III.17 Hydrogen Permeability and Integrity of Steel Welds

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Objectives

- Develop welding/joining technology that greatly reduces the capital cost and eliminates hydrogen embrittlement (HE) concerns in constructing new pipelines and converting existing pipelines for high-pressure hydrogen delivery.
- Quantify the effects of welding and joining on the resistance to HE of high-strength pipeline and other structural steels under high-pressure hydrogen.
- Develop the technical basis and guidelines to manage hydrogen, stress and microstructure in the weld region to ensure structural integrity and safety of hydrogen delivery systems.
- Develop risk assessment-based approach to manage the integrity and safety of hydrogen pipelines including weld joints.
- Determine the hydrogen transport behavior (absorption, diffusion, trapping, etc.) in steels.

Technical Barriers

This project addresses the following technical barriers from the Delivery section of the Fuel Cell Technologies Program's Multi-Year Research, Development and Demonstration Plan:

(D) High Capital Cost and Hydrogen Embrittlement of Pipelines
(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
(G) Storage Tank Materials and Costs
(K) Safety, Codes and Standards, Permitting

Technical Targets

This project is to develop the scientific understanding, technical basis and cost-effective engineering solutions to control and mitigate hydrogen embrittlement in the steel weld region of pipelines and other high-pressure hydrogen delivery infrastructure systems. Insights gained from this project will be applied toward the hydrogen delivery infrastructure that meets the following DOE 2017 hydrogen pipeline delivery targets:

- Capital cost: $490K/mile for transmission pipeline and $190K/mile for distribution pipeline.
- Cost of delivery of hydrogen <$1.00/gasoline gallon equivalent, gge
- Reliability/Integrity: Acceptable for H_2 as a major energy carrier.

Accomplishments

- Baseline high-pressure hydrogen permeation measurements established the effects of weld microstructure, surface conditions, temperature and hydrogen pressure on hydrogen permeation, diffusion and trapping of selected pipeline steels.
- Initial studies on friction stir welding of pipeline steels indicated considerable improvement of weld toughness and strength over the conventional arc welds.
- Testing with recently developed spiral notch torsion test (SNTT) and multi-notch tensile testing was able to quantify and rank the sensitivity of different microstructures in the weld region to hydrogen embrittlement.
- A general approach based on the finite element model has been developed to determine the fracture toughness of materials tested by SNTT.

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Introduction

The hydrogen energy delivery infrastructure will require extensive use of steels and other cost-effective structural and functional materials under high-pressure gaseous hydrogen (H_2) exposure. For example, high pressure (up to 3,000 psi) hydrogen pipelines are presently considered to be one of the most cost-effective and energy-efficient means to transport very large amounts of hydrogen to much of the market as is done currently for natural gas [1]. Under high hydrogen pressures, there are concerns about HE of steel pipelines and its potential catastrophic consequences [2]. Concerns regarding hydrogen embrittlement are not limited to steel pipelines; according to a recent DOE Basic Energy Science Office report [3], hydrogen embrittlement needs to be addressed for a variety of hydrogen storage and delivery system parts made of metallic materials that are exposed to hydrogen.

As in the case of natural gas and other energy carrier transmission pipelines, welding will be used to construct steel pipelines for high-pressure hydrogen delivery. Welding will be also widely used in fabrication of other system components for hydrogen production, storage, and delivery. However, welds in pipeline steels and other engineering materials are often the most susceptible regions to HE due to the formation of unfavorable microstructures and high tensile residual stresses. Indeed, recent studies [4] on pipeline steels have shown that the weld region exhibits delayed cracking (signature of hydrogen embrittlement) when exposed to high-pressure hydrogen gas. Furthermore, the weld region typically has substantially lower resistance to hydrogen crack initiation and higher crack growth rates, when compared to the baseline pipeline steel (base metal). **In this regard, the weld region can be the weakest link for the structural integrity and safety of hydrogen pipelines and hydrogen delivery infrastructure.** A systematic approach to deal with weld property degradation under high-pressure hydrogen gas is critical to ensure the safe, cost-effective operation and long-term reliability of the hydrogen delivery infrastructure.

