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HYDROGEN-STEEL COMPATIBILITY RESEARCH AT NIST-BOULDER[#]

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Abstract
The NIST Materials Reliability Division is outfitting a high pressure (100 MPa) hydrogen testing facility to collect mechanical and thermodynamic property data on various candidate structural materials, and is developing data on nondestructive sensors that can measure the content of hydrogen in steels. These data are becoming extremely important as the economics of hydrogen transport drive the consideration of a range of conventional steels for storage and distribution of hydrogen, and the infrastructure grows beyond pilot plants and demonstration facilities. Preliminary results with X-100 pipeline steel show a 100-fold increase in fatigue crack growth rate when charged with hydrogen. The two nondestructive sensors being evaluated are based on thermoelectric power and eddy-current concepts. Both have been found sensitive to hydrogen contents of less than one part per million, and are being used to validate permeation measurements of hydrogen through various pipeline steels.

Key Words: fatigue crack growth; hydrogen; mechanical testing; permeation; pipelines; test facility; workshop

1. Introduction
To support the drive towards a hydrogen economy, a very large and diverse infrastructure that can safely transport, store, and distribute hydrogen will be required. Existing data for the effect of hydrogen on pipeline steels (and associated hardware) are outdated and do not include data for more modern higher-strength materials. Gas pipelines are moving to newer steel grades, but designers lack the data necessary to support a fracture mechanics approach to assure their safe operation in pressurized hydrogen environments. To advance the knowledge database on various pipeline steels, the National Institute of Standards and Technology (NIST), Materials Reliability Division, is studying the influence of metallurgical factors in determining the susceptibility of high-strength steels to hydrogen embrittlement.

In 2007, NIST hosted a workshop to discuss the most critical needs for development of a hydrogen pipeline infrastructure [1]. The workshop comprised

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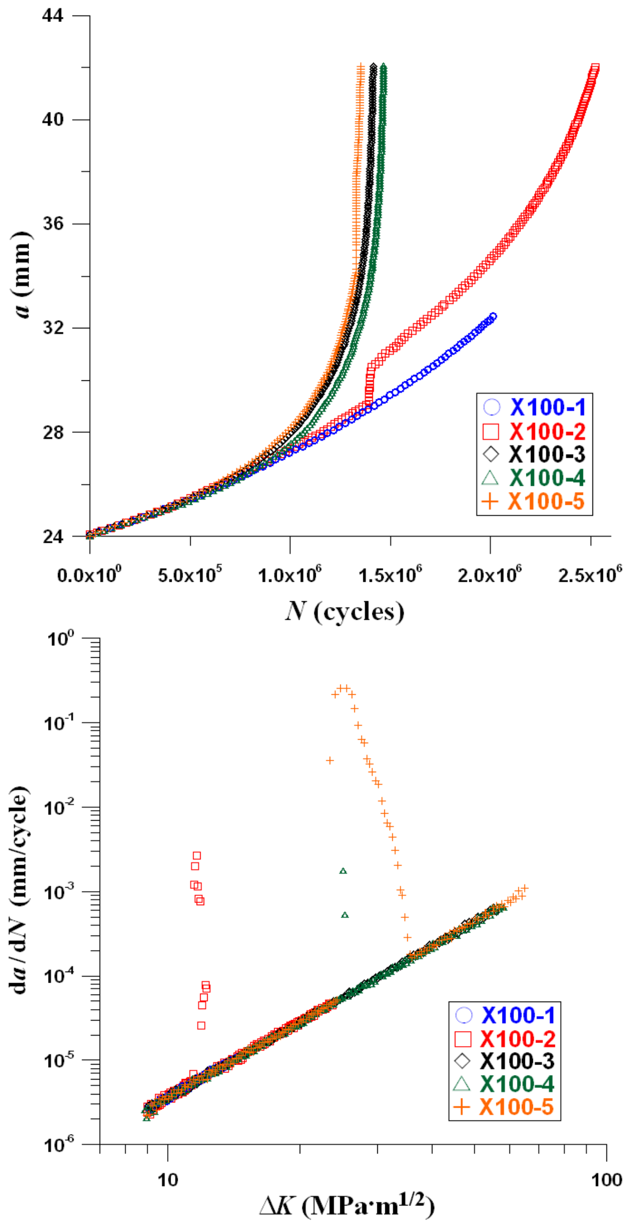
federal government (especially DOE and DOT), industry, and academic communities. The most critical needs for hydrogen pipeline research included: (1) Develop advanced hydrogen tools (measurement techniques, analytical methods, and models) that focus on current construction linepipe steels and weldments with yield strengths below 490 MPa (70 ksi), (2) Conduct round-robin performance testing to assess repeatability between laboratories, (3) Measure the performance of current pipeline construction materials (especially those in current use such as API-X52 and SA106B), (4) Study the effect of hydrogen pressure and steel microstructure, and (5) Evaluate nonmetallic linepipe and compare to metallic linepipe.

