THE INFLUENCE OF HYDROGEN ON THE ELASTIC MODULUS AND ANELASTIC RESPONSE OF COLD WORKED PURE IRON

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ABSTRACT

Understanding the influence of hydrogen on elastic deformation and anelastic response should contribute to our understanding of the influence of hydrogen on deformation and fracture. To accomplish this objective, samples of pure iron were cold-worked, charged with hydrogen, and examined in a dynamic mechanical analyzer. For these measurements, square wave loads were applied at different frequencies and the response of the sample quantified into time-independent and time-dependent components. These measurements were then analyzed to determine the influence of hydrogen on the time-independent, elastic, modulus and time-dependent, anelastic, relaxation. Hydrogen lowered the measured elastic modulus by a small, but statistically significant, amount.

INTRODUCTION

The mechanisms responsible for hydrogen-induced sub-critical crack propagation ("hydrogen embrittlement") have been the subject of considerable study, and there are a number of excellent reviews available in the scientific literature [1-5]. Many mechanisms have been proposed to explain hydrogen embrittlement in different materials and alloys including nucleation of gas filled voids and blisters [6-10], brittle hydride nucleation [5,11], reduced plasticity (dislocation pinning) [12,13], lattice decohesion [14,15], enhanced localized plasticity [16-20], and surface energy modification [21-23].

Whatever the mechanism or mechanisms of embrittlement may be, it is clear that hydrogen can influence fracture morphology by either: (i) modifying normal ductile fracture (e.g. enlarging dimples), (ii) inducing transgranular "cleavage-like" fracture features, (iii) inducing intergranular or interphase interface fractures, or (iv) nucleation of second phases (blisters or hydrides). Also, two or more of these fracture modes may be observed in the same alloy system depending on hydrogen

fugacity, strain rate, stress state, microstructure, and crack tip orientation with respect to susceptible interfaces. Hydrogen supersaturation by cooling or cathodic charging can result in interfacial cracking, blistering, or hydride cracking. Recent research has focused on hydrogen levels more representative of service conditions expected for a hydrogen fuel based economy and newer alloys. Typically, newer alloys are less susceptible to hydrogen induced intergranular fracture due to improvements in alloy chemistry and metallurgical practices. For these alloys and conditions, transgranular "cleavage-like" fractures are more common, and crack propagation is usually attributed to either decohesion [14,15] or enhanced localized plasticity [16-20].

Decohesion and enhanced plasticity mechanisms differ in the basic phenomena believed to be responsible for crack propagation. The decohesion mechanism attributes fracture to a lowering of the bond energy holding the lattice together resulting in a reduced cleavage stress. The enhanced plasticity mechanism assumes that increased dislocation activity localized to the crack tip plastic zone is responsible. While in real solids it may not be possible to alter one of these factors without influencing the other, understanding the contribution of each to embrittlement requires measuring the extent that hydrogen actually alters one or both of these factors. An experimental technique for accomplishing this objective would be to apply a cyclic square wave load to hydrogen charged and uncharged samples and compare the time-independent and time-dependent elastic and anelastic response of the solid. Since lowering the cohesive forces binding the lattice together will alter the curvature of the interatomic potential energy (Fig. 1), the underlying hypothesis of the decohesion mechanism means that a lower elastic modulus should be observed when hydrogen is present. On the other hand, if hydrogen increases dislocation activity, then an increase in the anelastic strains should be observed similar to that found in steels with increasing cold work [24].
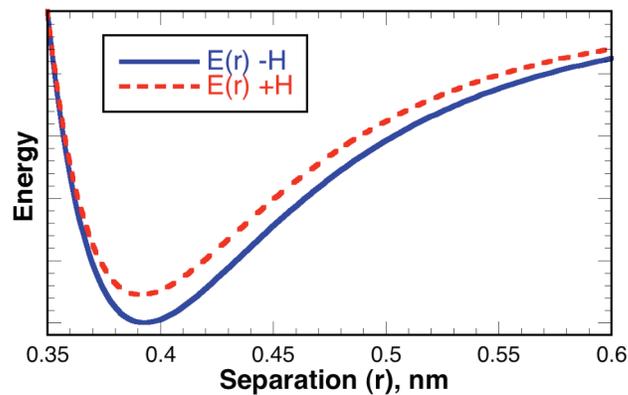

Figure 1: Diatomic potential energy vs. separation curves illustrating the change that hydrogen would have on curvature and modulus if it lowers attractive forces.

