VII.4 R&D for Safety, Codes and Standards: Materials and Components Compatibility

Aaron Harris (Primary Contact), Brian Somerday
Sandia National Laboratories
P.O. Box 969
Livermore, CA 94551-0969
Phone: (925) 294-4530
Email: apharri@sandia.gov

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

DOE Manager
Rick Farmer
Phone: (202) 586-1623
Email: Richard.Farmer@ee.doe.gov

Project Start Date: October 1, 2003
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Understand the effects of hydrogen on structural materials
- Support the development and improvement of design and safety qualification standards for material use and materials evaluation

Fiscal Year (FY) 2013 Objectives

- Support the development of design and safety qualification standards for components (SAE International [SAE] J2579, American Society of Mechanical Engineers [ASME] Article KD-10) and materials testing standards (Canadian Standards Association [CSA] CHMC1)
- Develop more efficient and reliable materials test methods in standards
- Execute materials testing to address targeted data gaps in standards and critical technology development
- Develop and maintain material property database and identify material property data gaps

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Safety, Codes ,and Standards section 3.8 of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Safety Data and Information: Limited Access and Availability

(F) Enabling National and International Markets Requires Consistent Regulations, Codes, and Standards

(G) Insufficient Technical Data to Revise Standards

Contribution to Achievement of DOE Safety, Codes and Standards Milestones

This project will contribute to achievement of the following DOE milestones from the Hydrogen Safety, Codes and Standards section of the 2012 Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

- Milestone 2.9: Publish technical basis for optimized design methodologies of hydrogen containment vessels to account appropriately for hydrogen attack. (4Q, 2014)
- Milestone 2.16: Demonstrate the use of new high-performance materials for hydrogen applications that are cost-competitive with aluminum alloys. (4Q, 2017)
- Milestone 2.18: Implement validated mechanism-based models for hydrogen attack in materials (4Q 2018)
- Milestone 3.3: Reduce the time required to qualify materials, components, and systems by 50% relative to 2011 with optimized test method development. (1Q 2017)
- Milestone 3.4: Develop hydrogen material qualification guidelines including composite materials (Q4, 2017)
- Milestone 4.9: Completion of the GTR Phase 2. (1Q, 2017)
- Milestone 5.2: Update materials compatibility technical reference (4Q, 2011-2020)
- Milestone 5.4: Develop and publish database for properties of structural materials in hydrogen gas. (2Q, 2013)

FY 2013 Accomplishments

- Completed test matrix to evaluate fatigue crack growth rate (da/dN) relationship corrections—two steels (SA372 Grade J and 34CrMo4) at three pressures (10, 45, 100 MPa):
  - For higher-strength steel, da/dN correction depends on hydrogen pressure and delta K level

  – For lower-strength steel, da/dN correction is less sensitive to hydrogen pressure
- Investigated effects of welding practice on hydrogen-exposed orbital welds in Type 316L tube:
  – Effect of low temperature evaluated for orbital tube welds
  – Tensile ductility of tubing and welds similar to data for bar materials
- Updated full public report on Technical Reference for Hydrogen Compatibility of Materials (SAND2012-7321), available on the Sandia National Laboratories' website (www.sandia.gov/matlsTechRef):
  – Data contributed to the White House OpenEI website (en.openei.org/wiki/Gateway:Hydrogen) initiative

✧ ✧ ✧ ✧ ✧

INTRODUCTION

A principal challenge to the widespread adoption of hydrogen infrastructure is the lack of quantifiable data on its safety envelope and worries about additional risk from hydrogen. To convince regulatory officials, local fire marshals, fuel suppliers, and the public at large that hydrogen refueling is safe for consumer use, the risk to personnel and bystanders must be quantified and minimized to an acceptable level. Such a task requires strong confidence in the safety performance of high pressure hydrogen systems. Developing meaningful materials characterization and qualification methodologies in addition to enhancing understanding of performance of materials is critical to eliminating barriers to the development of safe, low-cost, high-performance high-pressure hydrogen systems for the consumer environment.

APPROACH

The Materials and Components Compatibility project leverages decades of experience in high-pressure hydrogen systems, well-developed industry partnerships, world class technical expertise, and unique experimental equipment to focus on three critical activities: 1) optimize materials characterization methodologies, 2) generate critical hydrogen compatibility data for materials to enable technology deployment, and 3) provide international leadership by assembling and maintaining a technical reference that is populated with vetted data and includes a technical assessment of the data and its application.