Approach

While there have been extensive studies in the past on hydrogen embrittlement and hydrogen induced material property degradation of pipeline steels, the high-pressure hydrogen delivery pipeline presents some unique issues that are seldom addressed in the past. At the center of these issues is the hydrogen transport behavior in metal – the absorption, diffusion, and trapping of hydrogen in metal. At the present time, very limited knowledge is available about the rate of diffusion and amount of hydrogen in steel under high-pressure gaseous environment relevant to the hydrogen delivery infrastructure. Therefore, the first major effort in this project is directed toward high-pressure H_2 permeation and mechanical performance tests to systematically study the hydrogen permeation behavior and to evaluate the tolerance level to hydrogen of different steels before considerable mechanical property degradation would occur.

The weld joint in steel pipeline is expected to be a critical region mostly susceptible to hydrogen embrittlement due to the formation of unfavorable microstructure and the high residual stresses. The second major activity of this project focuses on developing new welding technology and/or improving existing welding technology to optimize weld microstructure and proactively control the weld residual stress for H_2 pipeline construction and repair. In addition, special testing methods need to be developed to quantify the degradation of mechanical properties in the weld region with complex microstructure and HE resistance gradients. Finally, a risk assessment-based approach will be developed to manage the integrity and safety of hydrogen pipelines including the weld joints.

Results

The Fiscal Year (FY) 2010 activities focused on the development of the SNTT method and associated finite element analysis for measuring the fracture toughness degradation of steel welds and base metals under high-pressure hydrogen.

Current standard methods for testing hydrogen-induced mechanical property degradation of base metal have shown to be inadequate when applied for the weld metal region due to the highly inhomogeneous microstructure and property gradients of the weld region [4]. In this project, we designed and fabricated miniaturized and self-loading testing devices for in situ measurement of mechanical property degradation of weld metal in high-pressure gaseous hydrogen environment. The compact size and self-loading mechanisms employed in the testing devices make it possible that the entire loading assembly and the test specimen be placed inside a relatively small high-pressure chamber. This minimizes the capital cost of the testing system and allows for multiple testing devices to be operated in a single high-pressure vessel to cost-effectively study and quantify the effects of the weld microstructure on HE resistance of different steels. The effects of high-pressure hydrogen on the stability of load sensors immersed in hydrogen have been solved with a novel sensor design.

In FY 2010, we focused on the further development of the SNTT method to test the fracture toughness of weld metal consisting of highly inhomogeneous microstructure. AISI 4340 high-strength steel samples with different level of microstructure inhomogeneity were studied. One sample was prepared by heat treatment at 850°C for one hour followed by oil quenching. The microstructure distribution was relatively uniform in this quenched sample. The other sample was prepared with simulated weld heating and cooling curves using the Gleeble system, a dynamic thermo-mechanical simulator. Highly non-uniform microstructure distribution was obtained resembling that encountered in the heat-affected zone of a weld.

Optical microscopy images of microstructure for the quenched sample at two transverse cross-sections are shown in Figure 1. The microstructure appears

