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The observation of compliance change in the transition from hydrogen to air environment during the fatigue test

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A compliance change was observed during fatigue testing of ASTM A710 HSLA steel using constant "K" CDCB specimen. The compliance decreased from 1.296×10^{-5} mm/N to 1.235×10^{-5} mm/N when the environment was changed from hydrogen to air under the fatigue test conditions of $f = 0.2$ Hz, $R = 0.1$ and $\Delta K = 10$ MPa$\sqrt{}$m. The compliance change was observed in all fatigue testing while changing the environment from hydrogen to air. This compliance change can be explained numerically using the differential method for the design factors of the CDCB specimen. It was found from the calculation that the compliance change corresponded to a 6.3% change in Young's modulus. It is proposed that the increased compliance resulted from the decreased Young's modulus, the reduced Young's modulus resulted from the increased lattice dilation which in turn resulted from a significantly increased hydrogen concentration at the crack tip region. The increased hydrogen concentration at the crack tip resulted from stress-induced hydrogen diffusion at the crack tip region. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

The effects of hydrogen on the mechanical properties of materials have been studied by many investigators [1–8]. It is commonly observed that hydrogen causes a loss of ductility in high strength materials. A number of mechanisms of hydrogen embrittlement in steel have been proposed. One mechanism proposed is a local enhancement of plastic deformation processes in the stress field of the crack in which the stress required for plastic deformation was locally decreased by the presence of hydrogen, i.e. hydrogen enhanced dislocation generation and mobility [9–14]. Dislocations pile up at grain boundaries or barriers which will induce crack nucleation. Birnbaum *et al.* [15–16] used an *in-situ* TEM technique and showed that hydrogen increased dislocation mobility and reduced the flow stress for fatigue crack growth. Another proposed mechanism is the decohesion model [17–18] in which hydrogen accumulates in the high stress region near the crack tip, lowering the cohesive strength of the lattice in that area and therefore making bond rupture easier. The experimental data [3–5] on iron based alloys indicates that hydrogen decreases the Young's modulus slightly for the equilibrium solubility concentration of 3 wppm.

The objective of this work is to report and discuss the origin of sample compliance changes observed during the fatigue test upon changing the environment from hydrogen to air. Compliance measurements have been used in this work to monitor the crack length during fatigue testing in a hydrogen environment (cathodic charging) and in air. This technique permits continuous determination of the crack length in fatigue tests performed initially in a hydrogen environment and subsequently in air.

2. Experimental procedures

The material used in this study was ASTM A710 (class 3) HSLA steel. The composition and mechanical properties of this steel are given in Tables I and II, respectively. The steel is a low carbon, quenched and tempered plate steel that has a nominal yield strength of 88.9 ksi (613 MPa). The steel is unique as its strength is derived from acicular ferrite microstructure and copper precipitation hardening.

Contoured double cantilever beam (CDCB) specimens were used which have a constant dC/da (where C = compliance, a = crack length) as a function of crack length, giving a stress intensity factor, K, that is dependent on load alone over a significant crack length range. This specimen, Fig. 1, was modified [19] from that originally developed by Mostovoy *et al.* [20].

The compliance calibration of ASTM A710 was conducted by fatigue testing in air under different load and stress ratios, R. The compliance values were recorded at each step when the load or stress ratio was changed.

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[*] This work was conducted at Illinois institute of Technology (IIT).

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TABLE I Chemical composition of ASTM A710 (wt.%)

Material	C	Mn	P	S	Cu	Si	Ni	Cr	Mo	Nb
ASTM A710	0.04	0.58	0.01	0.004	1.18	0.28	0.76	0.85	0.21	0.042

TABLE II As-received mechanical properties.

Material	YS (MPa)	UTS (MPa)	Elongation (%)	RA (%)	CVN energy at 211 K (J)
ASTM A710	613	696	35	77	68

Note: The material was austenitized at 899°C for 30 min, water quenched, tempered at 598°C for 30 minutes and furnace cooled.

The specimens were fractured after each test. The crack length corresponding to each compliance value was measured with an optical microscope. The determined relationship between the compliance and crack length is shown in Fig. 2 and Equation 1. With this relationship, the crack length can be calculated based on the measured compliance value.

$$C = -1.1696 \cdot 10^{-6} + 2.8371 \cdot 10^{-7} a \qquad (1)$$

Where, C = compliance (mm/N), a = crack length (mm).

