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ON THE INFLUENCE OF GASEOUS HYDROGEN IN DECELERATING FATIGUE CRACK GROWTH RATES IN ULTRAHIGH STRENGTH STEELS

J. Toplosky* and R. O. Ritchie**

*Department of Mechanical Engineering
Massachusetts Institute of Technology
**Department of Materials Science and Mineral Engineering
University of California, Berkeley

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Introduction

In general, high and ultrahigh strength low alloy steels, with yield strengths exceeding 1000 MPa, are known for their marked susceptibility to hydrogen-assisted cracking (1). Steels such as AISI 4340, for example, will initiate stable crack growth at stress intensities as low as 20% of K_{Ic} (the fracture toughness) in the presence of "hydrogen-producing" environments (i.e. H_2, H_2S, H_2O, etc.) or when internally-charged with hydrogen (e.g. 1-6). Similarly, under cyclic loading, crack propagation rates may be significantly enhanced in hydrogen environments compared to inert atmospheres (3,7,8). Although precise micro-mechanisms remain unclear (1), such observations are attributed to "hydrogen embrittlement" where entry of hydrogen atoms into the steel matrix at the crack tip results in some degradation in material properties such as decohesion at internal interfaces (9), hydrogen-affected plasticity (10) and so forth. The rate-limiting steps for such embrittlement appear to be related to surface reactions at the crack tip in the form of hydrogen chemisorption in gaseous hydrogen and metal oxidation in water/water vapor environments (6).

At very low growth rates below 10^{-6} mm/cycle, however, approaching the threshold stress intensity ΔK_o for no crack growth, the role of hydrogen in influencing fatigue crack propagation in lower strength steels (of yield stress 200-700 MPa) has been shown to be largely unrelated to such "classical" hydrogen embrittlement mechanisms (11-14). Although near-threshold growth rates can be two orders of magnitude faster in hydrogen gas compared to room air, the effect has been traced to the fact that hydrogen, as a dry environment, restricts the formation of crack flank fretting-corrosion deposits, thereby reducing oxide-induced crack closure, i.e. closure promoted by the wedging action of oxide debris (11-14).

In high and ultrahigh strength steels, however, hydrogen-affected near-threshold crack growth and the significance of such closure mechanisms have not been investigated, although threshold measurements by Stewart (12) have indicated identical ΔK_o values in air and hydrogen environments. The objective of the present note is to specifically document the effect of gaseous hydrogen on near-threshold crack growth and ΔK_o values in a high strength steel, and to compare behavior with that observed at higher growth rates and in moist air.

Experimental Procedures

The material studied was aircraft-quality, silicon-modified AISI 4340 (300-M) steel, austenitized at 870°C, oil quenched and tempered to two tensile strength levels of 2000 and 1200 MPa, namely at 300°C and at 650°C (hereafter referred to as T300 and T650 respectively). Microstructures were tempered martensitic, with a 20 μm prior austenite grain size, and have been described in detail elsewhere (15). Ambient temperature mechanical properties are listed in Table I.

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TABLE I

Ambient temperature mechanical properties of 300-M steel

Condition	Yield Strength Monotonic	Yield Strength Cyclic	U T S	% Elong.	K_{Ic}	K_{Iscc} (H_2 gas)
	(MPa)	(MPa)	(MPa)	(25.4mm gauge)	(MPa$\sqrt{m}$)	(MPa$\sqrt{m}$)
T300	1740	1700	2000	12	65	18-20
T650	1070	970	1200	18	152	-

Fatigue crack propagation rates were measured over a wide range of growth rates (10^{-8} to 10^{-2} mm/cycle) in plane strain, using 12.7 mm thick compact specimens tested in load control at 5 and 50 Hz (sinusoidal) at load ratios ($R = K_{min}/K_{max}$) of 0.05 and 0.70. Controlled environments of moist air (30% relative humidity) and ultrahigh purity, dehumidified hydrogen gas were examined at 23°C (138 kPa pressure). Using D.C. electrical potential crack monitoring, near-threshold growth rates were determined under standard load-shedding procedures, with the threshold ΔK_o defined in terms of a maximum crack growth rate of 10^{-8} mm/cycle. Full experimental details are described elsewhere (11,12,15).