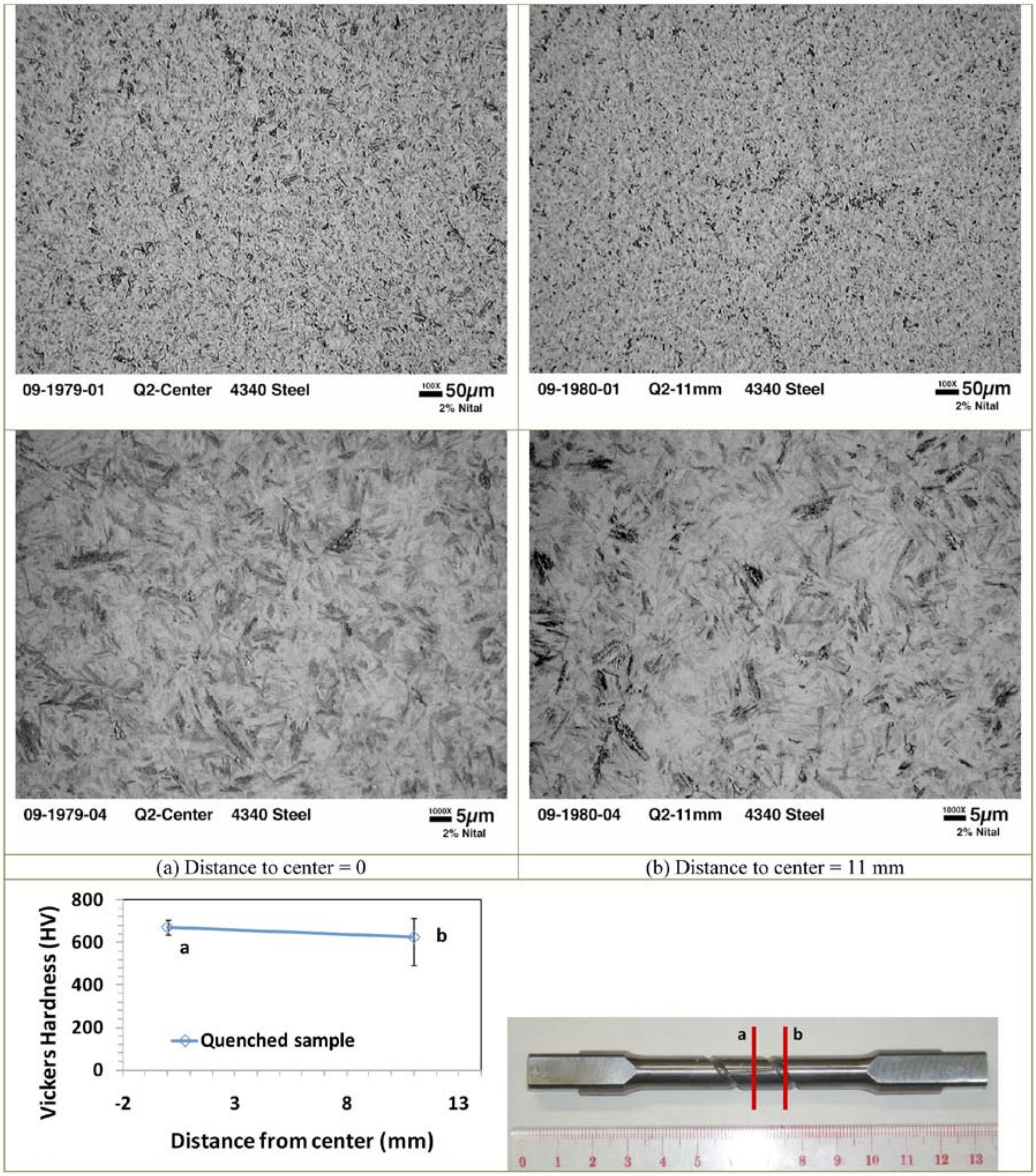


FIGURE 1. Distribution of Microstructure and Hardness in the Quenched Sample

to be predominantly martensite. The average prior austenite grain size is estimated to be roughly 250 μm. The average Vickers harness is about 650. The Gleeble sample exhibited very different microstructure than the quenched sample, as shown in Figure 2. Preliminary analysis indicates that the microstructure at the center appears to be a mixture of bainite and martensite, whereas that at 12 mm away from center is mostly bainite. It is noted that the martensite in the quenched sample is different from that in the Gleeble sample in terms of the chemical homogeneity. The rapid heating and cooling in Gleeble sample provides little time for the alloy elements to redistribute themselves in the microstructure. On the other hand, the microstructure in quenched sample is expected to be much more homogenous since the high-temperature holding permits the homogenization of alloying elements.