Equation 1 is only valid in a range of crack length between 25 to 60 mm.

3. Sample preparation

The CDCB specimens were carefully protected with Measurements Group/Vishay M coat J2-part polysulfide liquid polymer compound prior to hydrogen charging. The only part of the sample exposed to the hydrogen environment was a small region around the crack tip. Hydrogen charging was accomplished by immersing the CDCB specimen in a solution of 5N H_2SO_4 + 250 mg/l As_2O_3. The charging current was controlled at a constant cathodic current density of 5 mA/mm^2. The specimen was pre-charged for 12 h before fatigue testing.

4. Fatigue tests

The fatigue tests were conducted in a servohydraulic fatigue machine. The fatigue tests were performed at different applied stress intensity factor range, ΔK_{app}, and different applied frequencies while the specimen was still immersed in the hydrogen charging solution. The compliance was recorded periodically during the fatigue test. Once the crack propagation rate in the hydrogen environment was established, hydrogen charging was discontinued, the solution was drained from the bath, and the fatigue test was continued in air.

5. Results and discussion

Fig. 3 shows the relationship between the compliance and number of cycles at $\Delta K = 10$ MPa$\sqrt{\mathrm{m}}$, 0.2 Hz, and stress ratio, $R = 0.1$. The behavior is typical of all results. The compliance increased rapidly when the fatigue test was begun in a hydrogen environment after 12 h pre-charging. The compliance change reaches a steady state with dC/dN = 1.14 10^{-10} mm/N/cycle in this example. The electrolyte solution was removed after the compliance change reached a steady state.

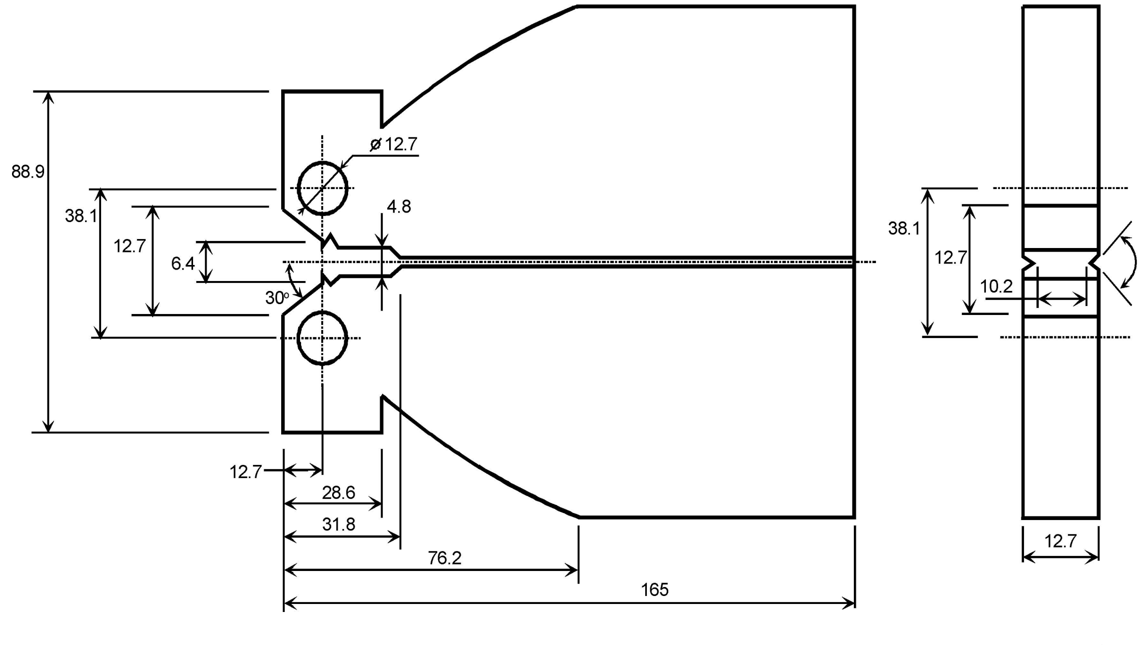

Figure 1 Schematic diagram of modified "Constant K" contoured double cantilever beam specimen with geometry factor, $m = 0.0524$ mm^{-1}. all dimensions are in mm.

