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Unification of hydrogen-enhanced damage understanding through strain-life experiments for modeling

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Abstract

Strain-life testing of a 4130 pressure vessel steel was conducted in hydrogen gas through the careful adaptation of an existing hydrogen-gas mechanical-testing apparatus. The strain-life mechanical results reveal that hydrogen has a significant effect on the strain-life, and impacts both the elastic and plastic responses of the material. Microscopy analysis shows a distinct difference in the microstructural development of the material after cyclic loading in air compared to after loading in hydrogen gas. These experimental results will inform coupled damage and deformation modeling.

1. Introduction

Recent studies [1] have highlighted both the importance of dislocation activity to the phenomenon of hydrogen embrittlement as well as the complexity of the phenomenon itself. While there is some developing consensus on the vital role that plasticity plays in establishing the conditions for hydrogen-enhanced failure, there is still a lack of understanding of the interplay between plasticity and hydrogen, as well as the regimes within which it is critical. For example, while a recent study [2] revealed the importance of dislocation activity to intergranular failure in distorting the grain boundaries as well as transporting and depositing hydrogen to the boundaries, it is important to note that it is not necessary for intergranular failure. Lassila and Birnbaum [3] showed that with sufficient aging, high levels of intergranular failure could be achieved in nickel, with the percentage of the fracture surface that was intergranular depending upon the aging time. Clearly, if sufficient hydrogen can accumulate in the grain boundaries, then failure will occur, at least in nickel, and the plasticity is merely a mechanism to accelerate the process. Iron is another matter, where calculations [4] show that ambient hydrogen pressures on the order of 510 MPa (5000 atm) would be needed to sufficiently lower the cohesive energy of the grain boundary to even 64% of its hydrogen-free value, which may still be insufficient to cause intergranular failure. As intergranular failure has been observed in iron [5] at hydrogen

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charging conditions well below this, it strongly suggests that another process, such as plasticity, is needed to achieve the process. Understanding the role of this plasticity is critical to understanding and predicting the fracture mechanics. The problem may be an issue of knowing which regimes are defined by the conditions at hand.

The question remains as to why these regimes have not been well established. Part of the issue is likely due to scale. Studies providing evidentiary support for the importance of plasticity have often focused at a scale where dislocation activity can be observed (transmission electron microscopy). Even when these studies are coupled to mechanical testing, the evidence comes from the microscopy, often in contradiction to the mechanical results. Likewise, at very small scales, such as those examined by nanopillar compression and atomistic modeling, other effects, such as surface effects or irradiation damage, may dominate, while dislocation activity may be artificially suppressed. Historically, the primary mechanical testing technique which supports the concept of increased plasticity in hydrogen is stress relaxation testing [6–9]. But there may be another mechanical testing technique, which has not been widely adapted in the hydrogen embrittlement field, which may help develop that insight: strain-life testing.

Strain-controlled fatigue testing, or strain-life testing, provides data useful to defining damage of a material system [10,11]. In the field of mechanics, damage has often been defined as dependent upon accumulated inelastic strain. Defining in terms of damage is useful, as damage similitude may be assumed between a notch-root and a smooth test specimen experiencing identical strain histories [10]. Additionally, most realistic geometric discontinuities, and certainly local regions near a crack tip, experience local displacement-controlled loading even when the macro-structure is experiencing load-controlled conditions. Consequently, if strain-controlled loading parameters are known, these local regions can be better understood and modelled.

It is for these reasons that the damage and failure modelling community favor strain-controlled testing. The benefits of data collected from strain-life testing include the ability to separate the effects of elastic strains from plastic or inelastic strains [12–15] and the ability to capture a material's cyclic evolution response, including yield-point and hardening phenomena [16,17]. These data are invaluable in creating constitutive, damage, and failure models for the material of interest. Having the ability to accurately model the constitutive response of the material to accumulated cycles in either air or hydrogen, and then to compare the results as a function of environment, enables the prediction of the relative effects of hydrogen-specific damage mechanisms. This work endeavors to quantify the effects of accumulated strain (both elastic and inelastic) on the constitutive response of a pressure vessel steel in both air and hydrogen with the goal of developing accurate fracture mechanics modeling. The use of strain-life provides separation between elastic and plastic components of damage and includes data on crack initiation. The damage accumulated as a function of environment is discussed in relation to supporting fractographic and microstructural analysis.

2. Materials and methods

2.1. Materials

Samples were cut directly from a standard hydrogen gas cylinder of 4130 steel. The Young's modulus, E , of this steel is 210 GPa. The cylinder was used for hydrogen service for 2 years, with a maximum in-service pressure of 41 MPa (6000 psi). The cylinder had an outer diameter of 230 mm (9 in.) and a wall thickness of 16.5 mm (0.65 in.) Samples for microstructural analysis were cut and mounted to investigate the three primary directions: longitudinal, circumferential, and through-thickness. Samples were mounted in a conductive metallography mount, and then polished to a mirror finish (0.04 μm colloidal silica). Samples with a mirror polish were characterized using electron backscattered diffraction (EBSD) to determine grain size, texture, and dislocation density. After initial scans showed that the system could not easily distinguish between martensite and ferrite, likely due to the highly tempered nature of this steel, all scans were set to index only ferrite. Samples were then etched with a 2% (by volume) nitric acid in methanol solution. The microstructural composition was then characterized using optical and scanning electron microscopy (SEM – operated at 30 kV).