Fracture Toughness Analysis for SNTT

A full three-dimensional (3-D) finite element analysis (FEA) model was developed to calculate the

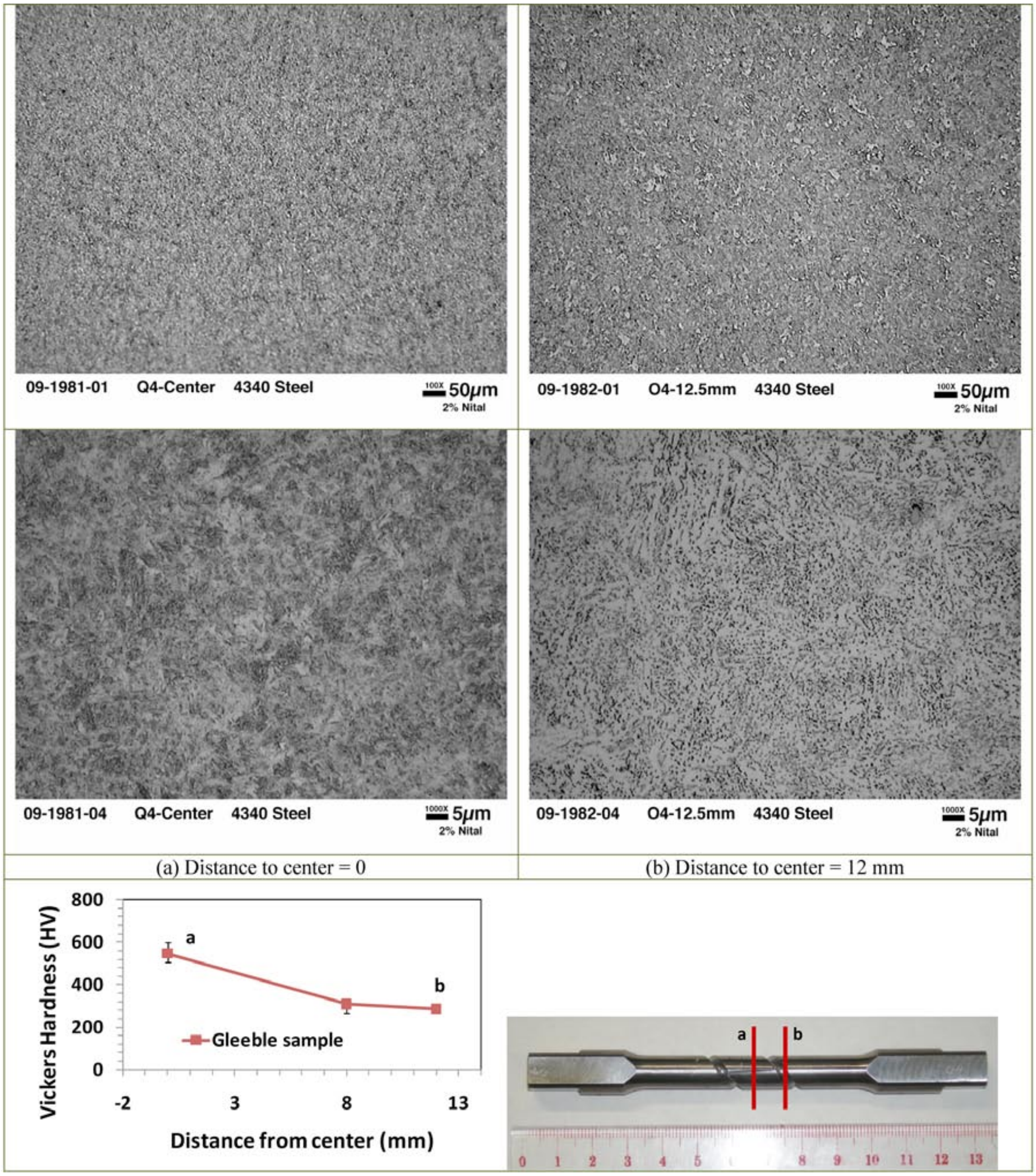


FIGURE 2. Distribution of Microstructure and Hardness in the Gleeble Sample

stress intensity factor and the fracture toughness of SNTT sample as a function of the fracture load recorded in the SNTT experiment. The model was used to study the effect of microstructure inhomogeneity on fracture toughness. Figure 3 displays the 3-D finite element model mesh of the SNTT specimen. In the analysis, one end of the sample is fully constrained, while the other end is rotated to provide the torsional load to the SNTT specimen.