RESULTS

Completed test matrix to evaluate correction method applied to fatigue crack growth relationships for two steels at three pressures

Hydrogen embrittlement has a great impact on the durability of metal components exposed to high-pressure hydrogen gas. Fatigue testing in high-pressure hydrogen helps ascertain material performance properties which inform the design of many parts and components used in high-pressure hydrogen service (i.e., ASME Article KD-10). The current fatigue crack growth test procedures in Article KD-10 are impractical, since test durations can be excessive at the prescribed load-cycle frequency (0.1 Hz). The test method can be improved to balance efficiency and data reliability. In FY 2011 and FY 2012 a modified test method was proposed and a validation test matrix was defined. The FY 2013 results represent completion of the validation test matrix consisting of two common pressure vessel steels in a range of hydrogen gas pressures. Table 1 provides a summary of the testing completed in FY 2013.

Figure 1 shows results from testing on the high-strength steel (34CrMo4) carried out following the matrix in Table 1. The results suggest that a possible test method modification could be implemented which would increase the efficiency of the test by applying a load-cycle frequency of 10 Hz (higher frequency = shorter test time). In concert, a correction factor to this high-rate data is determined by measuring the crack growth rate (da/dN) as a function of frequency at selected stress-intensity factor levels. There is a limiting frequency for the upper-bound da/dN, for example in the top graph of Figure 1 the 10-MPa pressure test reaches its upper-bound da/dN at approximately 1 Hz for both stress-intensity factors. The correction applied to the higher frequency test could be based upon the upper-bound da/dN measured at the limiting frequency. For the higher-strength 34CrMo4 steel, the correction factor applied to the high-frequency test data is dependent upon the pressure and the stress-intensity factor (delta K).

Similar to the high strength steels, the crack growth rate for the lower-strength SA372 Gr. J steel reaches an upper bound da/dN which is also defined by a limiting load cycle frequency (Figure 2). However, unlike the high-strength steel, the upper bound da/dN for the low-strength steel is similar for both 45 MPa and 100 MPa at both stress-intensity factors, which suggests that there is less sensitivity to hydrogen pressure. A modification to the test method may be the definition of a limiting test pressure in addition to the limiting frequency. These boundary conditions could enhance the efficiency of the test while ensuring that testing appropriately characterizes the material performance.

TABLE 1. Results of FY 2013 Testing

Steel	S_u (MPa)	H_2 Pressure (MPa)	Test Frequency (Hz)	Load Ratio	Status
SA372 Gr. J	890	10	10	0.1	Complete FY 2012-2013
		10	Variable	0.1	Complete FY 2012-2013
		45	10	0.1	Complete FY 2011-2012
		45	Variable	0.1	Complete FY 2011-2012
		100	10	0.1	In progress
		100	Variable	0.1	Complete FY 2012-2013
34CrMo4	1045	10	10	0.1	Complete FY 2012-2013
		10	Variable	0.1	Complete FY 2012-2013
		45	10	0.1	Complete FY 2012-2013
		45	Variable	0.1	Complete FY 2012-2013
		100	10	0.1	Complete FY 2012-2013
		100	Variable	0.1	Withdrawn

