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# Hydrogen Compatible Materials Workshop

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## ABSTRACT

This report serves as the proceedings of the Hydrogen Compatible Materials Workshop held virtually by Sandia National Laboratories on December 2-3, 2020. The purpose of the workshop was to assemble subject matter experts at Sandia and its national laboratory partners within the U.S. Department of Energy's (DOE) Hydrogen Materials Compatibility (H-Mat) Consortium with public and private stakeholders in the research, development and deployment of hydrogen technologies to discuss the topic of hydrogen compatible materials. This workshop was designed to build on past events and current research and development (R&D) efforts to develop a forward-looking vision that identifies gaps and challenges for the next decade. In particular, the workshop organizers sought to expand their understanding of hydrogen compatible materials needs for power, manufacturing and other industrial uses to enable deeper impact and widespread use of hydrogen while continuing to address open questions in hydrogen-powered transportation of concern to Original Equipment Manufacturers, hydrogen producers, materials & component suppliers and other private entities. The workshop was primarily organized as a series of panel-led discussions on the topics of hydrogen-enabled transportation, heating and power, and industrial uses. Each panel consisted of 2-3 subject matter experts who relayed their perspectives on a set of framing questions developed to facilitate discussion by the broader group of workshop participants. By the workshop's conclusion, the participants identified and prioritized a list of technical challenges for each panel topic where further R&D is warranted.

## ACKNOWLEDGEMENTS

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We also gratefully acknowledge the valuable ideas and insights contributed by the stakeholders who participated in this workshop. The willingness of these experts to share their time and knowledge has helped to identify current and emerging opportunities in hydrogen compatible materials.

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## EXECUTIVE SUMMARY

Since 2003, Sandia National Laboratories has hosted a series of workshops on Hydrogen Compatible Materials. These workshops brought together national laboratories, government agencies, codes & standards organizations and private industry to identify applications and components for which hydrogen compatible materials are relevant and data that currently existed or was missing with regard to meeting appropriate standards as well as technology needs. These workshops laid the foundation for the past decade research and development performed by U.S. national laboratories, as sponsored by DOE's Hydrogen and Fuel Cell Technologies Office (HFTO) within the Office Energy Efficiency and Renewable Energy (EERE), and other organizations.

Sandia National Laboratories and its national laboratory partners seek to revisit the topic of hydrogen compatible materials with public and private stakeholders to ensure that we develop a forward-looking vision that identifies the gaps and challenges for the next decade and beyond (e.g., heavy-duty vehicles, maritime, rail, aviation). In particular, this group aspires to apply knowledge developed over the past two decades from the transportation sector to address hydrogen compatibility questions of the power and heating sector and for industrial uses thus enabling deeper impact and widespread use of hydrogen. While doing so, the laboratories wants to ensure that its work continues to address open questions in hydrogen-powered transportation of concern to Original Equipment Manufacturers (OEMs), hydrogen producers, materials & component suppliers and other private entities.

The newest iteration of the Hydrogen Compatible Materials Workshop was held virtually by Sandia National Laboratories on December 2-3, 2020. From its inception, the purpose of this workshop was to:

- Increase industry awareness of hydrogen-materials compatibility R&D performed within the Hydrogen Materials Compatibility (H-Mat) consortium
- Assess current state-of-the-art technologies in hydrogen compatibility of materials for high-pressure gaseous hydrogen and liquid hydrogen use.
- Identify and prioritize unaddressed hydrogen-materials compatibility challenges that inhibit deployment of hydrogen-powered transportation, hydrogen-based energy conveyance and broader industrial use of hydrogen (hydrogen-natural gas blends, heating and power, steelmaking, chemical production, and other industrial processes).
- Brainstorm potential collaborative models to enable execution of projects that would provide these advances and enable technology transfer to end-use stakeholders.

To address this purpose, the workshop was organized around panel-led discussions on the topics of hydrogen-enabled **transportation, heating and power, and industrial uses**, three categories of energy consumption.