EXPERIMENTAL

Samples of pure iron (composition in Table 1) were cold rolled 47 % to a thickness of 0.83 mm. Pieces cut from the cold rolled strip were stacked and machined simultaneously to produce samples of nearly identical width (12.42 mm) and length (60 mm). The samples were tested in a commercially manufactured dynamic mechanical analyzer (DMA). This equipment consists of a furnace with a cryogenic (liquid nitrogen) cooling system capable of testing at temperatures from -150 °C to 600 °C and an electromagnetic driver capable of testing at frequencies from 0 Hz to 200 Hz and at applied loads up to 18 N. The closed-loop temperature control system uses a feedback thermocouple placed ≈ 3 mm from the test sample and is capable of controlling the temperature to ± 0.5 °C of the testing temperature (-100 °C). The force from the linear drive motor is applied with a frictionless air bearing and a three-point bending grip with a 50 mm span. An optical encoder with a resolution of 1.0 nm is used to measure displacement. The system is calibrated with the three-point bend grip in place to minimize errors from grip geometry and compliance.

Table 1: Chemical analysis of the Ferrovac E iron alloy. The identification of any commercial product or trade name does not imply endorsement or recommendation by the authors or NIST.

Element	Mass Fraction, %	Element	Mass Fraction, %	Element	Mass Fraction, %
Fe	Bal	Ni	0.03	Cu	0.001
C	0.006	Cr	0.01	Al	0.01
Mn	0.001	V	0.004	Sn	0.001
P	0.003	W	0.01	Pb	0.0006
S	0.007	Mo	0.001	O	0.026
Si	0.008	Co	0.003	N	0.0004

The samples were tested in three conditions: (1) uncharged, (2) hydrogen charged, and (3) hydrogen desorbed (desorbed). The samples were charged with hydrogen by polarizing them cathodically at room temperature in a solution of 0.1 mol/L NaOH for one hour using a closed-loop controller to hold the potential of the sample at -1.3 V with respect to a saturated calomel electrode. Diffusion calculations indicate that samples of this size will reach over 90 % of saturation at these conditions for hydrogen diffusion coefficients great than 4.0 E-11 m^2/s [25,26]. Following charging, the samples were immediately rinsed in water and alcohol, dried, and stored in liquid nitrogen until tested. The samples were tested in three point bending at -100 °C using a square wave load with a minimum force of 0.050 ± 2.0 E-7 N and a maximum force of 4.61327 ± 2.0 E-6 N, corresponding to a change in the bending stress in the sample of 40 MPa, at wavelengths of 6, 60, and 600 seconds. When the hydrogen charged tests were completed the samples were left in the grips untouched for a period of time sufficient to allow hydrogen desorption (overnight at ambient temperature). As with most elastic modulus measurements, the greatest source of uncertainty comes from sample dimensions, grips, and alignment. Re-testing the

same sample without repositioning it in the grips removes these sources of uncertainty [24]. No attempt has been made to correct for the influence of hydrogen content on sample dimensions. This correction requires additional measurements (i.e. hydrogen content) beyond the scope of the present work. However, it is well known that the iron lattice expands as the hydrogen content increases, which would reduce the displacements measured in three point bending for the same applied force if the elastic modulus were constant. Therefore, assuming that the sample dimensions are constant is a conservative test of the hypothesis that hydrogen lowers the elastic modulus.
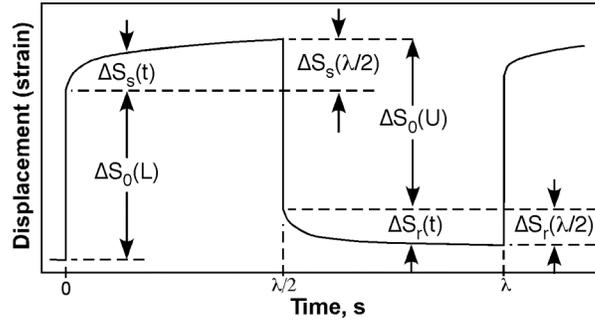

Figure 2: Schematic of the displacements produced by a square wave load with the magnitude of the time-dependent strains greatly exaggerated for illustration.

