Towards a Predictive, Physics-based Model of Hydrogen-Assisted Fatigue Crack Growth: Measurements of Strain Field and Isotope Effects*

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ABSTRACT

A predictive, physics-based model of hydrogen-assisted fatigue crack growth in pipeline steel is necessary to provide accurate lifetime predictions for current and future pipelines. It is necessary to inform such a model with physical data, namely crack tip strains and hydrogen diffusion rates. In this paper, we present measurements of the elastic crack tip deformation near cracks grown via fatigue in air and in a hydrogen environment. Drastic differences in both magnitude and spatial extent of the crack tip strain fields grown in each condition are demonstrated. We then present tensile and fatigue data for steel specimens measured in air, in hydrogen, and in deuterium, which present a measure of the role diffusion plays in hydrogen embrittlement and hydrogen assisted fatigue crack growth. A large diffusion effect is observed for hydrogen assisted fatigue crack growth rate, while only a small dependence is observed for hydrogen embrittlement measurements.

INTRODUCTION

Pipelines are the most likely means of transporting gaseous hydrogen to support clean power generation and clean transportation [1]. Although steels are a cost-effective solution for the construction of hydrogen gas pipelines, their fatigue and fracture properties are adversely affected by the presence of gaseous hydrogen [2-3]. The corrosive effect of hydrogen on steels manifests in fatigue crack growth rates (FCGRs) which are one to two orders of magnitude faster when grown in H_2 compared with those grown in air. Although the embrittlement effect has been observed since 1875[4], the exact mechanism (or mechanisms) that dominates remains to be elucidated. Determination of the mechanism(s) is necessary to develop designs for high-functioning hydrogen transportation and storage applications, which may, in turn, provide insight into hydrogen effects in other material classes. Until recently, most hydrogen embrittlement research comprised anecdotal material-specific observations, and concentrated on urgent technical problems [5]. However efforts to create and calibrate a physics-based predictive model for the damage has recently begun expanding to complement in-air and hydrogen assisted FCGR (HA-FCGR) data with physics-based modeling and a scientific corroboration of the prevailing mechanisms. A phenomenological model has been developed for HA-FCGR based on a closed-form solution to the crack tip deformation response (ie. elastic and plastic strain fields), hydrogen diffusion, and the coupling between them [6]. The model is phenomenological in that certain fitting parameters, which represent the crack tip deformation response and hydrogen diffusion, can be determined to fit an existing set of data. In order to push the phenomenological model toward a fully predictive, physics-based model, experimental determination of the crack-deformation response and hydrogen diffusion is needed.

Neutron-diffraction measurements of strain in steel are readily available to study elastic lattice deformation leading to HA-FCGR. In these measurements, a spatial mapping of the atomic lattice spacing is produced. With an appropriate measurement of an unstressed lattice spacing, the measured lattice spacing during mechanical loading can then determine the elastic lattice strain. Hydrogen diffusion through steel has been measured previously [7], however these measurements provided only effective diffusivity through an entire steel specimen, as the hydrogen traverses multiple steel microstructures, grain boundaries, and trapping sites. Microstructure and grain boundary specific diffusion rates are necessary for the physics-based model. Deuterium (D_2), an isotope of hydrogen which is twice as massive, provides a route to study the effect of diffusion rates on HA-FCGR. Because D_2 is chemically identical to H_2, it is expected that differences in FCGR between D_2 and H_2 to be due entirely to differences in diffusion rates, where gas phase D_2 diffuses approximately 70% as fast as H_2. While such a measurement does not provide an actual measure of the hydrogen diffusion rate through steel microstructures, such information does provide another data point for calibration of physics-based models of HA-FCGR.

MATERIALS AND METHODS

The material used for this study was an X70 pipeline steel. The material was chosen due to its heavy use in pipelines as well as the abundance of in-air and hydrogen-assisted FCGR data on the material. From optical microscopy, the X70 steel was determined to be polygonal ferrite and either acicular ferrite or bainite. There may be other constitutents that are not resolvable without employing more advanced analytical techniques.

Transmission Bragg Edge Spectroscopy (TBES) measurements were performed at the NIST Center for Neutron Research (NCNR) NG-6 beamline [8]. This beamline uses a pyrolytic graphite double monochromator system to vary the incident neutron wavelength. A LiF pixelated detector plate was used [9]. The detector plate was 28 cm × 28 cm in area, and the effective pixel pitch was 50 μm × 50 μm. For strain measurements, compact tension (CT) specimens with length W = 26.67 mm and thickness B = 6 mm was used. Fatigue cracks were grown with a load ratio R = 0.5, maximum load P_{max} = 3.4 kN, and a cycling frequency f =0.033 Hz. The loading frequency of the TBES crack growth was limited because of the constraints of a stepper motor on the load frame. Separate, identically prepared specimens were used for the in-air and in-H_2 TBES measurements. Each fatigue crack was cyclically loaded for at least N = 3000 cycles to ensure fresh crack growth in each environment. The specimens were then held at a given load during the strain measurements.