The starting microstructure, shown in Fig. 1, consists of a martensitic/ferritic structure. The microstructure has a directionality; though the steel was not rolled, the forming process, hot billet piercing followed by hot drawing, created a banded structure that, visually, has similarities to a rolled microstructure. In the through-thickness direction, the variations in microstructure are not neatly structured into bands but form random swirls. The dark bands consist of finer martensitic structures, while the lighter bands consist of larger ferrite grains. EBSD analysis calculates a grain size of 3.1 μm , which is likely an average of ferrite grain size and martensite packet size, rather than a prior austenite grain size.

Dog-bone shaped test specimens were extracted from the pressure vessel walls having loading orientations aligned with the vessel's longitudinal and circumferential orientations. While attempting to meet the criteria demanded in both ASTM E8 and ASTM E606 [18] standards, the specimen design was devised such that the largest possible specimen could be extracted from the circumferential orientation, given the limits posed by the wall thickness and diameter of the vessel. Due to these limitations, the overall specimen length does not meet the ASTM suggested proportion relative to the gage section diameter. All other dimensions fall within suggested limits. The test specimen geometry used for this work is provided in Fig. 2. Note that the gage sections of all specimens were hand-polished post-machining in the loading direction to the surface finish required by the ASTM standards.

2.2. Strain-life mechanical testing

Fully-reversed strain-life tests were conducted on the 4130 steel. The steel had a 0.2% offset yield strength of (696 ± 17) MPa and an ultimate tensile strength of (793 ± 12) MPa in the longitudinal orientation. The uncertainty is one standard deviation of the mean. Strain-life tests followed ASTM E 606 [18]. Tests were conducted in ambient air and in hydrogen gas pressurized to 18 MPa. The tests in hydrogen gas used a chamber described previously [19]. This chamber was designed for testing in tension only, so a few modifications were

necessary to conduct fully-reversed strain-life experiments which include large compressive loads. Fig. 3 shows a drawing of the chamber and associated parts. As seen on the left side of the figure, a special “compression clevis” has been introduced consisting of two large (165 mm diameter) and thick (25 mm) steel plates joined by 8 bolts and nuts. This clevis provides the compressive force necessary to attach the load frame actuator to the pull rod through the test vessel, while having a lateral stiffness which exceeds that of the actuator rod of the load frame, in order to maintain alignment.

Inside the test vessel is the specimen, two extensometers, a load cell, and custom specimen grips. The cylindrical geometry of the specimen, Fig. 2, enables the use of a linear extensometer. Two extensometers are attached to the specimen by way of rubber bands or springs. They are placed 90–120° apart, which provides information on sample bending during a test: the two extensometer readings will deviate from each other if the specimen bends. The specimen grips are designed to compressively hold the samples tightly against counter-faces in order to endure the tensile and compressive loads of testing, with the design allowing up to ± 24 kN (5.5 kip).

Alignment of all components to the actuator of the load frame is crucial for fully-reversed loading. The large compressive loads seen during these tests, over 20 kN in some cases, can cause bending of the specimen if the equipment is not properly aligned. The parameters measured and derived for strain-life will also be inaccurate if the loading includes appreciable bending stresses. Alignment of the load train can be done many ways, but we chose to first align our bottom anchoring plate, onto which one end cap (right side in Fig. 3) of our test vessel attaches, with the actuator of the load frame. This was accomplished by use of a laser alignment tool attached to a carefully-machined holder which screws into a stud that threads into the actuator of the load frame.

Strain-life testing is generally performed over a wide range of strain amplitudes, which in this case will be used to inform a model on both elastic and plastic response of this 4130 steel. Table 1 shows the pertinent parameters of the strain-life tests conducted both in air and in hydrogen gas. Every effort was made to ensure as much overlap as possible between strain amplitudes run in air and in hydrogen gas. However, larger strain amplitude tests, which can be run in air, cannot be run in hydrogen gas because of the much shorter lifetimes (number of cycles until failure) in hydrogen gas. Therefore, the largest strain amplitude run in hydrogen gas was 0.025, whereas a test at a strain amplitude of 0.1 was run in air. The range of strain amplitudes in air and in hydrogen gas were sufficient to characterize the mechanical behavior of the 4130 steel. Table 1 also provides the strain-life test results, including the elastic and plastic strain amplitude along with the cycles to failure. Strain rates for these tests were 0.008 s^{-1} in air and 0.002 s^{-1} in hydrogen. The hydrogen tests had a lower strain rate such that the test frequency would always be at or below 1 Hz to provide time for hydrogen to diffuse to any stress concentration within the material. Previous studies have shown that air tests are insensitive to frequency in this range [20].

2.3. Fractography and EBSD

Samples that were cycled until full failure (separation of two sample halves) were examined by optical profilometry and SEM analysis (30 kV). To compare the microstructure after

mechanical testing, the failed tensile bars were sectioned and prepared for metallographic analysis. One section was made 5 mm below the fracture surface, and another section was made 5 mm below that, resulting in a ~ 5 mm thick section. The cut face originally nearest to the fracture surface was mounted and polished to a mirror finish (as described above). Optical, SEM, and EBSD analyses were performed. In particular, high resolution (0.25 μm steps) EBSD scans were performed to analyze differences in the geometrically necessary dislocation (GND) density between the various samples. Grain size values from the EBSD scan represent areas of similar orientation, which for such a complicated microstructure will likely be an average of the ferrite grain size and the martensite packet size, as opposed to the prior austenite grain size usually reported for such steels. In the grain size calculation, grains less than 1 μm in size (< 4 pixels of the scan) were ignored.