For the quenched sample, the fracture torque during testing is 1,100 in·lbf. Using the 3-D model, the critical fracture energy (J_{Ic}) is found to be 33 kJ/m^2. For simplicity, it is assumed that the plastic component of J-integral is much smaller than the elastic component. Therefore, the fracture toughness K_{Ic} can be converted from J_{Ic} by

$$J_{Ic} = \frac{K_{Ic}^2}{E}(1-\nu^2),$$

and is found to be 84.1 MPa·$\sqrt{m}$ (76.5 ksi·$\sqrt{in}$). This value is in good agreement with the reported fracture toughness ranging from 67 to 86 ksi·$\sqrt{in}$ based on the compact tension test of 4340 base steel available in the

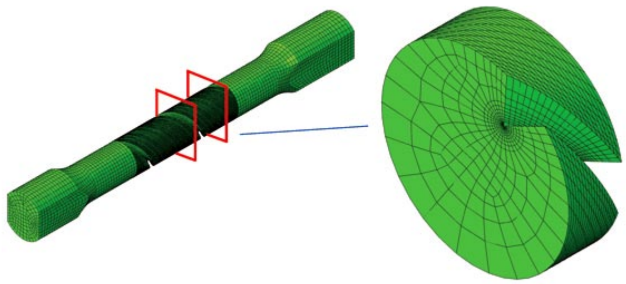


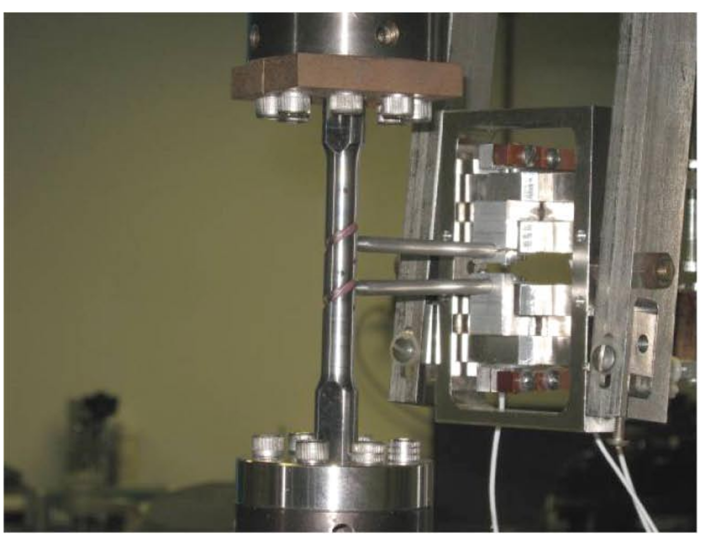
FIGURE 3. Mesh used in the Full 3-D Finite Element Model

literature [5]. On the other hand, the Gleeble sample failed at a lower fracture torque of 77 kN·m (680 in·lbf). The post-test examination reveals that the fracture initiates from the central region of the sample where the hardness is highest and the microstructure consists of a mixture of bainite and martensite. The fracture toughness is calculated to be 51.8 MPa·$\sqrt{m}$ (47.1 ksi·$\sqrt{in}$), i.e., 62% of that of quenched sample. The difference in fracture toughness between the Gleeble and quenched samples is largely due to the local microstructure. The microstructure in the quenched sample consists of mostly fine martensite, whereas the microstructure in the fractured region of Gleeble sample consists of a mixture of bainite and martensite. Furthermore, as discussed previously, the microstructure in the quenched sample is expected to be more chemically homogenous than that in the Gleeble sample.