Measurement of the FCGR was performed according to ASTM E647[11] for CT specimens (length W = 26.67 mm and thickness B = 3 mm) with a Crack Mouth Opening Displacement (CMOD) gauge attached to the load line. All CT specimens were fatigue pre-cracked in air to obtain a sharp initial crack. The pre-crack length for all specimens was approximately 10 mm. All FCGR measurements were performed at a load ratio R = 0.5 and maximum load P_{max} = 1.7 kN. A larger P_{max} was used for the strain measurements compared to the FCGR measurements because of the larger specimen thickness, to ensure that cracks were grown in identical stress intensity factor ranges (ΔK) for the FCGR and strain measurements. A cycling frequency f = 1 Hz was used for the H_2 and D_2 test and a cycling frequency of f = 10 Hz was used for the air test. Research-grade (99.9995 % pure) H_2, and CP-grade (99.7% isotopic purity) D_2 were used for testing. CP-grade D_2 is chemically pure, however small partial pressures of H_2 gas may have been present during the test. Analysis of each test gas indicated O and H_2O concentrations below the detection limits of 0.5 ppm for O and 1 ppm for H_2O. Test pressure was maintained to within 10% of the set pressure. Measurement of the stress-strain curve was performed according to ASTM E8 for 6.35 mm diameter notched round tensile specimens [10].

RESULTS

Contour images of the measured through-thickness strain fields in air and in H_2 for a loading P=5.15 kN are shown in Figure 1. Note that TBES measures the strain in the direction of the neutron beam; in this case in the direction of the through-thickness of the CT specimen. Because tensile load is applied at the pin holes, the in-plane strain near the crack tip is tensile, and the measured out-of-plane strain is compressive due to a Poisson effect. The contour images show a larger compressive crack tip strain for the crack grown in H_2 as compared to air by a factor of nearly two. The results of this study suggest that the effect of hydrogen is to enhance the crack-tip strain field for a given applied load beyond that observed in air.

Stress-strain curves and FCGR data for in-air, in-H_2, and in-D_2 tests are shown in Figure 2. An embrittlement effect was observed in the steel specimens in both hydrogen and in deuterium, as indicated by a decrease in the elongation to failure compared with air. The extent of the embrittlement, quantified by the change in elongation to failure compared to air, appears stronger in the H_2 case compared to the D_2 case, though variability in tensile property measurements make the differences difficult to quantify with the current data set. In fatigue, the steel specimens presented a strong susceptibility to hydrogen assisted FCGR, with FCGRs an order of magnitude larger than for cracks grown in air. In contrast, there was minimal, and possibly no, indication of deuterium assisted FCGR.

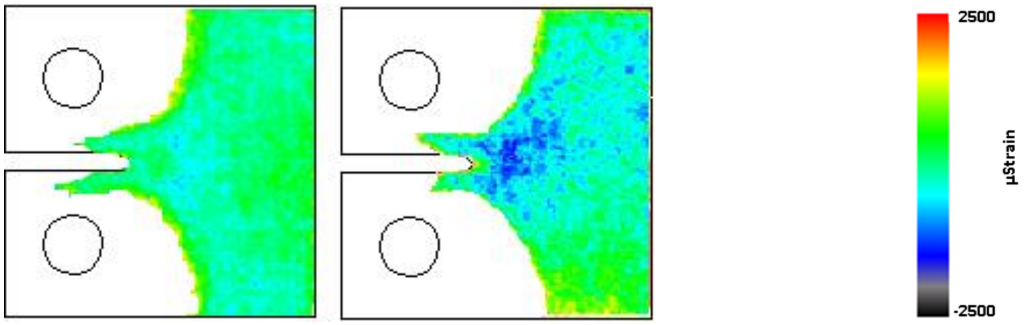

Figure 1: Measured elastic strain fields for the cracks grown in air (left) and in H2 (right). The strain direction measured is in the direction of the through-thickness of the CT specimen. The tensile applied load at the pinholes lead to tensile in-plane strains at the crack tip, which give rise to the compressive strain field in the through-thickness direction, as presented here.

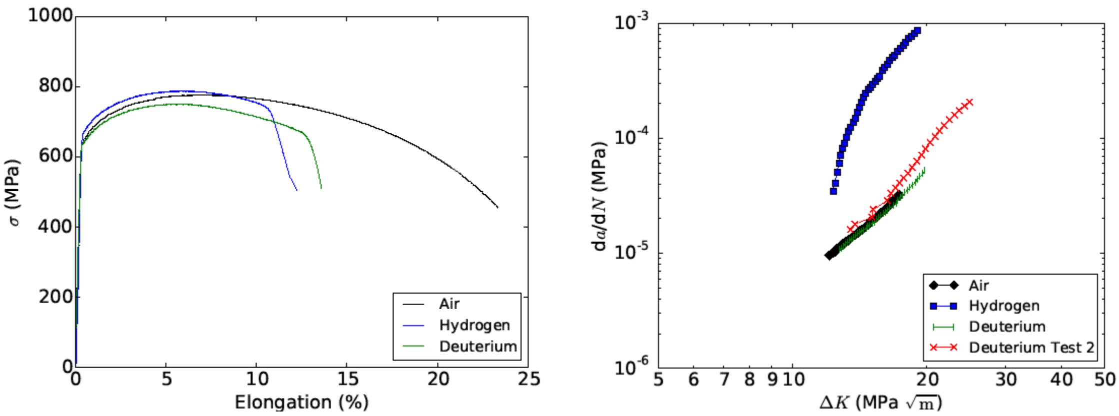

Figure 2: Stress-strain curves for steel specimens measured in air, hydrogen, and deuterium (left). Both hydrogen and deuterium present an embrittlement effect as compared to air, indicated by a decrease in the elongation to failure. Fatigue data in the three environments (right) show a strong hydrogen assisted FCGR as compared to air, with negligible deuterium assisted FCGR.