3. Results

3.1. Strain-life tests in air

Fully reversed ($R = \epsilon_{min}/\epsilon_{max} = -1$) strain-controlled data were collected for six 4130 specimens oriented in the longitudinal direction and 3 specimens oriented in the circumferential direction, relative to the pressure vessel geometry. Data from a typical test is shown in Fig. 4. Tests were stopped when either the specimen broke in half or the stress-strain (force-displacement) cyclic response clearly decayed.

The data presented in Fig. 4(a), which shows the first, half-life, and final cycles (defined below) of the test, indicates that the pressure vessel material experienced cyclic softening during the initial stages of the test, and this was observed in all samples tested. The material evolution stabilized, as expected, to a predictable linear force-cycle response, Fig. 4(b), after the initial softening. The linearly stabilized material response is used to predict the failure criterion, where the failure was defined as a reduction of 10% in the maximum load carrying capacity per cycle of the specimen from the stabilized response. From the number of cycles to failure, the half-life (or “stabilized cycle”) was determined by dividing the total cycles to failure by two. The half-life cycle is subsequently used as the characteristic hysteresis loop representing the material’s stabilized deformation response, as indicated in Fig. 4(a). The effect of the applied strain amplitude on the stabilized hysteresis loop shape is shown in Fig. 4(c).

The hysteresis loops for the half-life cycles were then decomposed into elastic and plastic strain portions for the purpose of calibration of strain-life parameters, Fig. 4(a). The plastic strain range at half-life was determined as the strain remaining at zero load application, or the width of the half-life hysteresis loop at zero stress. The elastic strain range was determined as the total strain range minus the measured plastic strain range.

The elastic strain amplitude, $\frac{\Delta\epsilon_{elastic}}{2}$, versus cycles to failure, N_f , was used to calibrate the Basquin relationship:

$$\frac{\Delta\epsilon_{elastic}}{2} = \frac{\sigma'_f}{E}(2N_f)^b \quad (1)$$

The variables in Eq. (1) include the fatigue strength coefficient, σ'_f , the modulus of elasticity, E , and the fatigue strength exponent, b . Twice the number of cycles, or $2N_f$, is often referred to as the number of reversals. Similarly, the plastic strain amplitude, $\epsilon_{plastic}/2$, versus cycles to failure was used to calibrate the Coffin-Manson relationship

$$\frac{\Delta\epsilon_{plastic}}{2} = \epsilon'_f (2N_f)^c \quad (2)$$

where ϵ'_f is the fatigue ductility coefficient and c is the fatigue ductility exponent. When combined, the Basquin and Coffin-Manson relationships describe the total strain-life curve given by

$$\frac{\Delta\epsilon}{2} = \frac{\sigma'_f}{E} (2N_f)^b + \epsilon'_f (2N_f)^c \quad (3)$$

where ϵ is the total strain range ($\frac{\Delta\epsilon}{2}$ being the strain amplitude, ϵ_a). The calibrated strain-life constants for the 4130 pressure vessel steel tested in air are provided in Table 2, and the strain-life data separated into total strain, elastic strain, and plastic strain components is plotted in Fig. 5, which also includes the calibrated strain-life (ϵ -N) curve from Eq. (3).

In addition to the strain-life curve fitting, the data collected were also fit to the cyclic stress-strain relationship [21],

$$\epsilon = \frac{\sigma}{E} + \left(\frac{\sigma}{K'} \right)^{1/n'} \quad (4)$$

where ϵ is the strain, σ the stress, E the modulus of elasticity, and n' and K' are material-specific constants. The calibrated cyclic stress-strain curve is plotted as the black line along with the half-life hysteresis loops of different strain amplitude tests in Fig. 4(c). The calibrated cyclic stress-strain constants are provided in Table 2. The 95% confidence intervals were calculated for the strain life constants using the ASTM E739 standard [22], and are presented in Table 2. Due to the manner of calculating the intervals for these tests, they are not symmetrical about the calculated value.

3.2. Hydrogen mechanical results

Data collected during strain-control testing of the 4130 pressure vessel steel in 18 MPa (2600 psi) gaseous hydrogen was also analyzed to determine the strain-life and cyclic stress-strain constants. The strain-life data collected in 18 MPa hydrogen are provided in Fig. 6 where each point is delineated into total, elastic, and plastic strain amplitudes. The calibrated strain-life constants for the steel tested in 18 MPa gaseous hydrogen are provided in Table 3. Similarly as for the in-air tests, the 95% confidence intervals calculated using ASTM E739 for the strain-life constants are also presented in the table. The 95% confidence intervals appear tighter for the hydrogen tests than for the air tests. This is likely due to differences in the experimental set-up required by the presence of the hydrogen chamber.

Attempts were made to cover as much of the same strain amplitude space as in air, though this was not possible at the higher strain amplitudes due to the drastic reduction in strain life in hydrogen. The resulting test matrix covers much of the same strain-life (or cycles to failure) parameter space under both conditions.