The workshop included informed panel presentations and rich discussion from the participants and panelists. Both high-level and detailed elaboration of industrial usages, practices and needs were shared. At the conclusion of each panel, a survey was conducted regarding the most common information and research gaps relevant to each topic. Participants were asked to vote for the top 3 issues of importance for each topic from their perspective. While the list of issues did not incorporate

every aspect of the discussions, the survey results provide a snapshot of some of the highest priority issues for hydrogen compatible materials research and development. The top priorities from the real-time survey of the participants within each topic are:

### **Transportation**

- Establishment and population of a common database of materials properties
- Data on material properties in cryogenic hydrogen
- Understanding similitude of different environments (i.e., electrochemical vs precharging vs in-gas) and transferability of test results
- Characterizing the performance of welds

### **Heating and Power**

- Characterizing the performance of high-strength alloys in combustion/burner equipment (e.g., nickel alloys)
- Assessing the effect of degrading impurities (e.g., hydrogen sulfide)
- Assessing corrosion effects and the synergy of such effects with hydrogen
- Stress hold in fatigue; Fatigue frequency and transferability to very low frequency

### **Industrial Uses**

- Fatigue life assessments and design methods with hydrogen
- Characterizing the performance of high-strength, pressure-containing alloys
- Understanding hydrogen-induced crack initiation/nucleation
- Characterizing the effect of hydrogen in high-temperature environments

For this list, the top 4 issues were taken from the surveys for each of the panel sessions. In addition, we removed duplication in our surveys, noting that welds were a priority in all three panel themes, but is only listed in the transportation theme. Future national lab research should reflect at least some of these areas, as well as other areas described in this report and determined from follow-on discussion with industry partners.

## ACRONYMS AND DEFINITIONS

Abbreviation	Definition
AHJ	authority having jurisdiction
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
DOE	U.S Department of Energy
EERE	Office of Energy Efficiency and Renewable Energy
EPRI	Electric Power Research Institute
GTR	Global Technical Regulations
HCM	Hydrogen Compatible Materials
H-Mat	Hydrogen-Materials Compatibility (Consortium)
HFTO	Hydrogen and Fuel Cell Technologies Office
HTHA	high temperature hydrogen attack
LCRI	Low-Carbon Resources Initiative
LH <sub>2</sub>	liquid hydrogen
NDE	non-destructive evaluation
Ni <sub>EQ</sub>	Nickel equivalent
OEM	original equipment manufacturer
PCRI	Pipeline Research Council International
R&D	research and development
RA	reduction of area
RRA	relative reduction of area
SAE	Society for Automotive Engineers
SSRT	slow strain rate testing
TBC	thermal barrier coating

## 1. WORKSHOP BACKGROUND AND PURPOSE

### 1.1. Background and History of the Hydrogen Compatible Materials Workshop

In 2003, Sandia National Laboratories hosted the Hydrogen Materials Compatibility Workshop, which brought together national laboratories, government agencies, codes & standards organizations, and private industry to define the framework and content of a Technical Reference for Materials Compatibility with Hydrogen. Breakout sessions were used to discuss the target audience for this reference, their likely needs and a potential format for the reference. Also discussed were identifying applications and components for which hydrogen compatible materials are relevant and data that currently existed or was missing with regard to meeting appropriate standards. This workshop provided insights on long-term needs for research on hydrogen compatible materials, framing objectives for proposed national laboratory research and development (R&D).

In 2010, a second iteration of this workshop produced a prioritized list of technical gaps in data & phenomenology, technology development, and codes & standards. The four highest-priority gaps and R&D pathways were determined to be:

- 1) measurement of mechanical properties of structural metals in high-pressure hydrogen gas, in particular fatigue properties (both crack initiation and crack propagation) and testing protocols for materials evaluation,
- 2) development and population of a database for properties of structural materials in hydrogen gas,
- 3) characterization of the influence of welds on hydrogen compatibility of structures,
- 4) development of high-strength, low-cost materials for long-life hydrogen service.

In 2012, Sandia partnered with the U.S. Department of Energy (DOE) in organizing a meeting on the use of polymer and composite materials in hydrogen applications. Participants identified material knowledge gaps in six different topical areas, motivated by safety, performance, and reliability concerns.