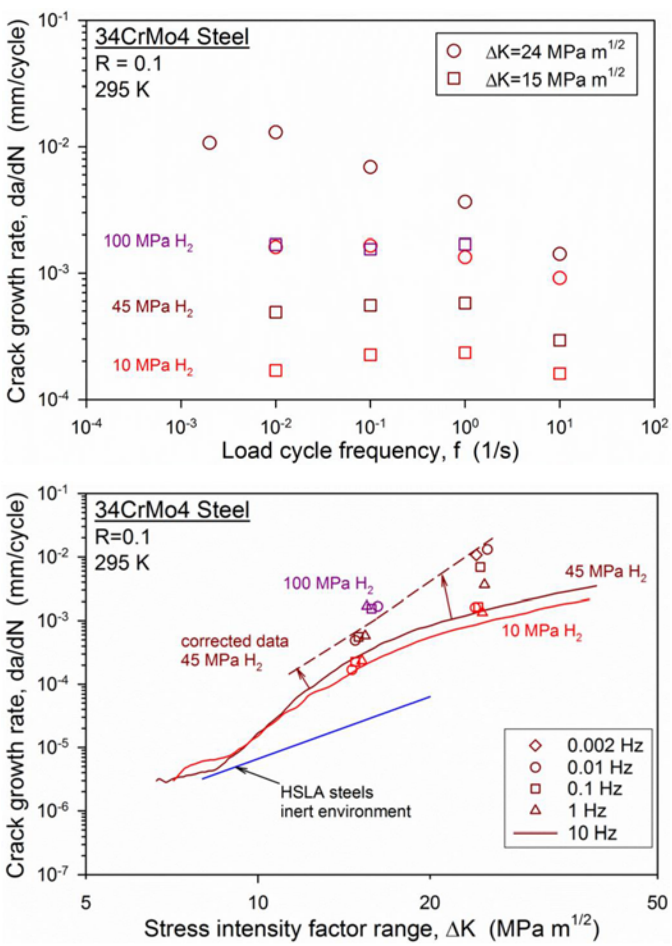

FIGURE 1. Top: summary of results for high strength steels shown as crack growth rate as a function of cycle frequency at different pressures for selected stress intensity factors. Bottom: test results for high strength steel demonstrating the validation of the correction factor applied to high-frequency data (improved efficiency).

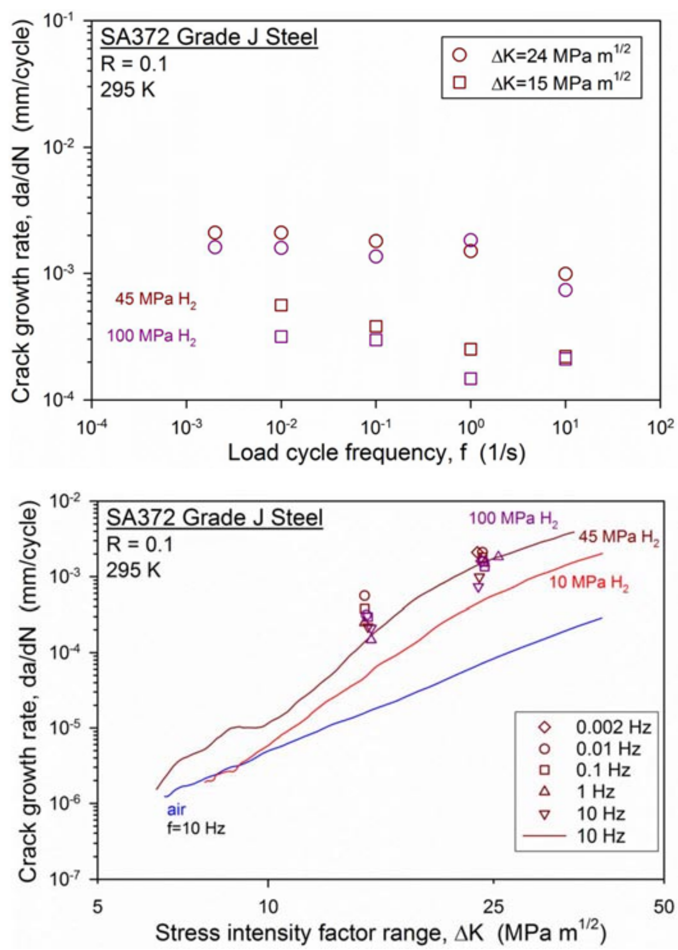

FIGURE 2. Top: summary of results for low strength steels shown as crack growth rate as a function of cycle frequency at different pressures at selected stress intensity factors. Bottom: test results for low strength steel demonstrating the validation of the correction factor applied to higher frequency testing (improved efficiency).

Investigation of welding practice for hydrogen-exposed orbital tube welds in Type 316L

While material characterization establishes safety margins for the performance of materials there are other factors which must be considered with regard to the practical use of those materials in the application. Orbital welding is a popular and well trusted method for joining tubing. This process is often automated and highly repeatable. All welding practices, regardless of automation, introduce microstructure alterations and residual stress to the material in and around the weld location. This activity investigated the performance of orbital tube welds with respect to non-welded tubes and traditional coupon samples from bar stock. Figure 3 shows the results of the testing. Weld A was produced by the industry partner and Weld B was created at Sandia using commercial welding equipment. Although the data set from these experiments is limited, the results suggest that welding practice can affect resistance to hydrogen embrittlement. Weld A retained ductility similar to the non-welded sample while Weld B shows a greater effect of hydrogen. Despite the manifestation of hydrogen embrittlement (reduced tensile ductility) in both welds, the absolute ductility values remain quite high (a key factor in safety of the tubing). The correlation of nickel content with greater resistance to hydrogen embrittlement has been substantiated with the results of tensile tests on the tubing and the orbital welded specimens compared to bar material as shown in Figure 4. The unexpected performance of Weld B is under investigation.