A comparison of the strain-life curve of 4130 steel in air with the strain-life curve in 18 MPa H₂ gas is shown in Fig. 7. For a given strain amplitude, the pressure vessel steel experiences approximately two orders of magnitude longer life in air compared with in 18 MPa hydrogen. Another way to look at it is that a given strain-life occurs at approximately an order of magnitude lower strain amplitude in hydrogen compared to air. Strain-life is considered a useful parameter in that comparable strain-lives are expected to result in comparable levels of damage [10,11].

3.3. Early microstructural and fracture results

The appearance of the fracture surface depends strongly on the test conditions. Given the differences in strain-life behavior between the in-air and in-H₂ conditions, it makes sense to compare samples at a given strain-life, where, according to strain-life theory, damage is expected to be comparable. In air, at moderate strain amplitude (0.0098), the fracture surface was inclined relative to the sample cross-section, with a distinct hump towards the later stages of failure, Fig. 8. The total height difference is on the order of 1.4 mm, with half of that accounted for by the hump at the end. Closer examination of the features, Fig. 9, shows fatigue striations in the earlier and flatter area of failure. The features in this area are very flat, likely due to complete closure of the crack during the compression portion of the cycle. Various microvoids can also be seen to have been intersected by the fracture surface. The region forming the hump is composed of microvoids. This suggests a fatigue process dominating early crack growth, followed by rapid ductile failure.

In hydrogen, comparing a sample with very similar strain-life (~ 1200 cycles), and therefore expected similar damage, but different strain amplitude (0.0098 in air, 0.0046 in H₂), the fracture surface, Fig. 8, is significantly flatter than in air (less than 400 μm in hydrogen). Even considering the “flat” section of the air specimen, prior to fast fracture, the height variation is around 800 μm compared to less than 400 μm for the entire hydrogen-assisted surface. At the micro-scale, Fig. 9, the hydrogen fracture features are extremely flat, with divisions on the order of 100 μm ; significantly larger than any microstructural feature. There are suggestions of striations, but they are disguised by what is likely the effect of crack closure and compression. Unlike the air fracture surface, there does not appear to be clear evidence of microvoids intercepting the hydrogen fracture surface. These differences are expected based upon the difference in environment.

Optical microscopy of the sections reveals a distinct change in the microstructure, Fig. 10. There is a definite refinement after loading, and a “mixing” effect, wherein the clear stratification (areas with clearer martensitic laths separated from areas of larger ferrite grains) of the initial microstructure is lost. In particular, the larger light-colored grains, associated with ferrite in the original structure, have been refined and appear more distributed around rounder areas of lath structures. The microstructure in air appears tighter and more refined than that in hydrogen. EBSD measurements (averaged over ~ 1500 grains

in each scan) suggest that, from a starting grain size of $(3.19 \pm 0.05) \mu\text{m}$, the “in air” deformed sample had a final grain size of $(2.54 \pm 0.04) \mu\text{m}$, while the “in H_2 ” deformed sample had a final grain size of $(2.93 \pm 0.06) \mu\text{m}$ (the uncertainty calculated is the standard error of the mean).

The EBSD scans for the starting microstructure and the microstructure of the sections after cycling in air and in hydrogen for approximately 1200 cycles are shown in Fig. 11. As seen in the top row, showing the inverse-pole-figure colored maps for the out-of-plane direction, the overall distribution of the grain sizes does not appear to drastically change after loading. However, the preponderance of green grains present in the map indicates that a considerable amount of reorientation appears to have occurred after loading in air, which did not occur after loading in hydrogen. This reorientation, which is also clearly seen in the inverse pole figure below the map, is towards the $\langle 1\ 0\ 1 \rangle$ direction. Note that only the $[1\ 0\ 0]$ (out of plane) inverse pole figure is shown. Due to the round bar geometry of the sample, it is not possible to determine the orientation of in-plane directions with respect to the original longitudinal and circumferential plate directions, rendering comparisons between the scan x- and y-directions meaningless. The $\langle 1\ 0\ 1 \rangle$ direction is significant as this is the slip direction in body-centered cubic ferritic iron. Deformed crystals tend to rotate towards their slip direction, though grains in a polycrystalline material will be subject to constraint by the surrounding grains. Therefore, the sample tested in air showed significant rotation of grains towards the dislocation slip direction, while this rotation did not happen in the presence of hydrogen.

The calculated geometrically necessary dislocation (GND) density maps, bottom row of Fig. 11, also show a distinct difference between the starting microstructure and final two states, despite the average dislocation densities over the areas scanned being similar. Due to the complicated quench and tempered martensitic/ferritic starting microstructure, it is not surprising that there is a reasonably high starting GND density, or that it is segregated, with higher densities in some grains, and very low densities in others. Similarly, as the material exhibited macroscopic softening due to the cyclic loading, it is not surprising that the average dislocation density did not change significantly, though rearrangement of the dislocation structures did occur. After testing in air, there is significant refinement: the areas of low dislocation density (blue) are much smaller, and the areas of higher density (green to yellow) appear finer. In contrast, the GND density map for the hydrogen-tested specimen is closer to the initial microstructure, though some refinement has occurred, and fewer large low density grains (blue) are evident.