NIST participated in the DOE Hydrogen Working Group to develop a collaborative plan to accomplish goals set in the 2007 NIST workshop [1]. NIST is participating in round robin mechanical and gaseous permeation testing on various linepipe steels.

2. Fatigue Data

Some of the first research that NIST has conducted on high-strength linepipe steel was on the effect of hydrogen on fatigue crack growth rate (FCGR). Fatigue tests were conducted in a servo-hydraulic fatigue test machine using API-X100 pipeline steel specimens precharged in gaseous hydrogen. The samples were charged in a high-pressure chamber until saturated, removed from the chamber and quickly tested in an ambient environment. The diffusion of hydrogen from the charged specimens prior to fatigue testing was reduced by coating the specimens with tin. The crack growth and FCGR curves (from Ref. 2) for the tests performed at a loading ratio equal at 0.1 (specimens X100-1 through X100-5) are presented in Figures 1 (a) and (b). The results in Figure 1 (b) show a pronounced effect of hydrogen embrittlement from the gaseous hydrogen pre-charging. The hydrogen embrittlement effect is especially seen in specimens with a hydrogen barrier coating (tin), samples X100-2 and X100-5, applied to retain the hydrogen content as long as possible (by minimizing losses from free surfaces). The hydrogen embrittlement effect lasted for 87 min in specimen X100-2 and 91 min in specimen X100-5. These periods of time are substantially longer compared to those for specimens that were not tin-coated [2]. Specimen X100-4 (not tinned) shows some limited effects of the hydrogen charging before the hydrogen quickly diffused (within approximately 5 min) from the specimen. In terms of the relationship between the degree of crack growth enhancement and ΔK *(stress intensity)*, the results suggest that there is a peak of embrittlement in the Paris regime. This embrittlement peak occurs at a ΔK between 20 to 40 $MPa \cdot m^{1/2}$, and is in agreement with values reported by Mittal, et al. [3]. These ΔK values are considered to be in a relatively high-level stress intensity range. The diffusivity time comparison between tinned specimens, X100-2 and X100-5 (about 90 min) and the specimen without a hydrogen barrier, X100-4, (about 5 min) clearly shows the limits of testing hydrogen-charged specimens in air.



(a)

(b)

Figure 1: Influence of hydrogen on (a) crack growth and on (b) fatigue crack growth rate as a function of stress intensity on various tests performed at a loading ratio equal to 0.1 [2].

The results in Figures 1 (a) and (b) confirm the detrimental effect that hydrogen can have on fatigue crack growth rates and demonstrate the need for high-pressure test facilities, where long-term fatigue studies can be conducted under uniform conditions (gaseous hydrogen with known levels of other gases instead of hydrogen pre-charging). As a result, NIST constructed a new hydrogen testing facility for gaseous hydrogen in-situ mechanical testing capabilities.

3. Capabilities of the Hydrogen Testing Facility

As of February 2009, the construction of the hydrogen testing facility is complete and it is being commissioned. The new hydrogen testing facilities are pictured in Figure 2. One building houses mechanical test systems and high-pressure hydrogen chambers, while the other building is the control room (about 25 m away from mechanical test systems) for the personnel to operate the facility and collect the data. The hydrogen testing facility will be the location for the mechanical testing portion of the round robin, which focuses on the effect of hydrogen on fatigue crack growth rate, and hydrogen permeation measurements. Nondestructive hydrogen sensors are also being designed to monitor the level of atomic hydrogen in high strength steel specimens during static and dynamic loading in gaseous hydrogen environments. The nondestructive sensors will also be used to measure permeation rates of hydrogen through various steel specimens and will be validated by comparing results with those obtained through traditional techniques. The following paragraphs give some further details about the mechanical testing system and hydrogen permeation measurements (including a nondestructive permeation technique).