Combined, these discussions laid the foundation for the past decade of R&D performed by U.S. national laboratories, as sponsored by DOE's Hydrogen and Fuel Cell Technologies Office (HFTO) within the Office of Energy Efficiency and Renewable Energy (EERE), and other organizations. HFTO-sponsored projects at Sandia on hydrogen compatibility of materials have had significant industry impact:

- Foundational data for fatigue design curves, resulting in American Society of Mechanical Engineers (ASME) Code Case 2938 (approved December 2018) that harmonizes design, removes need for expensive testing, and leads to longer design life.
- Demonstration of Type 1 pressure vessel reliability in high cycle fatigue for hydrogen forklift trucks, paving way to broader acceptance and growth of fuel cell technology for this application.
- Understanding of fatigue crack growth rates of various American Petroleum Institute (API) pipeline grades in hydrogen, which, when combined with testing at NIST-Boulder, provided

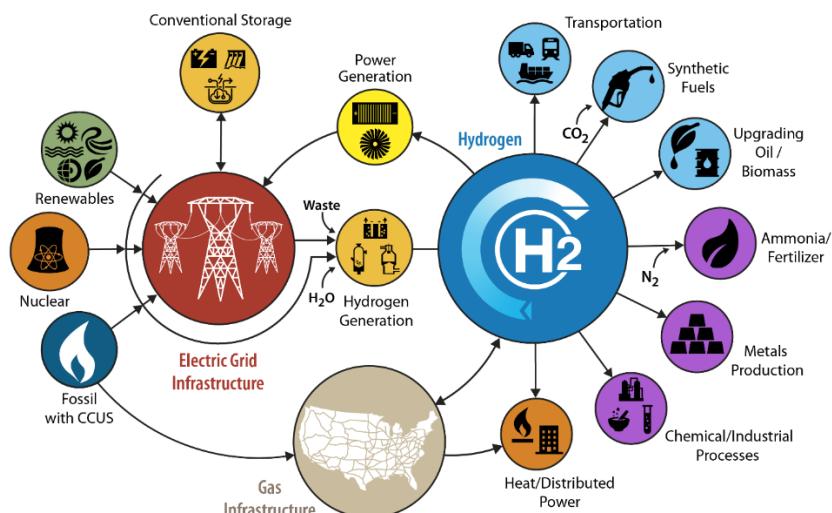
the basis for design curves accepted into ASME B31.12 Hydrogen Piping and Pipelines code for fracture mechanics-based design.

- Development of a performance-based metric for hydrogen compatibility of materials that are used in fuel systems onboard hydrogen-powered vehicles and standardized in SAE J2579.

## 1.2. H-Mat, H2@scale and next phase of HFTO-sponsored R&D

Now that hydrogen fuel cell vehicles and technology are a reality and there is growing interest in looking beyond transportation. This perspective has led to the H2@Scale initiative led by the HFTO. Figure 1 provides an overarching vision for how hydrogen can enable energy pathways across applications and sectors and realize its potential to meet existing and emerging market demands. Materials compatibility challenges are present across all energy sectors in the H2@Scale initiative. This realization led to the initiation of the Hydrogen Materials Compatibility (H-Mat) consortium. The goal of H-Mat is to provide foundational research that impacts and advances hydrogen usage. In particular, several of the more enduring issues (such as high-strength, low-cost materials and advanced protocols) have become focal thrusts within the H-Mat consortium, with the objectives of gaining a foundational understanding of hydrogen-materials interactions and degradation mechanisms, while also developing engineering solutions for high-pressure structures and technologies.

Sandia National Laboratories and its national laboratory partners within H-Mat seek to revisit the topic of hydrogen compatible materials with public and private stakeholders to ensure that we develop a forward-looking vision that identifies the gaps and challenges for the next decade and beyond (e.g., heavy-duty vehicles, maritime, rail, aviation, etc.). In particular, H-Mat aspires to apply knowledge developed over the past two decades from the transportation sector to address hydrogen compatibility questions of the power and heating sector and for industrial uses thus enabling deeper impact and widespread use of hydrogen. While doing so, H-Mat wants to ensure that its work continues to address open questions in hydrogen-powered transportation of concern to Original Equipment Manufacturers (OEMs), hydrogen producers, materials & component suppliers and other private entities.



**Figure 1: Conceptual H2@Scale vision. Hydrogen generation can derive from varied resources and serve the diverse needs of the entire energy portfolio.**

## 1.3. Workshop Purpose and Goals

From its inception, the purpose of this workshop was to:

- Increase industry awareness of hydrogen-materials compatibility R&D performed within the H-Mat consortium
- Assess current state-of-the-art technologies in hydrogen compatibility of materials for high-pressure gaseous hydrogen and liquid hydrogen use.
- Identify and prioritize unaddressed hydrogen-materials compatibility challenges that inhibit deployment of hydrogen-powered transportation, hydrogen-based energy conveyance and broader industrial use of hydrogen (hydrogen-natural gas blends, heating and power, steelmaking, chemical production, and other industrial processes).
- Brainstorm potential collaborative models to enable execution of projects that would provide these advances and enable technology transfer to end-use stakeholders.