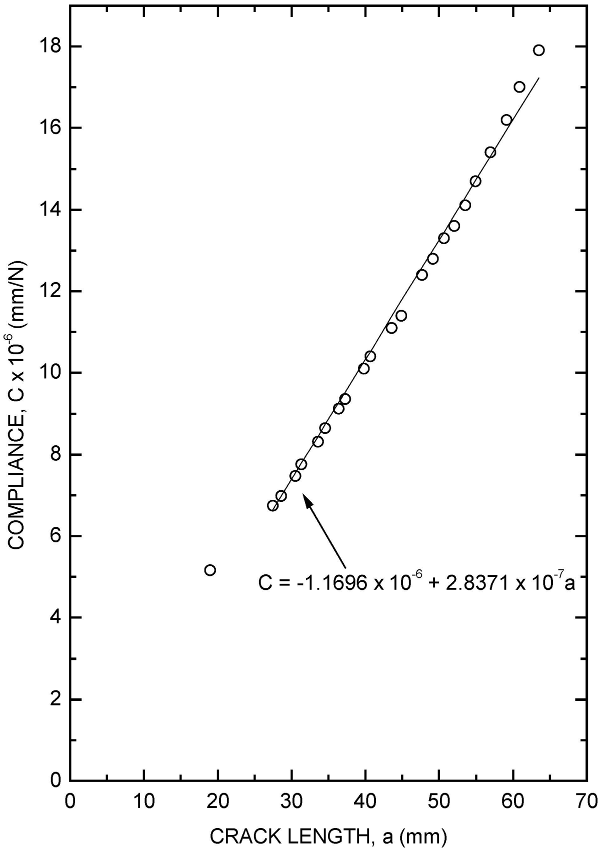

Figure 2 The relationship between the compliance and the crack length for the double cantilever beam (CDCB) specimen with geometry factor, $m = 0.0524\ \text{mm}^{-1}$ of ASTM A710, tested in air.

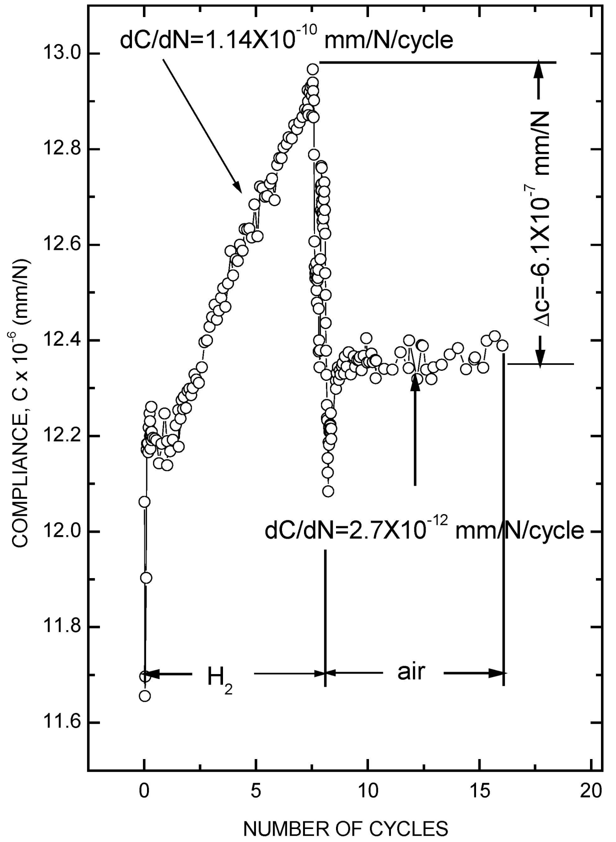

Figure 3 The relationship between the compliance and the number of cycles of the ASTM A710 for the fatigue test at $\Delta K = 10.0\ \text{MPa}\sqrt{\text{m}}$, $f = 0.2$ Hz and R = 0.1 with a geometry factor, $m = 0.0524\ \text{mm}^{-1}$.

After a transition region, the compliance change once again reached a steady state in air with $dC/dN = 2.7 \times 10^{-12}$ mm/N/cycle. The crack growth rate decreased from a steady state value of 4.02×10^{-4} mm/cycle in the hydrogen environment to 9.52×10^{-6} mm/cycle at steady state in air.