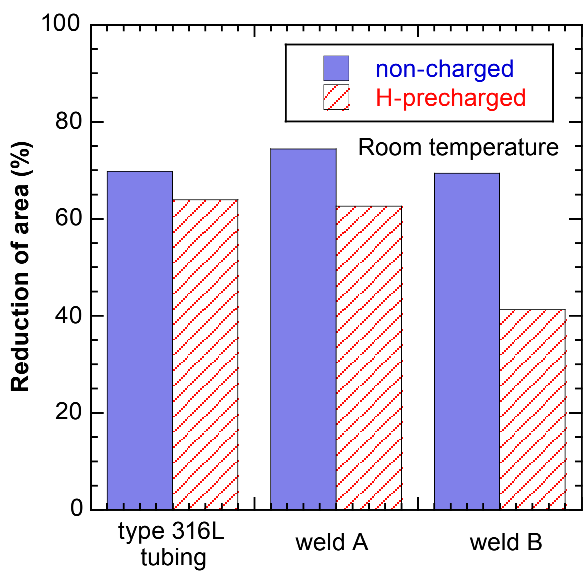

FIGURE 3. Results of weld practices upon the performance of welds in Type 316L tubing. The Type 316L tubing is non-welded, Weld A was produced by the industrial partner and Weld B was produced at Sandia using commercial welding equipment.

Investigation of temperature on hydrogen-exposed orbital tube welds

Another consideration with regard to the performance of welds in high-pressure hydrogen environments is the effect of low service temperatures. It is well known that hydrogen embrittlement of stainless steels is maximum at sub-ambient temperature, thus this environmental variable must be explored for stainless steel weld performance as well. Figure 5 shows that hydrogen-affected ductility at sub-ambient temperature is similar for the orbital tube welds compared to the non-welded tube and bar stock.

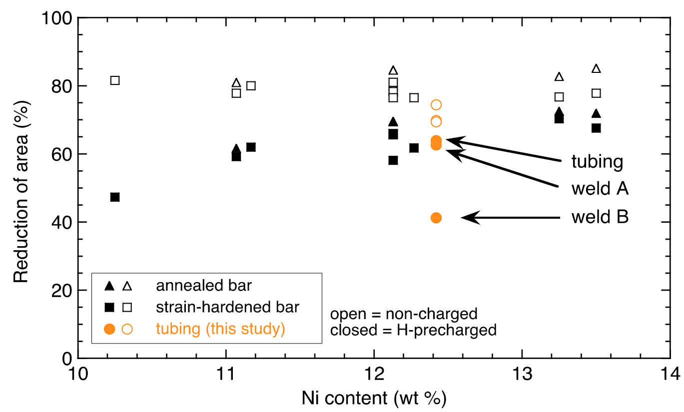

FIGURE 4. The results of the tubing and orbital tube welds is consistent with the correlation of nickel content with greater resistance to hydrogen embrittlement.

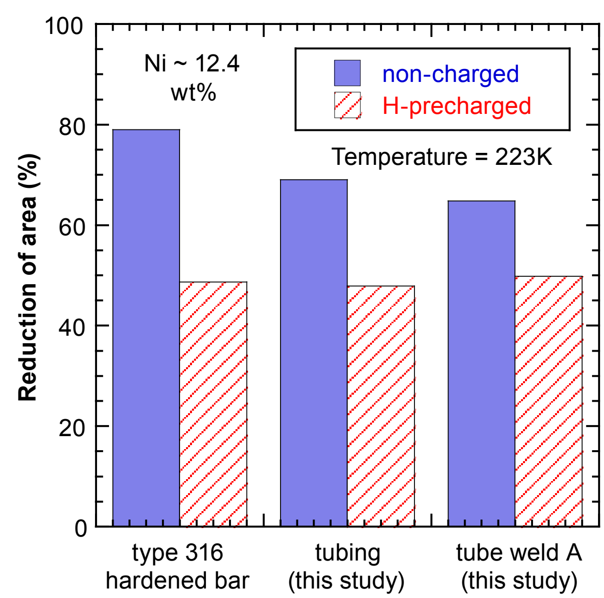

FIGURE 5. Tensile ductility results for 316 stainless steel bar stock, tubing and welded tubing at low temperatures.

