydrogen—assisted fatigue crack propagation at growth rates in excess of  $10^{-5} \text{mm/cycle}$  may be ascribed to hydrogen embrittlement mechanisms, significant enhancements in crack velocities due to hydrogen at near-threshold levels ( $<10^{-6} \text{mm/cycle}$ ) appear

to result more from the absence of corrosion deposits formed within the crack surfaces. Such concepts of oxide-induced crack closure are shown to be consistent with effects of load ratio and environment at near-threshold levels, and further highlight certain inconsistencies in the reproducibility of threshold fatigue data.

# ACKNOWLEDGEMENT

The work was supported under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, with Dr. S. M. Wolf as contract monitor.

## REFERENCES

- Austen, I. M., and P. McIntyre (1979). Metal Science, 13, 420-428.
- Benoit, D., R. Namdar-Tixier, and R. Tixier (1980). <u>Mater. Sci. Eng.</u> 25, in press. Brazill, R. L., G. W. Simmons, and R. P. Wei (1979). <u>J. Eng. Matl. Tech., 101</u>, 199-204.
- McEvily, A. J., and R. P. Wei (1971). <u>Proceedings of Intl. Conf. on Corrosion</u> Fatigue, Chemistry, Mechanics, Microstructure, NACE, pp. 381-395.
- Nelson, H.G. (1976). Proceedings of 2nd Intl. Conf. on Mechanical Behavior of Materials, ASM, pp. 690-694.
- Nordmark, G. E., and W. G. Fricke (1978). J. Test. and Eval., 6, 301-303.
- Oriani, R. A., and P. H. Josephic (1974). Acta Met., 22, 1065-1075.
- Paris, P. C., R. J. Bucci, E. T. Wessel, W. G. Clark, and T. R. Mager (1972). In Stress Analysis and Growth of Cracks, ASTM STP 513, pp. 141-176.
- Ritchie, R. O., (1977). J. Eng. Matl. Tech., 99, 195-204.
- Ritchie, R. O., (1980). In G.C.Sih (Ed.), Analytical and Experimental Fracture Mechanics, Sijthoff and Noordhoff, The Netherlands.
- Ritchie, R. O., S. Suresh, and C. M. Moss (1980). J. Eng. Matl. Tech., 102, in press.
- Stewart, A. T. (1980). Engr. Fract. Mech. 13, in press.
- Tu, L.K.L., and B. B. Seth (1978). J. Test. and Eval., 6, 66-74.
- Wei, R. P., and J. D. Landes (1969). Mater. Res. Stds., 9, 25.
- White, C. S. (1980). S. B. Thesis, Massachusetts Institute of Technology.
- Zappfe, C., and C. Sims (1941). Trans. AIME, 145, 225-261.