4. Discussion

When plotting the air and hydrogen strain-life data for the 4130 pressure vessel steel on the same axis, as is done in Fig. 7, one can appreciate the differences in damage accumulation between the two environments. But, it is difficult to determine the primary life-limiting mechanism from the data as presented in the figure. In an attempt to elucidate the relative contributions to the total damage accumulation as a function of environment, Fig. 12 plots the power law fits of the elastic strain amplitude versus number of reversals and plastic strain amplitude versus number of reversals for both environments.

The data in Fig. 12 indicates that, for all conditions, hydrogen influences both the elastic and plastic response of the material. For a given elastic strain amplitude (green lines), the 4130 material exhibits over three orders of magnitude longer life in air than in gaseous hydrogen. The data also indicates that for a given plastic strain amplitude (red lines), the material exhibits nearly two orders of magnitude longer life in air than in gaseous hydrogen. The net effect is a shift in the cross-over point between plastic and elastic dominance. In hydrogen, the cross-over occurs at both a lower strain amplitude, and a lower strain life. As a result, more of the behavior in hydrogen is dominated by the elastic response. This shift is likely due to a shift in regimes of mechanism dominance, as discussed below.

Interestingly, the effect of hydrogen on the elastic portion of the material's strain-life response decreases with decreasing strain amplitude, while the effect of hydrogen on the plastic portion of the response increases with decreasing strain amplitude. This can be seen in the differences in slope (b & c from Tables 2 and 3), where b (elastic) shows a 23% decrease in value between air and hydrogen and where c (plastic response) shows a 10% increase between in-air and in-hydrogen. While this effect is overwhelmed by the shift in cross-over point between elastic and plastic, it still indicates a difference in hydrogen effect. The uncertainty in the fit (Tables 2 and 3) means that this difference in slope could be less, but likely still significant. While further work will focus on exploring these differences in slope and understanding this change with respect to hydrogen embrittlement mechanisms, some early conjectures can be made based upon these results as well as the shift in the cross-over point.

While exposure to hydrogen decreases the strain-life of this material across all the strain ranges tested, the subtle differences in the power-law fits may provide insight to the dominant damage mechanisms. Specifically, the plastic response in air yields a more pronounced regime of plastic strain-dominance from low cycle fatigue than that of hydrogen, with a regime of elastic strain-dominance from high cycle fatigue starting at around 10,000 reversals (5000 cycles) in air. Conversely, in hydrogen, the plastic response dominates the strain-life response of the material for a relatively short period, with the elastic strain-dominated "high-cycle" fatigue regime starting at around 1000 reversals (500 cycles). The more negative power law slope for the plastic response in hydrogen results in a decreased effect on life for a given change in applied mechanical strain, relative to air, suggesting that the material is less sensitive to plastic deformation when exposed to hydrogen. The converse is true for the elastic response in hydrogen. The less negative power-law slope for the elastic response in hydrogen, as compared to air, indicates that the material is more susceptible to elastic deformation when exposed to hydrogen.

These observations may indicate a few things. First, exposure to hydrogen may result in a decrease in life resulting from the Hydrogen Enhanced Localized Plasticity (HELP) mechanism [23] in the low cycle regime. That is, the localized increase in plasticity resulting from hydrogen exposure decreases the life of the material when compared to similar tests in air. Second, the dominance of the elastic deformation response in hydrogen, particularly at lower strain amplitudes, would indicate that other considerations may have an effect on the deformation response in the "high cycle" regime. A simple explanation is that the Hydrogen Enhanced Decohesion (HEDE) mechanism [24,25] is more dominant, though, given the

amount of plasticity that still occurs, it is likely that the situation is more complicated than that. It is understood that, through the HELP mechanism, dislocation activity can occur at stresses below the yield stress in the presence of hydrogen. Though this has not been specifically addressed with cyclic loading, the premise should be similar, with dislocation activity potentially occurring even during the elastically dominated regime. This hydrogen-enhanced dislocation activity is often different in behavior from that in air, with closer packing and suppressed cross-slip resulting in different dislocation structures than formed in air. Recent work in nickel [26] has shown that this change in dislocation behavior results in a different global deformation appearance, including a reduction in grain rotation due to applied stress, similar to that observed in this study. The resulting different microstructure establishes the condition for decohesion processes to occur [27,28], whether intergranular or transgranular in character. At lower strain amplitudes, the lifetime may increase partly due to the number of cycles needed to develop the microstructure necessary for decohesion processes to occur. Note that the dominance of an elastic deformation response may result from an increase in elastic deformation, or a decrease in plastic deformation, or for the threshold stress for dislocation activity, for all other things being equal.

The postulated effect of hydrogen on the strain-controlled life of the material is born out in the microscopy provided in Figs. 8–11. Specifically, the specimen tested in air, having a strain-life of 1200 cycles (2400 reversals), is predicted to have a plastically-dominated deformation response. The microscopy shows a refinement in grain size, a re-distribution of the dislocation density, and significant grain rotation, resulting in a fracture surface with ample evidence of plastic failure. The specimen tested in hydrogen with a similar strain-life is expected to have a similar amount of damage, and yet distinct differences were observed suggesting a mixture of processes supported by the fact that the deformation response had a stronger elastic component. Refinement of the microstructure was still observed after testing in hydrogen, with the original microstructure significantly disturbed, resulting in the refinement of the grain size and redistribution of the dislocations. However, while some reorientation of the grains occurred, it was significantly less than observed after loading in air. This change in deformation occurred without significantly changing the average dislocation density, suggesting a difference in dislocation behavior, as proposed by the HELP mechanism. It is likely that this deformation, along with accumulated solute hydrogen, significantly changed the weakest path through the material resulting in a flatter fracture surface. The lack of clear facets on the fracture surface suggests that boundary failure did not occur, but transgranular fatigue failure occurred and was accelerated by hydrogen-enhanced decohesion of the HELP-deformed grains. The microscopy supports the hypothesis from the previous paragraph that the HELP mechanism influenced the deformation leading to the conditions where HEDE processes can occur. While further analysis is needed to confirm these findings under multiple strain-life regimes, these preliminary results support the postulated hydrogen-influences based upon the mechanical results.