The crack length was calculated from the compliance data based on the relationship between the compliance and the crack length (Equation 1). The compliance measurements indicate a decrease in crack length as the specimen goes through the transition region from the hydrogen charged to the uncharged condition. The effect was reproducible and, since crack length decrease is not possible, constraint of crack closure due to corrosion product was considered as a possible explanation. This explanation is rejected because there is likely not enough time to build up corrosion products at the crack tip due to the high crack propagation rate in the hydrogen environment. SEM study indicated that no corrosion products were found on the fracture surfaces.

The geometry of the CDCB sample is such that the compliance change with crack length is approximately constant. The geometry factor of the CDCB specimen is defined as [20]:

$$m = \frac{3a^2}{h^3} + \frac{1}{h} \tag{2}$$

Where, m=geometry factor (1/mm); a = crack length (mm) h = crack height (mm).

In the case of elastic deformation, the compliance is related to the Young's modulus for CDCB specimen by:

$$\frac{dC}{da} = \frac{8m}{Eb} \tag{3}$$

Where; dC/da = change in compliance/crack length; m = specimen geometry factor (1/mm); E = Young's modulus (GPa); b = specimen thickness (mm).

Integration of Equation 3 will give

$$C = \frac{8m}{Eb}a + C_0 \tag{4}$$

Partial differentiation of Equation 4 with respect to hydrogen content [H], gives the following equation:

$$\begin{aligned}\frac{\partial C}{\partial[H]} &= \frac{8a}{Eb}\cdot\frac{\partial m}{\partial[H]} + \frac{8m}{Eb}\cdot\frac{\partial a}{\partial[H]} - \frac{8ma}{bE^2}\\ &\quad\cdot\frac{\partial E}{\partial[H]} - \frac{8ma}{Eb^2}\cdot\frac{\partial b}{\partial[H]} + \frac{\partial C_0}{\partial[H]}\end{aligned} \tag{5}$$

The geometry factor, m, is a constant value in the design of the CDCB specimen resulting from the relationship between the crack length, a, and crack height, h, based on Equation 2. Therefore, the partial differential of m with respect to the hydrogen content, $\frac{\partial m}{\partial[H]} = 0$. The specimen thickness, b, is also a design parameter of the CDCB specimen which will not change with the hydrogen content. Therefore, the partial differential of b with respect to the hydrogen content, $\frac{\partial b}{\partial[H]} = 0$. As previously discussed, the partial differentials of the a value with respect to the hydrogen content, $\frac{\partial a}{\partial[H]} = 0$. The constant, C_0, is an integration constant, therefore, the partial differential of the C_0 with respect to the hydrogen content, $\frac{\partial C_0}{\partial[H]} = 0$. Therefore, the change of compliance due to the change of hydrogen content [H] can be simplified as:

$$\frac{\partial C}{\partial[H]} = -\frac{8ma}{bE^2} \cdot \frac{\partial E}{\partial[H]} \tag{6}$$

Fig. 3 shows that the compliance increased when the test environment changed from air to hydrogen during the fatigue testing. Therefore, $\frac{\partial C}{\partial[H]} > 0$ when the hydrogen content increased. The m, a, and E^2 values are positive based on their nature. Therefore, $\frac{\partial E}{\partial[H]} < 0$ will be true which represents a Young's modulus decrease when the test environment is changed from air to hydrogen.

If Equation (6) is valid for both the air and hydrogen tests, the observed compliance drop can be explained by an increase in the Young's modulus locally at the crack tip and crack surface on decreasing the hydrogen concentration. That is, the Young's modulus returns to the normal value for the steel from a reduced value caused by the presence of hydrogen. The hydrogen content [H] is largest at the crack tip due to stress gradient induced diffusion. Therefore, modulus variations in this region will give sensitive results to the compliance, C.

From Fig. 3, the change in compliance with respect to hydrogen content is approximately, $\frac{\partial C}{\partial[H]} = 6.1 \times 10^{-7}$ mm/N/∂ [H]. Therefore, the change in Young's modulus with respect to hydrogen content can be determined from:

$$\frac{\partial E}{\partial[H]} = -\frac{\partial C}{\partial[H]} \cdot \frac{bE^2}{8ma} \tag{7}$$

where:

$b = 10.2$ (mm)
$E = 197.89$ (GPa)
$m = 0.0524$ (1/mm)

$a = 46.77$ (mm) when the environment was changed from hydrogen to air which resulted in a compliance value in air of $C = 1.21 \times 10^{-5}$ mm/N based on Equation 1 Therefore,

$$\frac{\partial E}{\partial[H]} = -12.43(\text{GPa}/\partial[\text{H}]) \tag{8}$$