To address this purpose, the workshop was organized around panel-led discussions on the topics of hydrogen-enabled **transportation, heating and power, and industrial uses**. These topics are loosely based on the H2@scale vision and the three categories of energy consumption.

### 1.3.1. *Framing Questions*

Each panel is comprised of subject matter experts who conveyed their perspectives on the set of framing questions listed below (in relation to the aforementioned topics) and facilitated discussion by the broader group of workshop participants.

1. What applications suffer from a lack of materials options for hydrogen use? Are there materials that could be suitable that haven't been considered or evaluated?
2. How could materials that are already used in hydrogen be improved or better characterized?
3. Where does industry lack understanding of the required metrics for materials selection in hydrogen environments?
4. What are the largest hurdles (cost, manufacturability, supply chain reliability, performance, etc.) to materials selection for hydrogen service?
5. What standards, test methods, performance metrics, and design requirements are missing to support broader implementation of hydrogen technologies?
6. Are there materials issues associated with large-scale storage of hydrogen (such as geologic storage) and the infrastructure necessary to support hydrogen utilization at scale?
7. Are there materials' advances necessary to enable broader use of cryogenic hydrogen?
8. Are there open questions about joining and welding of materials for use in hydrogen?

### 1.3.2. **Workshop Agenda**

All times listed below are Pacific Standard Time [PST]

#### Day 1 – December 2, 2020

- 6:00-6:30 am: Welcome, Select Introductions, Workshop Purpose (SAND2020-13297PE<sup>1</sup>)
- 6:30-7:15 am: Orientation of H-Mat consortium and current activities (SAND2020-13399PE<sup>1</sup>)
- 7:15-7:45 am: Discussion on Framing Questions
- 7:45-8:00 am: Break
- 8:00-9:30 am: Panel-led brainstorming session on **transportation**
  - *Panelists:*
    - Matthias Kuntz – Robert Bosch GmbH
    - Amy Ryan – Toyota Motor North America R&D
  - *Moderators:*
    - Charles (Will) James – Savannah River National Laboratory
    - Brian Kagay – Sandia National Laboratories
  - 8:00-8:30 am: Panel answers to framing questions
  - 8:30-9:30 am: Group brainstorming on R&D gaps
- 9:30-10:00 am: Day 1 review (including R&D gaps identified) and outline of Day 2 agenda

#### Day 2 – December 3, 2020

- 6:00-6:30 am: Special presentation/ Impacts of R&D on Hydrogen Compatibility of Materials (SAND2020-13398PE<sup>1</sup>)
- 6:30-8:00 am: Panel-led brainstorming session on **heat and power**
  - *Panelists:*
    - John Scheibel and Jonathan Parker – Electric Power Research Institute
    - Kang Xu – Linde
    - Hemanth Satish – TC Energy
  - *Moderators:*
    - Zhili Feng – Oak Ridge National Laboratory
    - Joseph Ronevich - Sandia National Laboratories
  - 6:30-7:00 am: Panel answers to framing questions
  - 7:00-8:00 am: Group brainstorming on R&D gaps
- 8:00-8:15 am: Break
- 8:15-9:45 am: Panel-led brainstorming session on **industrial uses**
  - *Panelists:*
    - Anders Werme - ArcelorMittal
    - Gerhard Schiroky - Swagelok
    - Neeraj Thirumalai - ExxonMobil
  - *Moderators:*
    - Kevin Simmons - Pacific Northwest National Laboratory
    - Christopher San Marchi - Sandia National Laboratories
  - 8:15-8:45 am: Panel answers to framing questions
  - 8:45-9:45 am: Group brainstorming on R&D gaps

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<sup>1</sup> All referenced “SAND” reports are public documents available as <https://osti.gov>.