5. Future work

In order to appropriately capture the salient features of the hydrogen effect on plasticity, especially under cyclic loading, two different modeling components need to be developed

and properly combined: a coupled hydrogen diffusion-accumulated deformation constitutive model and a damage accumulation model. Ideally, the combination of these models would be valid in both air and various pressures of hydrogen gas; the goal of the fully-reversed strain-controlled testing presented in this work is to provide the data to properly calibrate the model to these conditions and apply to fracture mechanics-based predictive modeling.

A historical coupled hydrogen-diffusion and accumulated-deformation modelling framework is being implemented and used to support this work [29–32]. An example of the application of such a model would be to compare the three disparate test methods recommended for evaluating pressure vessel steels for hydrogen service [33]: a burst disk test, wedge opening test, and a fracture toughness test. The main concern of oversight bodies is that these tests are not comparable, preventing groups which prefer one test from using data from another group. Recently, constitutive damage modelling was performed on this 4130 pressure vessel steel based on the strain-life testing results in air [34], which predicts the number of cycles to critical damage resulting in failure. Our goal is to use a damage parameter compared to cycles to failure in order to plot the different test methods on the same curve as our fatigue data, allowing direct comparisons between the test results. Then, as the data from the hydrogen tests presented here are analyzed, it will provide insight into how to best calibrate the critical damage model to account for hydrogen-assisted damage and eventually provide a mechanism-based model for hydrogen-assisted failure.

6. Conclusions

Fully-reversed strain-life testing provides insight into the effect of hydrogen on the elastic and plastic responses of a material. Although several technical challenges exist to conducting these tests in high pressure hydrogen gas, the preliminary results presented in this work show that the data is informative as to the influence of hydrogen on both the plastic and elastic cyclic response of a material. In the case of a 4130 martensitic pressure vessel steel, hydrogen was observed to decrease the strain-life of the steel by around 2 orders of magnitude. Additionally, while both the elastic and plastic components are affected by the hydrogen, the elastic response is the most sensitive to hydrogen, which is dominant over a larger regime than in air, especially at low strain amplitudes and longer strain-life. This low strain amplitude and longer strain-life probably best represents the in-use conditions of a pressure vessel. Corresponding to the reduction in strain-life due to hydrogen is a drastic change in fracture from a ductile appearing surface to a flat, brittle-appearing surface, as well as a change in the development of the plastically-deformed microstructure resulting from the cyclic loading. As this work is ongoing, clearly more effort is needed to understand these results in terms of hydrogen embrittlement mechanisms, though an initial effort is shown here, connecting results with possible acting mechanisms. However, these data are critical for informing and calibrating constitutive models under development. If successful, these models would provide predictive capabilities that would have applicability to fields such as standards for materials selection.