RESULTS AND DISCUSSION

When a square wave cyclic force is applied to a sample, the resulting displacements should consist of nearly instantaneous displacements when the load is applied and removed ($\Delta S_0(L)$ and $\Delta S_0(U)$ in Fig. 2) followed by a period of time equal to half the wavelength where the displacement is essentially constant. Small time-dependent microstructural relaxations, $\Delta S_s(t)$ and $\Delta S_r(t)$, occur during these periods of static stress as shown in Fig. 2. These strains are several orders of magnitude smaller than the time-independent strains, and they are due to relaxation of microstructural defects in the applied stress. The magnitude of this relaxation depends on the population of microstructural defects and the ability of these defects to respond to the applied stress and produce an increment of strain [27,28]. Since cold work increases the magnitude of these time-dependent strains [24], dislocations are one of the types of microstructural defects that contribute to these strains. The goal of the present study is not to evaluate these mechanisms, but to determine if these strains are modified by the presence of hydrogen in a manner consistent with the decohesion or enhanced localized plasticity mechanisms for hydrogen embrittlement. For this purpose, the time-independent strains will be quantified by the displacements measured on load application or removal, $\Delta S_0(L)$ and $\Delta S_0(U)$ respectively, and the time-dependent strains will be quantified by the relaxation over the half cycle at maximum load, $\Delta S_s(\lambda/2)$, and the recovery during the half cycle at the minimum load, $\Delta S_r(\lambda/2)$. Since the sample dimensions and the applied forces are constant,

changes in the measured displacements will be inversely proportional to the changes in the modulus.

The time-independent strains were examined by first comparing response during loading and unloading, $\Delta S_0(L)$ and $\Delta S_0(U)$, and no statistically significant difference could be determined. Also, no significant trend could be discerned with increasing cycle count. A slightly greater range was observed for the first load application and attributed to seating of the sample in the grips. Therefore, these measurements, minus the first loading transient, were grouped together for the evaluation of the effects of hydrogen desorption. To minimize experimental uncertainties, the samples were left mounted in the grips with the chamber closed during desorption (overnight at ambient temperature). Table 2 summarizes the results of this comparison and shows that displacements were slightly smaller for the same loading conditions after hydrogen desorption. However, a t-test for the statistical significance of this difference found essentially zero probability that this difference could be due to measurement uncertainty. Therefore, it is concluded that removal of the hydrogen cathodically charged into the samples resulted in a small increase in the observed elastic modulus. While this difference may not actually be due to a change in the interatomic bonding forces and other hydrogen microstructure interactions could be responsible, one cannot rule out decohesion as a potential mechanism for hydrogen embrittlement, as this observation is consistent with the fundamental hypothesis of this mechanism.

Table 2: Analysis of the influence of hydrogen on the elastic displacement measured when the applied force is stepped between the minimum and maximum.

		Sample A	Sample B
After H Charging $\Delta S_0(+H)$	Mean, μm	87.528	95.030
	Std Dev, μm	0.061	0.099
	n (meas.)	15	15
After H Desorption $\Delta S_0(-H)$	Mean, μm	87.090	93.998
	Std Dev, μm	0.032	0.069
	n (meas.)	15	15
Statistical Test of Significance	ΔMean, μm	0.439	1.031
	t-Test Statistic	26.399	35.143
	DOF	28	28
	t-Test Prob	1.35E-20	5.79E-24