The increase of compliance due to an increase of hydrogen content is approximately of 6.1×10^{-7} mm/N/∂ [H]. This will lead to a change in the Young's modulus of steel by −12.43 GPa/∂ [H]. This corresponds to a 6.3% decrease in the Young's modulus on a macro scale if the elastic deformation is the only contributing factor. However, the hydrogen content does not change in most of the specimen but only locally at the crack tip. The plastic deformation zone will be the area in which there is increased hydrogen content. For ASTM A710 with a yield stress of 620 MPa, the plastic zone size is approximately 13.8 μm for $\Delta K = 10$ MPa$\sqrt{\text{m}}$. It is proposed that the change in Young's modulus results from a dilation of the lattice. Lattice dilation results from the solution of hydrogen in steel at the crack tip region. However, the hydrogen concentration would have to be many orders of magnitude larger than the equilibrium value to reach the lattice dilation required to explain the observed compliance change. Such a high concentration of hydrogen at the crack tip could result from stress gradient driven hydrogen diffusion (Gorsky effect [21]). A detailed finite element model based on this idea has been published elsewhere [19].

6. Conclusions

A compliance change has been observed in fatigue testing of ASTM A710 HSLA steel as the specimen went through a transition region from a hydrogen environment to an air environment. The compliance decrease from 12.96×10^{-6} mm/N to 12.35×10^{-6} mm/N is equivalent to a 6.3% increase in Young's modulus. It is proposed that the decrease of compliance results from the increased Young's modulus due to hydrogen diffusion away from the crack tip. This phenomenon can be explained by the lattice dilation at the crack tip region caused by the stress gradient induced diffusion of hydrogen which resulted in a decrease of Young's modulus locally.

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References

1. H. A. WRIEDT and R. A. ORIANI, *Scripta Metall.* **8** (1974) 203.
2. E. S. FISHER, D. G. WESTLAKE and S. T. OCKERS, *Phys. Status Solidi* **28A** (1975) 591.
3. P. BASTIEN and P. AZOU, *Compt. Rend.* **231** (1950) 147.
4. T. Y. ZHANG, F. X. JIANG, W. Y. CHU and C. M. HSIAO, *Metall. Trans. A* **16A** (1985) 1655.
5. M. ORTIZ and J. OVEJERO-GARCIA, *J. Mater. Sci.* **26** (1992) 6777.
6. S. ASANO and R. OTSUKA, *Scripta Metall.* **10** (1976) 1015.
7. C. D. BEACHMAN, *Metall. Trans.* **3** (1972) 437.
8. S. X. XIE and J. P. HIRTH, *Corrosion* **38**(9) (1982) 486.
9. H. MATSUI, H. KIMURA and S. MORIYA, *Mater. Sci. Eng.* **40** (1979) 207.
10. P. BASTIEN and P. AZOU, in Proc. Of the First World Metallurgical Conf., ASM, Metals Park, OH, 1951.
11. P. LYNCH and N. E. RYAN, in Proc. 2nd Int. Conf., paper 3D12, Oxford, Pergamon Press (on behalf of the International Association for Hydrogen Energy), 1977.
12. C. A. HIPPSLEY, *Mat. Sci. Tech.* **3** (1987) 912.

13. J. D. FRANSDEN and H. L. MARCUS, *Scripta Metall.* **9** (1975) 1089.
14. J. D. FRANSDEN and H. L. MARCUS, *Metall. Trans. A* **8A** (1977) 265.
15. T. TABATA and H. K. BIRNBAUM, *Scripta Metall.* **18** (1984) 231.
16. H. K. BIRNBAUM, to be published.
17. A. R. TROIANO, *Trans. ASM* **52** (1960) 54.
18. R. A. ORIANI, No. 1637, Edgar C. Bain Laboratory for Fundamental Research, United States Steel, Monroeville, PA, Dec. 1971.
19. G. LIU-NASH, Ph.D. Thesis, "Accelerated Test Method for Collecting Near-Threshold Fatigue Data", Illinois Institute of Technology, May 1998.
20. S. MOSTOVOY, P. B. CROSLEY and E. J. RIPLING, *J. Mater.* **2**(3) (1967) 661.
21. W. S. GORSKY, *Phys. Z. Sowjetunion* **8** (1935) 457.

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