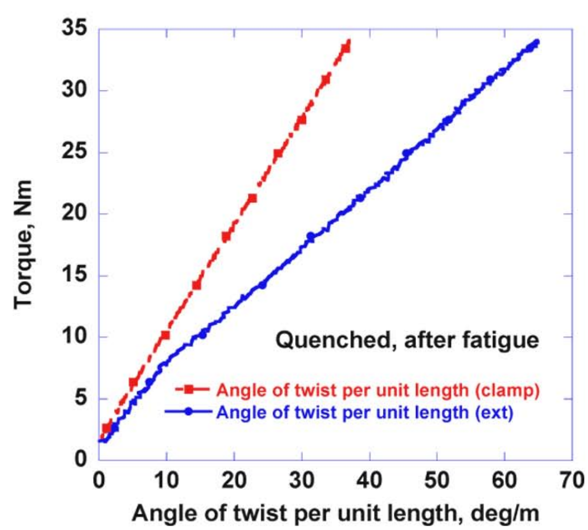
The significance of the above results is the following. Firstly, the SNTT tested fracture toughness of quenched sample is very consistent with that based on the standard ASTM compact tension test. This demonstrates that SNTT is a sound and accurate technique for measuring fracture toughness. Secondly, the miniature specimen design and high constraint in SNTT offers potential advantages over the standard compact tension test when testing mechanical property degradation due to HE in high-pressure hydrogen. As reported in the literature, it is difficult to test weld fracture toughness in hydrogen using the compact tension test due to the irregular crack growth in non-uniform microstructure [4]. As demonstrated in the Gleeble sample, the ability to test fracture toughness in the sample with a highly non-uniformed microstructure provides a solid basis for testing the weld in high-pressure hydrogen using SNTT.

Further Enhancements to SNTT

The SNTT testing technique was further improved in the following two areas. First, an extensometer was installed to accurately measure the local rotational displacement during testing. Figure 4(a) shows the in-house biaxial extensometer with a gage length of 0.5 inch. The relationship between the applied torque and rotation angle measured from the rotary variable differential transformer and the extensometer is shown in Figure 4(b). It can be seen that under the same applied torque, the angle of twist per unit length measured by the extensometer was larger than that from the rotary variable differential transformer. This indicates that the middle section of the SNTT specimen underwent a larger twist deformation than the average of the whole sample. The deformation measured from the extensometer, a more realistic representation of the actual deformation in the notched section, will be used to further validate the 3-D model.



(a)



(b)

FIGURE 4. (a) SNTT testing utilizing a biaxial extensometer; and (b) applied torque versus rotation angle per unit length measured from rotary variable differential transformer and extensometer.

Another improvement to SNTT is that sharp pre-cracks at the groove roots were induced using cyclic fatigue. Two samples were studied: One sample was machined in the as-received annealed condition; while the other was first annealed at 850°C for 1 hour and then oil-quenched to room temperature. Fatigue cycling was performed at room temperature for 10,000 cycles at 1 Hz frequency. The maximum and minimum torques applied during fatigue pre-cracking were 300 and 30 in·lbf, respectively. The pre-fatigued samples were then tested at an applied loading rate of 20 in·lbf/s.

Postmortem surface examination was performed on the fracture surfaces of the two samples using a stereo optical microscope and a scanning electron microscope (SEM). The photographs of the fracture surface of the samples are shown in Figure 5. As shown in the figure, for the as-received material, the fracture surface contains three regions. Region A appears to be smooth from a macroscopic point of view, while region B and region C appears to be rough. For the quenched material, the fracture surface contains only two regions, in which region A appears to be smooth and region B appears to be rough. Region A in both samples were suggested to be precracks introduced by fatigue loading, and region B in both samples were suggested to be the fast growth region of crack during final fracture. A possible cause for the occurrence of region C in the as-received material is that during the torsion test, the as-received sample was loaded and unloaded twice prior to the final fracture. So region C was probably introduced during the first two loading cycles. Region B exhibited a cleavage fracture feature, which is typical for the rapid growth region of cracks. The shape of region A is well-defined, and the crack length is similar measured from different parts of region A. This verifies the strong material constraint at the crack front in SNTT specimen.

Detailed FEA of a model with fatigue precrack is ongoing to calculate the fracture toughness from the fracture load. The above enhancements are expected to further improve the consistence and accuracy of the tested fracture toughness using SNTT. This is especially important for testing fracture toughness in high-pressure hydrogen.

Conclusions and Future Directions

This project focuses on the resistance of HE in the weld region of steels. Such region is regarded as the weakest link for the structural integrity and safety of hydrogen pipeline and hydrogen delivery infrastructure. In FY 2010, we have successfully demonstrated the SNTT method for testing fracture toughness of non-uniform microstructures in the heat-affected zone and weld region.