To evaluate the effect of hydrogen on the magnitude of anelastic relaxations, the total relaxations over the half wavelength ($\lambda/2$) at the maximum and minimum loads of each load cycle were compared with and without hydrogen over a sequence of 3 cycles. These results are shown in Fig. 3 with error bars determined from the standard deviations of the measurements. This figure shows that the anelastic relaxations determined for the static period at the maximum load (ΔS_s) were greater with hydrogen in the lattice for all cycles for $\lambda/2$ of 3 s and 30 s and for the first cycle at 300 s. The anelastic strain recovered over the static period after the load was

reduced from the maximum (ΔS_r) was not significantly different with hydrogen content for any of the loading cycles and periods except for the first cycle with $\lambda/2=3$ seconds. Since there is greater error in these measurements and the error bars frequently overlap, these conclusions are not as strong as those for the time-independent response, but Fig. 3 shows that greater relaxations were observed at the maximum stress when hydrogen was present in the lattice. Since the measurements include all mechanisms of microstructural relaxations one cannot conclude that dislocation activity was increased when hydrogen was present [29]. However, one can conclude that removal of hydrogen from the samples reduced the magnitude of the observed relaxations consistent with the hypothesis that hydrogen increases dislocation activity.
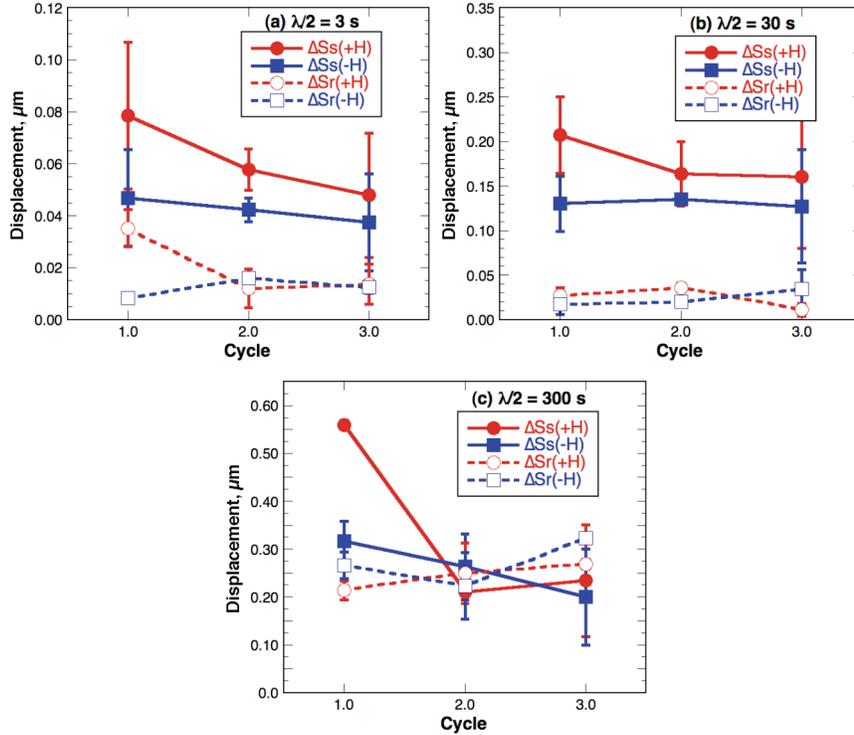

Figure 3: Comparison of the anelastic relaxations at maximum load with hydrogen present and after desorption ($\Delta S_s(+H)$ and $\Delta S_s(-H)$) and after release of the maximum load with hydrogen present and after desorption ($\Delta S_r(+H)$ and $\Delta S_r(-H)$) as a function of the cycle count for three cycles with a half wavelength ($\lambda/2$) of (a) 3 s, (b) 30 s, and (c) 300 s.

CONCLUSIONS

There were three objectives to these experiments: (i) test the hypothesis that hydrogen lowers the elastic modulus, (ii) test the hypothesis that hydrogen increases anelastic relaxations, and (iii) evaluate dynamic mechanical analysis as a measurement tool for investigation of fundamental interactions contributing to hydrogen embrittlement. These experiments accomplished all three objectives although the change in the anelastic response was not definitive. While the changes in the time-independent and time-dependent responses were consistent with these mechanistic hypotheses, it is premature to conclude these mechanisms are the only mechanisms that could be responsible for the observations. Additional testing and analysis will be required to evaluate and eliminate other mechanistic possibilities before this can be concluded unequivocally. In any event, dynamic mechanical analysis has proven to be an effective tool for investigating the influence of hydrogen on mechanical properties.

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