Figure 2: Photograph of the NIST hydrogen test facility, showing the hydrogen building (12) in the left foreground and the building (8) that contains the control room back and to the right.

a. Mechanical Testing

The first load frame has a capacity of 100 kN and is being fitted with a small test chamber (about 1 liter in volume) that can be pressurized at pressure greater than

100 MPa. This pressure exceeds those proposed for pipelines, and matches the highest pressures currently proposed for mobile storage tanks. This chamber is designed to contain standard ASTM E8 tensile compact tension C(T) specimens. A second, larger load frame has a capacity of 500 kN and will be fitted with a larger chamber (about 40 L in volume) that can be pressurized to 35 MPa. This pressure exceeds the maximum pressure now being discussed for pipelines. The larger volume allows us to use much larger specimens (such as full-thickness curved wide plate sections from pipelines, middle-crack tensile specimens, and crack tip opening angle specimens). Data from these larger specimens are needed by pipeline designers to estimate the performance of the full-scale structure.

b. Permeation Testing

Techniques to monitor and quantify hydrogen contents form the basis for developing a better understanding of the role of hydrogen in high strength steels. Two common nondestructive tools have been developed to monitor hydrogen content in steels and steel weldments. Both tools are capable of providing hydrogen content measurements as a function of time. In turn, these measurements can be correlated to traditional measurements of permeation rate, where gaseous hydrogen is held on one side of a sample and the period taken for hydrogen to travel to the opposite side (determined by pressure drop) of the sample is used to calculate the diffusion coefficient. The nondestructive tools are based on thermoelectric power and eddy current concepts. With careful calibration, both techniques provide a very accurate means to non-destructively monitor hydrogen content in many materials. The eddy current technique is especially useful because it provides non-contact hydrogen concentration measurements as a function of depth. This permits measurement of the hydrogen content at specific locations, such as crack-tip plastic zones [4-7].

Figures 3 (a) and (b) (from Ref. 7) show the thermoelectric power coefficient and low frequency impedance measurements plotted as a function of time for hydrogen-charged grade X65 steel specimens. The X65 steel specimen was deoxidized prior to hydrogen charging at 7 MPa for 912 h at 100˚C. These plots show the sensitivity of nondestructive electronic tools for measuring hydrogen concentration for a given period. Equilibrium levels less than one part per million can be determined. The data from the two different electronic tools agree well, indicated by the minimal changes in impedance and thermoelectric power coefficients after approximately 500 s for both techniques. This decreasing trend is a result of hydrogen diffusing out of the specimen. While both techniques yield equivalent times to achieve equilibrium, the low frequency impedance (eddy current) measurements are generally more accurate at lower hydrogen concentrations.

Since these nondestructive test methods have been shown to yield reproducible results, preliminary calibrations are being performed for both thermoelectric power and low frequency impedance (eddy current) for measuring hydrogen concentrations in different pipeline materials. The effects of microstructure and hydrogen gas pressure must also be determined, so that calibrations will account for these factors.

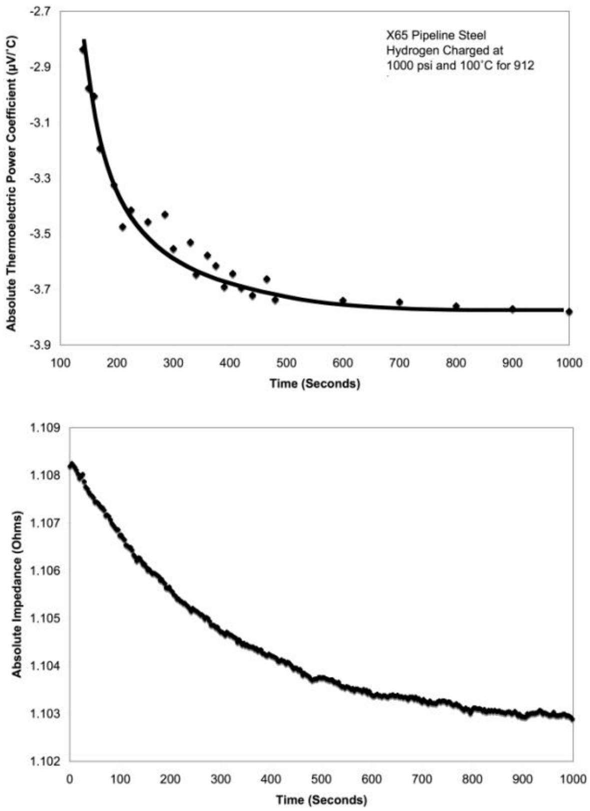


Figure 3: (a) Thermoelectric power coefficient as a function of time (as hydrogen diffuses out) and (b) low frequency impedance as a function of time (as hydrogen diffuses out) for a gaseous hydrogen pre-charged X65 steel pipeline specimen [7].

Expansion of this program may require additional staff. If interested, please contact Tom Siewert at siewert@boulder.nist.gov

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