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References

- [1]. Robertson IM, Sofronis P, Nagao A, Martin ML, Wang S, Gross DW, et al. Hydrogen embrittlement understood. *Metall Mater Trans A* 2015;46(6):2323–41.
- [2]. Martin ML, Somerday BP, Ritchie RO, Sofronis P, Robertson IM. Hydrogen-induced intergranular failure in nickel revisited. *Acta Mater* 2012;60(6):2739–45.
- [3]. Lassila DH, Birnbaum HK. The effect of diffusive hydrogen segregation on fracture of polycrystalline nickel. *Acta Metall* 1986;34(7):1237–43.
- [4]. Wang S, Martin ML, Robertson IM, Sofronis P. Effect of hydrogen environment on the separation of Fe grain boundaries. *Acta Mater* 2016;107:279–88.
- [5]. Wang S, Martin ML, Sofronis P, Ohnuki S, Hashimoto N, Robertson IM. Hydrogen-induced intergranular failure of iron. *Acta Mater* 2014;69:275–82.
- [6]. Oriani RA, Josephic PH. Hydrogen-enhanced load relaxation in a deformed medium-carbon steel. *Acta Metall* 1979;27(6):997–1005.
- [7]. Sirois E, Birnbaum HK. Effects of hydrogen and carbon on thermally activated deformation in nickel. *Acta Metall Mater* 1992;40(6):1377–85.
- [8]. Birnbaum HK, Sofronis P. Hydrogen-enhanced localized plasticity—a mechanism for hydrogen-related fracture. *Mater Sci Eng A* 1994;176(1):191–202.
- [9]. Abraham DP, Altstetter CJ. Hydrogen-enhanced localization of plasticity in an austenitic stainless steel. *Metall Mater Trans A* 1995;26(11):2859–71.
- [10]. Dowling NE. Fatigue failure predictions for complicated stress-strain histories, theoretical and applied mechanics. University of Illinois at Urbana-Champaign; 1971.
- [11]. Morrow J. Cyclic plastic strain energy and fatigue of metals, internal friction, damping, and cyclic plasticity. ASTM International; 1965.
- [12]. Smith RW, Hirschberg MH, Manson SS. Fatigue behavior of materials under strain cycling in low and intermediate life range. National Aeronautics and Space Administration, Cleveland OH Lewis Research Center; 1963.
- [13]. Manson S, Hirschberg M. Fatigue-an interdisciplinary approach. Syracuse, NY: Syracuse University Press; 1969 p. 133.
- [14]. Coffin LF Jr. A study of the effects of cyclic thermal stresses on a ductile metal. *Trans ASME* 1954;76:931–50.
- [15]. Tavernelli J, Coffin L Jr. A Compilation and interpretation of cyclic-strain fatigue tests on metals. *Trans ASM* 1959;51:438–53.
- [16]. Chaboche JL. Time-independent constitutive theories for cyclic plasticity. *Int J Plast* 1986;2(2):149–88.
- [17]. Chaboche JL. Constitutive equations for cyclic plasticity and cyclic viscoplasticity. *Int J Plast* 1989;5(3):247–302.
- [18]. ASTM Standard E 606–04 E1. Standard practice for strain-controlled fatigue testing. West Conshohocken, PA; 2004.
- [19]. Slifka AJ, Drexler ES, Nanninga NE, Levy YS, McColskey JD, Amaro RL, et al. Fatigue crack growth of two pipeline steels in a pressurized hydrogen environment. *Corros Sci* 2014;78:313–21.
- [20]. Cialone HJ, Holbrook JH. Effects of gaseous hydrogen on fatigue crack growth in pipeline steel. *J Metall Trans A* 1985;16(1):115–22.
- [21]. Bannantine J, Comer J, Handrock J. Fundamentals of metal fatigue analysis. Englewood Cliffs, NJ: Prentice Hall; 1990.

- [22]. ASTM E739–10 standard practice for statistical analysis of linear or linearized stress-life (S-N) and strain-life (e-N) fatigue data. ASTM International; 2015.
- [23]. Martin ML, Dadfarnia M, Nagao A, Wang S, Sofronis P. Enumeration of the hydrogen-enhanced localized plasticity mechanism for hydrogen embrittlement in structural materials. *Acta Mater* 2019;165:734–50.
- [24]. Johnson HH, Morlet JG, Troiano AR. Hydrogen, crack initiation, and delayed failure in steel; 1958 Medium: X; Size: 528–36.
- [25]. Song J, Curtin WA. Atomic mechanism and prediction of hydrogen embrittlement in iron. *Nat Mater* 2012;12:145. [PubMed: 23142843]
- [26]. Bertsch K. Hydrogen effects on the evolution of plastic deformation in polycrystalline nickel: a mechanism for intergranular failure, materials science and engineering. University of Illinois at Urbana-Champaign; 2017.
- [27]. Nagao A, Smith CD, Dadfarnia M, Sofronis P, Robertson IM. The role of hydrogen in hydrogen embrittlement fracture of lath martensitic steel. *Acta Mater* 2012;60(13):5182–9.
- [28]. Pioszak GL, Gangloff RPJM, A MT. Hydrogen environment assisted cracking of modern ultra-high strength martensitic steels 2017; 48(9): 4025–45.
- [29]. Sofronis P, McMeeking RM. Numerical analysis of hydrogen transport near a blunting crack tip. *J Mech Phys Solids* 1989;37(3):317–50.
- [30]. Di Leo CV, Anand L. Hydrogen in metals: a coupled theory for species diffusion and large elastic-plastic deformations. *Int J Plast* 2013;43:42–69.
- [31]. Amaro R, Long B, Slifka A, Drexler E, O'Connor D. Application of a model of hydrogen-assisted fatigue crack growth in 4130 steel, international hydrogen conference (IHC 2016): materials performance in hydrogen environments. ASME Press; 2017.
- [32]. O'Connor D, Long B, Slifka A, Drexler E, Amaro R. Computational modeling of hydrogen-assisted fatigue crack growth in pipeline steels, international hydrogen conference (IHC 2016): materials performance in hydrogen environments. ASME Press; 2017.
- [33]. B.S.I. ISO, London, 11114–4. Transportable gas cylinders-compatibility of cylinder and valve materials with gas contents, Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement; 2005.
- [34]. Looney CP. Accumulated inelastic strain based damage modeling of pressure vessel steels in air [M.S. thesis]. Colorado School of Mines; 2018.

Fig. 1. Starting microstructure of 4130 steel. Figure composed from three optical micrographs taken from sections in the three directions of the cylinder wall: circumferential (C), through-thickness (T), and longitudinal (L). Samples etched with a 2% nitric acid in methanol solution.

Fig. 2.

Drawing of the cylindrical specimen geometry used for strain-life tests in both air and hydrogen. Dimensions indicated are in inches. Gage width (0.25 in.) is 6.35 mm, and gage length (0.875 in.) is 22.23 mm.

Fig. 3.
Drawing of the test vessel and associated parts for strain-life testing in pressurized hydrogen gas.

Fig. 4.