Results and Discussion

The variation of fatigue crack propagation rates (da/dN) as a function of the alternating stress intensity (ΔK) at R = 0.05 for the higher strength T300 microstructure is shown in Fig. 1 for environments of moist air and dry hydrogen. The data plotted represent mean values from several individual tests. As reported for lower strength steels (16), two distinct regimes appear to exist where crack growth behavior is influenced by hydrogen, namely above $\sim 10^{-5}$ mm/cycle and at near-threshold levels. Above 10^{-5} mm/cycle, although growth rates in air and hydrogen are similar at 50 Hz, lowering the frequency to 5 Hz results in significantly faster growth rates in hydrogen. This behavior, which has been widely reported by others (3,7,8), has been attributed to hydrogen embrittlement mechanisms, consistent with an increase in intergranular fracture observed for hydrogen-assisted failures. What is intriguing, however, is the observation that at growth rates below 10^{-6} mm/cycle at 50 Hz frequency, the presence of hydrogen gas actually results in a *deceleration* in near-threshold propagation rates and a 16% higher threshold ΔK_o value compared to air. Similar behavior is seen in the lower strength T650 microstructure where, at both high and low load ratios (R = 0.05 and 0.70) at 50 Hz, growth rates in air and hydrogen are similar until near-threshold levels, whereupon they become slower in hydrogen (Fig. 2). Threshold ΔK_o values in hydrogen are again between 11 to 15% higher than in air. Since the decelerating influence of hydrogen is both small and surprising, the validity of the data in Fig. 2 was checked by performing a constant ΔK test near the threshold. A crack was grown in hydrogen gas, after load-shedding to just above ΔK_o at $\Delta K = 9.3$ MPa$\sqrt{m}$, whereupon the environmental chamber was evacuated and flushed with air. The resulting two-fold increase in near-threshold growth rates when air was introduced provides an indication that decelerating effect of hydrogen is real (Fig. 3). Fractographically, little difference was apparent between near-threshold cracks grown in either environment: characteristic flat, featureless transgranular fracture surfaces were observed with isolated intergranular facets.

Similar effects have been recently observed in high strength NiCrMoV rotor steels tested in air and hydrogen (17), although earlier data on a similar material (where no growth rates were measured) showed threshold ΔK_o values to be identical for both environments (12).

Such observations appear to be at variance with conventional mechanisms of corrosion fatigue crack growth, involving hydrogen embrittlement or active path corrosion models (1), and are more surprising in view of the well-known susceptibility of high strength steels such as 300-M to embrittlement from hydrogen, particularly when tempered to peak strength conditions (i.e. at 300°C). Further, unlike behavior in lower strength steels (11,13), the observations are also inconsistent with fretting oxide-induced crack closure mechanisms for near-threshold corrosion fatigue (11-14), since closure would only be significant at low load ratios, and lower effective stress intensities would be expected for the moist air environment where presumably oxide formation and hence crack closure would be enhanced. However, the role of such corrosion debris in high strength materials is still unclear at this time (13) since oxide thicknesses are considerably less than in low strength steels. This apparently follows from reduced fretting-oxidation effects arising from less plasticity-induced closure and less abrasion of the oxide debris on the harder steel substrate, and from the fact that the extent of oxide build-up is limited by the smaller crack tip opening displacements (13,14). Auger measurements of oxide thicknesses in the present steel, using Ar^+ sputtering techniques (14), revealed excess thicknesses of approximately 0.01 μm at $R = 0.05$, which are comparable with the cyclic crack tip displacements (ΔCTOD) at threshold. However, such measurements approached background noise levels and it was difficult to detect any changes in oxide thickness between the two environments or at different crack lengths.

Other models for the role of hydrogen involving hydrogen-affected plasticity (10) and hydrogen-induced Mode II crack branching (18) were discounted since no evidence of hydrogen-induced hardening or softening was seen in monotonic and cyclic tests on hydrogen-charged hour-glass specimens, nor was there any evidence of more secondary or shear cracking on fracture surfaces in hydrogen.

It appears, that unlike behavior in lower strength steels (11-14), the role of hydrogen gas, compared to moist air, in affecting near-threshold fatigue crack propagation in ultra-high strength steels may still be associated with hydrogen embrittlement mechanisms. However, the experimental observations (Figs. 1-3) suggest that, at the partial pressures and periods (reciprocal frequency)associated with the near-threshold conditions, hydrogen uptake into the matrix, and hence the extent of embrittlement may be somewhat more efficient for water vapor compared to gaseous hydrogen. This is contrary to experience in steels at higher growth rates (2), yet similar to behavior in aluminum alloys (19), and presumably occurs because at the small ΔCTODs associated with near-threshold levels, where fretting oxidation promotes enhanced oxide growth even in nominally dry environments (14), crack tip oxide deposits may be considerably thicker than naturally-formed oxides. Since it is this nucleation and growth of oxide on the crack surface which is the source of hydrogen for water vapor environments, whereas the oxide provides a barrier for hydrogen permeation for hydrogen gas phase environments, moist air atmospheres may well be more aggressive in terms of hydrogen embrittlement mechanisms associated with near-threshold fatigue crack growth. Such ideas are currently under investigation.