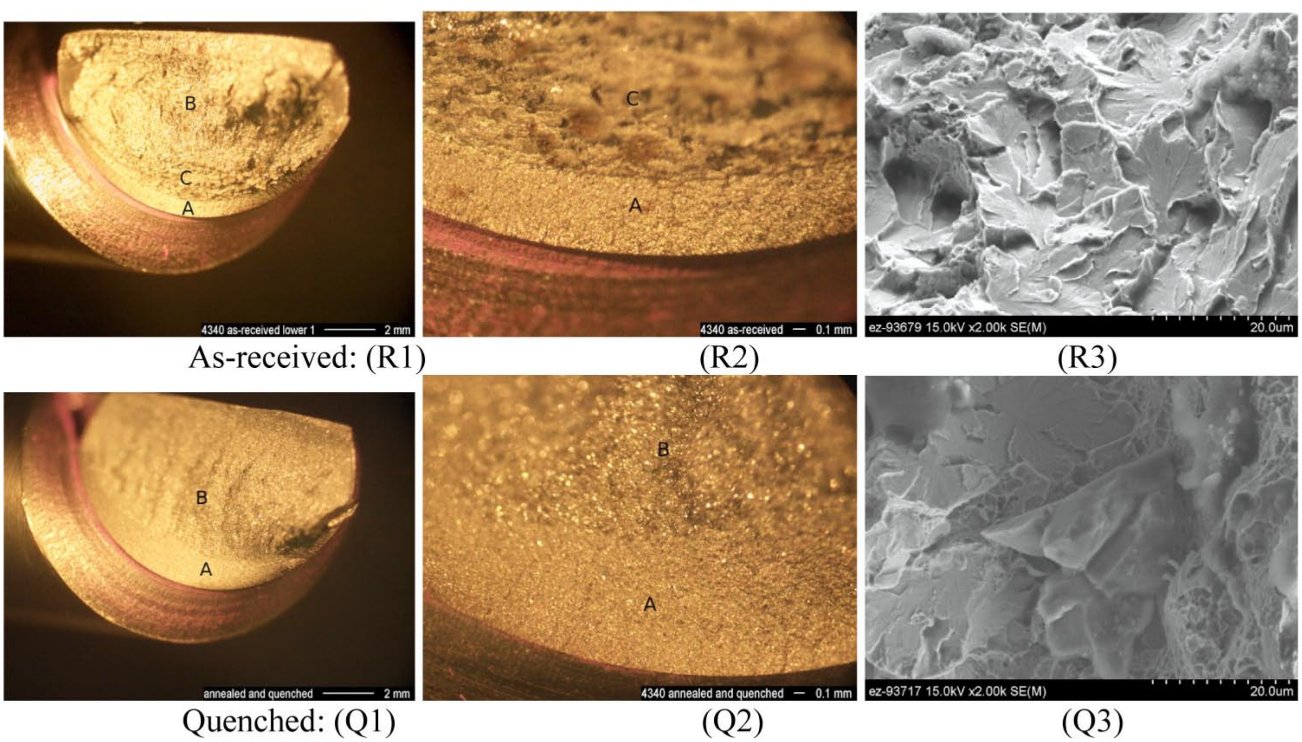


FIGURE 5. Photographs of the Fracture Surfaces of the Samples As-received: (R1) low-mag, (R2) high-mag, and (R3) SEM image of region C. Quenched: (Q1) low-mag, (Q2) high-mag, and (Q3) SEM image of region C.

The project plan for the remaining of FY 2010 includes: (1) completing the development of SNTT method for fracture toughness testing in high-pressure hydrogen, and (2) performing tests on different arc welds and friction stir welds of pipeline grade steels and establishing a database of material performance in high-pressure hydrogen.

FY 2010 Publications/Presentations

1. Wei Zhang, Zhili Feng and Jy-An Wang: Measurement Of Fracture Toughness Of Materials With Non-Uniform Microstructure Based On Spiral Notch Torsion Test, ASME PVP 2010, Bellevue, WA.

2. 2010 DOE Hydrogen Program Review – Washington, DC, June 2010.

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5. Bandyopadhyay et al, *Metallurgical Transactions A*, **14**(5), 881-888 (1983).