Updates to the Technical Reference for Hydrogen Compatibility of Materials

The White House, in collaboration with the Department of Energy, initiated a project to publish energy data, called OpenEI. The OpenEI initiative hopes to leverage the success of publication of U.S. Geological Survey data that spawned the mobile GPS industry. In support of this initiative, Sandia posted two sets of information to the OpenEI website (en.openei.org/wiki/Gateway:Hydrogen). The Technical Reference for Hydrogen Compatibility of Materials was updated as a full public report and made available through the website (www.sandia.gov/matlsTechRef) and the OpenEI (en.openei.org/wiki/Gateway:Hydrogen). In addition, new datasets for fatigue crack growth in gaseous hydrogen not yet featured in the Technical Reference were included in the OpenEI database.

International Institute for Carbon-Neutral Energy Research (I2CNER)

Sandia provides leadership for the Hydrogen Structural Materials Division within the I2CNER. This research division in I2CNER is focused on understanding fundamental mechanisms of hydrogen embrittlement and developing new materials for hydrogen service—two areas that are critical to the Safety, Codes and Standards sub-program. Support of this task will enable Brian Somerday (division lead principal investigator) to interface the research performed in I2CNER with the DOE Fuel Cell Technologies Office, providing a conduit for research information between this international institute and the Fuel Cell Technologies Office.

Brian Somerday attended the I2CNER Annual Symposium at Kyushu University, Japan, in January 2013, presenting an overview of research progress in the Hydrogen Structural Materials Division. In addition, he served as a session chair at the HYDROGENIUS & I2CNER Research Symposium on Structural Materials, which featured presenters from eight different countries. Brian Somerday also met with collaborators in I2CNER, exchanging views and providing guidance on basic research that complements the applied research in the Materials Compatibility activity.

In June 2013, Brian Somerday traveled to Kyushu University for the Ministry of Education, Culture, Sports, Science, and Technology Site Visit, essentially an annual review of the Institute. As lead principal investigator, he represented the Hydrogen Structural Materials Division in the review.

National Institute of Advanced Industrial Science and Technology (AIST)

The DOE and the Ministry of Economy, Trade and Industry have coordinated R&D efforts in the area of hydrogen safety, codes, and standards. One of these coordinated activities is collaboration between AIST-Tsukuba and Sandia to develop standardized test methods for fracture threshold and fatigue crack growth measurements of steels in high-pressure hydrogen gas and to define the mechanisms of hydrogen-assisted fracture in stainless steels. An evolving project plan initiated in FY 2012 outlines the details of coordinated research between AIST-Tsukuba and Sandia in these two topic areas. The collaboration is expected to involve reciprocal visits to the U.S. and Japan.

This activity was reduced due to budget constraints. The reduction eliminated experiments on pressure vessel steels at Sandia that complement companion experiments at AIST. Brian Somerday met twice with his project-lead counterpart at AIST, once at AIST and another time at Sandia, to discuss progress on testing pressure vessel steels in hydrogen gas at AIST. Chris San Marchi visited AIST/Tsukuba for two weeks in March (expenses paid by AIST), presenting seminars at AIST and at Kyushu University (Hydrogenius). Chris San Marchi also visited Nippon Steel and Sumitomo Metals to share experience with testing in gaseous hydrogen and explore opportunity for collaboration with a steel manufacturer.

AIST-Tsukuba continued to conduct experiments on pressure vessel steels in hydrogen gas which formed the basis for discussions in project meetings hosted at Sandia throughout FY 2013. Sandia is provided test specimens from a U.S. pressure vessel steel specification for inclusion in the AIST test matrix. Dr. Bai An from AIST visited Sandia in May 2013 to continue the collaboration.