(a) Representative hysteresis loops for the first, half-life, and final cycle of a strain-life test ($\epsilon = 0.1$, $R = -1$, $\dot{\epsilon} = 0.008$ 1/s) with overlaid relevant parameters marked on the half-life (or stabilized) cycle and (b) representative maximum force versus cycle data collected for strain-life test shown in (a). (c) Half-life hysteresis curves for multiple strain amplitude tests encompassing a range of applied strain amplitudes from $\epsilon_a = 0.0033$ (red squares) to $\epsilon_a = 0.0196$ (yellow triangles). The black line shows the cyclic stress-strain relationship for this material, as calculated from Eq. (4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5.

Strain-life data and model fits presented as a function of total strain, elastic strain, and plastic strain ($R = -1$, $\dot{\epsilon} = 0.008$ 1/s). The elastic strain is fit to the Basquin relationship (Eq. (1)), the plastic strain is fit to the Coffin-Manson relationship (Eq. (2)), while the ϵ -N curve is fit to Eq. (3).

Fig. 6. 4130 pressure vessel steel strain-life data tested in 18 MPa gaseous hydrogen ($R = -1$, $\dot{\epsilon} = 0.002$ 1/s). The data is fit to curves analogously to those in Fig. 5.

Fig. 7.
Stain-life curves for 4130 pressure vessel steel tested in air and 18 MPa Hydrogen.

Fig. 8.

Fracture surfaces of strain-life specimens failed in air (left) and in hydrogen gas (right). Top images show optical images (composite of high resolution images). Bottom images show height profile reconstructions based upon focal distance of optical system. Note very different height scales in the left and right reconstructions. All images are oriented with crack initiation on the left side.

Fig. 9. SEM micrographs of fracture features of strain-life specimens failed in air (left) and in hydrogen gas (right). Areas of striations are indicated with black arrows, and voids are marked with white arrowheads.

Fig. 10.

Optical micrographs showing the initial microstructure in the longitudinal direction, microstructure perpendicular to the tensile axis (longitudinal direction) after failure in air, and microstructure perpendicular to the tensile axis (longitudinal) after failure in hydrogen gas.

Fig. 11.

EBSD analysis of microstructure prior to loading (longitudinal direction) and after strain-life testing to failure in air (center) and in hydrogen gas (right). Scans are $150\ \mu\text{m} \times 150\ \mu\text{m}$ with $0.25\ \mu\text{m}$ steps. Top images show inverse pole figure colored map (color based upon crystallographic direction out of plane). Center row shows the inverse pole figure summarizing the orientations shown in the top images. Bottom row is a map showing the geometrically necessary dislocation densities calculated from the kernel average misorientation in the top maps. Dark blue represents areas of lowest dislocation density, and increasing dislocation density to green, yellow and red at the highest. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 12. 4130 pressure vessel strain-life data fits delineated by elastic and plastic strain amplitudes for both air and 18 MPa gaseous hydrogen.

Table 1

Parameters for strain-life tests conducted in air and in pressurized hydrogen gas (18 MPa), where L denotes longitudinal direction and C denotes circumferential direction.

Test type	Target strain amplitude ϵ_a	Number of cycles to failure N_f	measured plastic strain amplitude $\epsilon_{\text{plastic}}$	elastic strain amplitude $\epsilon_{\text{elastic}}$
Air, L	0.1	49	0.08900	0.01100
Air, L	0.04	103	0.03250	0.00740
Air, L	0.0399	153	0.03260	0.00720
Air, C	0.0399	81	0.03320	0.00670
Air, L	0.0196	1631	0.01370	0.00590
Air, L	0.0196	1381	0.01350	0.00610
Air, C	0.0186	1201	0.01280	0.00580
Air, L	0.0084	16,000	0.00330	0.00500
Air, C	0.0084	20,121	0.00330	0.00510
Hydrogen, L	0.025	7	0.02093	0.00397
Hydrogen, C	0.01	87	0.00677	0.00319
Hydrogen, C	0.0092	93	0.00608	0.00308
Hydrogen, C	0.0084	131	0.00549	0.00288
Hydrogen, C	0.0046	1232	0.00216	0.00243
Hydrogen, C	0.0046	567	0.00220	0.00240
Hydrogen, C	0.0035	2433	0.00108	0.00242
Hydrogen, C	0.0021	27,957	0.00024	0.00018

Table 2Strain-life and cyclic stress-strain curve calibration values ($R = -1$, $\dot{\epsilon} = 0.008$ 1/s) in air.

σ_{UTS} (MPa)	σ'_f (MPa)	b	ϵ'_f	c	K' (MPa)	n'
793	3268	-0.113	0.6592	-0.501	1277	0.18
95% confidence intervals						
σ'_f (MPa)		b		ϵ'_f		C
Lower	Upper	Lower	Upper	Lower	Upper	Lower Upper
1231	11,277	-0.083	-0.399	0.168	1.818	-0.406 -0.744

Table 3

Strain-life and cyclic stress-strain curve calibration values for 4130 pressure vessel steel in 18 MPa gaseous hydrogen ($R = -1$, $\dot{\epsilon} = 0.002$ 1/s).

σ'_f (MPa)	b	ϵ'_f	c	K' (MPa)	n'		
1003	−0.093	0.124	−0.559	1195	0.14		
95% Confidence Interval							
σ'_f (MPa)	b		ϵ'_f		C		
Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper
869	1286	−0.07354	−0.1281	0.07591	0.2391	−0.4902	−0.6496