DISCUSSION

One of the two prevailing mechanisms for hydrogen embrittlement is the Hydrogen Enhanced Decohesion (HEDE) mechanism [5]. In the HEDE mechanism, interstitial accumulation of hydrogen at locations of high triaxial stresses lead to the weakening of Fe-Fe bonds (intragranular decohesion) and grain boundary interaction strength (intergranular decohesion) once the hydrogen reaches a critical concentration. The strain field results presented here are consistent with the HEDE mechanism; as H absorbs into the material, the presence of hydrogen in the lattice decreases the Fe-Fe interaction energy, leading to larger elastic strains for a given applied load. It should be noted that because TBES measures only elastic strain, the measurement technique is more sensitive to the HEDE mechanism, though activation of other mechanisms is possible. For example, the delivery of hydrogen into the material is believed to be driven by large localized plastic strains, as in the Hydrogen Enhanced Localized Plasticity (HELP) [5,11]. Results from solely the TBES technique alone cannot preclude the activation of mechanisms in addition to HEDE. However, the power in the strain measurements presented here lies in the possibility to quantify the extent of the enhanced elastic strain field ahead of the crack tip as a function of applied load, gas pressure, and crack length. Such information can be utilized in models of hydrogen embrittlement and hydrogen assisted FCGR at both ends of the modeling procedure: by informing the models with a quantification of the intragranular decohesion due to hydrogen, and by providing a direction measurement of the strain fields, for which results of finite element modeling can be compared and validated.

The results of the deuterium FCGR tests are surprising; current modeling of diffusion rate dependence of hydrogen assisted FCGR predict FCGRs 85-90% of those observed in hydrogen for deuterium if the differences are due entirely to differences in diffusion rates [6]. However, the FCGR results presented here show a drastic isotope effect, where any enhancement of FCGR due to deuterium is negligible. Even more surprising is that tensile tests indicate that steel is still susceptible to deuterium embrittlement effects. Hydrogen embrittlement and hydrogen assisted FCGR are thought to be intimately related, where the existence of the former implies the latter. It is therefore instructive to consider the hydrogen pathway which leads to enhanced FCGR, in order to discern possible differences between hydrogen and deuterium beyond diffusion rate. Although the exact physical mechanisms leading to hydrogen embrittlement are not well understood, the mechanism by which hydrogen enters the material is well accepted. Diatomic hydrogen first adsorbs on the surface of the solid, then dissociates to atomic hydrogen at the surface and chemisorbs. The hydrogen then diffuses either through the metal lattice or through grain boundaries and accumulates near internal stress centers such as dislocations or crack tips. At this stage, hydrogen then corrodes the metal through either the HEDE, HELP, or some other mechanism. The adsorption of hydrogen has been found to conform well to a Langmuir isotherm [12]. Physical parameters for the Langmuir isotherm are the binding energy and the vibrational frequency. Because adsorption is driven by Van der Waals forces, and H_2 and D_2 are chemically identical, the binding energy of the two molecules should be identical. On the other hand, the extra mass of the D_2 molecule will decrease the vibrational frequency, leading to a higher surface coverage for a given temperature. At the dissociation stage, differences in dissociation energy could lead to the observed FCGRs. However, in the gas phase the dissociation energies of for H_2 and D_2 are 432 kJ/mol and 439 kJ/mol, a difference of only 1.6% [13]. The remaining stages are dependent on the diffusion rate of D_2 through the lattice and grain boundaries, and the dependence on the activated embrittlement mechanisms. It is therefore likely that the role of diffusion plays a much more important role in the hydrogen assisted FCGR mechanisms than currently incorporated in the model.

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- **M.J. Connolly**, P. Bradley, A. Slifka, and E. Drexler, "Chamber for Mechanical Testing in a Gaseous Environment with Observation by Neutron or X-ray Scattering", under revision, Review of Scientific Instruments
- M.W. Roth, L. Firlej, B. Kuchta, **M.J. Connolly**, E. Maldonado and C. Wexler (2016).
- "Simulation and Characterization of Tetracosane on Graphite: Molecular Dynamics Beyond the Monolayer." The Journal of Physical Chemistry C, 120(2), 984-994.
- **M.J. Connolly**, M.W. Roth, C. Wexler and P.A. Gray (2008), "Explicit hydrogen molecular dynamics simulations of hexane deposited onto graphite at various coverages", Langmuir 24, 3228.

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