Codes and Standards Support

This project affects many codes and standards, both directly and indirectly. The following list summarizes that direct participation:

- CSA CHMC1
  - Materials testing and data application standard
  - Sandia provides leadership in technical committee and document preparation
  - Publication of Part 3 expected in 2013
- SAE J2579
  - Hydrogen vehicle fuel system standard
  - Sandia serves as U.S. technical lead on addressing hydrogen embrittlement
  - Publication expected in 2013
- ASME Article KD-10
  - Standard on high-pressure hydrogen tanks for transport and storage
  - Sandia provides data on exercising and improving materials test methods

- Reporting progress on optimizing fatigue crack growth testing to former chair of ASME Project Team on Hydrogen Tanks

CONCLUSIONS AND FUTURE DIRECTIONS

- Fatigue crack growth results for high strength steel (34CrMo4) and low-strength steel (SA372 Gr.J) in three hydrogen gas pressures suggest that test method efficiency could be improved without compromise of data reliability.
  - Future work – communicate the results of testing to ASME and support further action by the technical committee.
  - Future work – Develop validated methodology to account for fatigue crack initiation life in steel H_2 pressure vessels for consideration in ASME Article KD-10.
  - Future work – Leverage results on fatigue crack growth of pressure vessel steels in H_2 to enhance understanding of basic physics in collaboration with I2CNER.
  - Future work – Develop R&D project with industry partner(s) to evaluate and improve resistance of high-strength structural metals to H_2-assisted fracture.
  - Future work - Critically evaluate test method ("safety factor method") in CHMC1 Part 3 for qualifying materials for hydrogen service.
- Orbital tube welding practices for stainless steels may have an influence on the performance in hydrogen gas, however all welds retained significant tensile ductility. The performance of hydrogen-exposed orbital tube welds at strong sub-ambient temperature is similar to non-welded tubes and stainless steel bar stock.
  - Future work – Measure fatigue crack initiation resistance of H_2-exposed stainless steel tube welds.
  - Future work – Develop R&D program with industry partner(s) to evaluate and improve resistance of high-strength structural metals to H_2-assisted fracture.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. K. Nibur, B. Somerday, C. San Marchi, J. Foulk, M. Dadfarnia, and P. Sofronis, "The Relationship Between Crack-Tip Strain and Subcritical Cracking Thresholds for Steels in High-Pressure Hydrogen Gas", *Metallurgical and Materials Transactions A*, vol. 44A, 2013, pp. 248-269.

2. T. Michler, C. San Marchi, J. Naumann, S. Weber, M. Martin: "Hydrogen environment embrittlement of stable austenitic steels". *Int J Hydrogen Energy*, vol. 37, 2012, pp.16231-16246.

3. C. San Marchi, B. Somerday. "Technical Reference for Hydrogen Compatibility of Materials", Sandia National Laboratories Report SAND2012-7321, 2012.

4. (invited presentation) C. San Marchi, "Overview of Gaseous Hydrogen Embrittlement Testing at Sandia", Korean Society of Mechanical Engineering, Annual Fall Meeting, Special International Session on Hydrogen Effects in Materials, Chagwon, Korea, Nov. 2012.

5. (invited presentation) C. San Marchi, A. Harris, D. Dedrick, "Investigation of the Hydrogen Release Incident at the AC Transit Emeryville Facility", Korea Research Institute of Standards and Science (KRISS), Daejeon, Korea, Nov. 2012.

6. (invited presentation) C. San Marchi, "Standards for Qualifying Materials for Hydrogen Service", Korea Research Institute of Standards and Science (KRISS), Daejeon, Korea, Nov. 2012.

7. B. Somerday, K. Nibur, and C. San Marchi, "Measurement of Fatigue Crack Growth Rates for SA-372 Gr. J Steel in 100 MPa Hydrogen Gas Following Article KD-10", ASME PVP2013, Paper No. 97455, 2013, submitted.

8. B. An, H. Itouga, T. Iijima, C. San Marchi, and B. Somerday, "Hydrogen-assisted twin boundary fracture of type 304 austenitic stainless steel at low temperature investigated by scanning probe microscopy", ASME PVP2013, Paper No. 97355, 2013, submitted.

9. C. San Marchi, L. Hughes, B. Somerday, and X. Tang, "Hydrogen-Assisted Fracture of Type 316L Tubing and Orbital Welds, ASME PVP2013, Paper No. 97538, submitted.