Conclusions

From studies of fatigue crack propagation in ultrahigh strength 300-M steel, quenched and tempered at 300°C and 650°C to tensile strengths of 2000 and 1200 MPa respectively, and tested in ambient temperature moist air and dehumidified gaseous hydrogen, the following conclusions can be made:

1. Two distinct growth-rate regimes exist where crack growth behavior is influenced by hydrogen, namely above $\sim 10^{-5}$ mm/cycle and at near-threshold levels below $\sim 10^{-6}$ mm/cycle.

2. *Above* 10^{-5} mm/cycle, growth rates are similar in air and hydrogen at 50 Hz. At 5 Hz, however, the presence of hydrogen gas results in significantly *faster* growth rates, associated with predominately more intergranular cracking on fracture surfaces.

3. *Below* 10^{-6} mm/cycle, the presence of hydrogen gas results in *slower* near-threshold growth rates, with threshold ΔK_0 values 13% lower in air. The decelerating influence of gaseous hydrogen is observed for both tempers at 50 Hz, at high and low load ratios, and is associated with no apparent change in fracture morphology.

4. The observed influence of gaseous environment on near-threshold fatigue crack growth is significantly different to behavior reported for lower strength steels (UTS = 300 - 800 MPa), and is rationalized in terms of hydrogen embrittlement and oxide-induced crack closure mechanisms.

Acknowledgement

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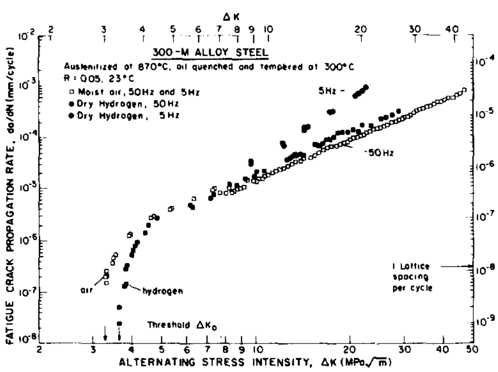

FIG. 1 Effect of moist air and dry hydrogen on fatigue crack growth in 300°C temper at 5 and 50 Hz (R = 0.05).

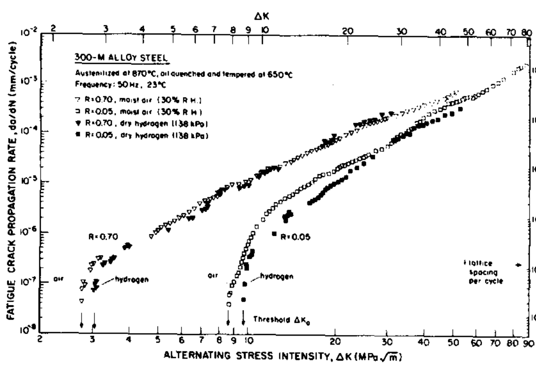

FIG. 2 Effect of moist air and dry hydrogen on fatigue crack growth in 650°C temper at R = 0.05 and 0.70 (50 Hz).

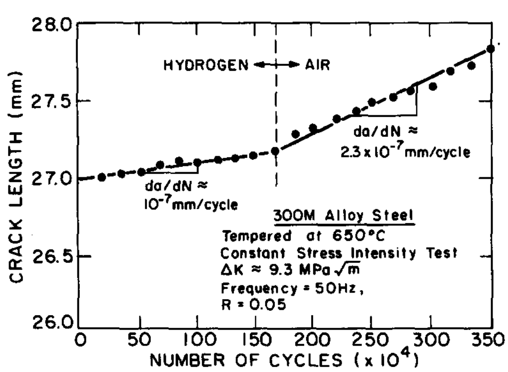

FIG. 3 Showing two-fold acceleration in near-threshold growth rates in 300-M, tempered at 650°C, on changing environment from dry hydrogen to moist air. Test performed at constant $\Delta K = 9.3$ MPa$\sqrt{m}$ ($R = 0.05$) at 50 Hz.