- 9:45-10:15 am: Day 2 review (including R&D gaps identified) and next steps

## 1.4. Summary of opening presentations

### 1.4.1. *Welcome presentation and introduction to workshop*

To start the Hydrogen Compatible Materials (HCM) Workshop, Jon Zimmerman presented a typical categorization of world energy consumption as largely falling into three sectors: transportation, heat and power (generally residential and office use of electricity and comfort heating), and industrial uses (which includes chemical and energy usage for manufacturing). This division is reflected through the H<sub>2</sub>@Scale concept and vision for use of hydrogen to satisfy these energy needs and has been discussed at length in multiple roadmaps developed between 2017 and 2020, starting with the USDRIVE Technical Team Roadmaps for Hydrogen Production, Delivery, Storage and Codes & Standards. Themes on materials that appear within these roadmaps include:

- Codes and standards that specify material requirements and testing procedures
- Materials with resistance to hydrogen-induced fracture, fatigue and damage to avoid leakage
- Manufacturing of specialized materials and components
- Low-cost
- Adaptable to heavy-duty applications and industrial uses

Jon then relayed technical challenges present for this use due to the question of compatibility of component materials with hydrogen environments. Sandia's vision for its Hydrogen Research is to conduct foundational-to-applied research uncovering the science of materials for hydrogen production, delivery, storage and use; utilize its research to inform the safe, reliable use of hydrogen fuel cell technology; and partner with industry, codes & standards organizations, and international institutes and participate in demonstration applications to get scientific findings in the hands of practitioners. Realization of this vision is accomplished by developing state-of-the-art methods and tools to assess hydrogen compatibility of materials through discovery of the mechanisms responsible for hydrogen-materials interactions and using this understanding and these methods to inform science-based strategies to design the microstructure of metals with improved resistance to hydrogen degradation. Jon then reviewed outcomes from previous workshops, such as the development of a technical reference for materials compatible with hydrogen, high priority technical issues for which R&D on structural metals was needed (see Section 1.1), and information gaps pertaining to use of polymer and composite materials in hydrogen. He also reviewed several impacts made by Sandia National Laboratories since those workshops occurred (the last one in 2012), and the formation of the Hydrogen Materials Compatibility (H-Mat) consortium, a multi-lab partnership sponsored by the U.S. Department of Energy's (DOE's) Hydrogen and Fuel Cell Technologies Office (HFTO). Jon concluded by reviewing the Workshop's purpose, desired outcomes, agenda, and topics for panel-led discussion. Slides presented can be found in SAND2020-13297PE.

### **1.4.2. HFTO opening remarks**

HFTO Hydrogen Technologies Program Manager Ned Stetson stressed the importance of the issue of materials compatibility to HFTO's entire portfolio of projects in hydrogen production, storage and utilization. Ned commented on the broad interest in hydrogen, not only for transportation but also for industrial applications, e.g., steelmaking, and other activities that require large-scale production, storage and delivery of hydrogen. Work in HCM is critical for safe use of materials and components, and Ned emphasized the importance of getting the information and understanding developed into the hands of codes and standards communities, as well as to regulators and AHJs (authorities having jurisdiction).

HFTO Technology Manager Neha Rustagi then spoke to introduce the next presentation on the Hydrogen-Materials Compatibility (H-Mat) consortium. Neha stressed the critical role that the workshop would play in gathering input from industry stakeholders on the HCM gaps, information needed by DOE to inform their yearly funding solicitations. Particularly sought are areas of research and development that could lead to improvements in (hydrogen technology) component cost and durability.

### **1.4.3. Discussion of framing questions**

A short discussion was led by Jon Zimmerman regarding the completeness of this set of framing questions. Some additional questions and comments that emerged from this discussion included:

- Are there methods for enhancing the compatibility of materials or components with hydrogen environments, e.g., in-line coatings?
- How do we optimize materials selection decisions? Should long-term value be used? How to ensure reliability over long periods of time? How do we baseline initial quality?
- Aside from structural materials, what are the effects on reliability of materials used in measurement and control (probes, meters, T / P sensors, etc.)?
- What is the impact of changing industrial processes to enable use of hydrogen?
- What about applications that use advanced manufacturing techniques? What is the effect of using hydrogen on such materials and systems?
- What are the differences between hydrogen precharging and testing in air versus in gas (*in situ*) testing? Are different mechanisms of embrittlement/degradation active, i.e., trapping phenomena (for precharging) versus diffusion phenomena (for in gas testing)?
- What are the effects of impurities, i.e., gas mixtures, on hydrogen embrittlement and fatigue behavior? [In the Teams Meeting chat, it was noted that one of the challenges with impurities is that every source has different impurities, which makes drawing broad conclusions difficult.]

- For existing piping and pipelines, especially given that they have been exposed to various threats over their service, how does hydrogen blending and transport affect the reliability?
  - With regard to hydrogen blending, do we have confidence in extrapolating pure-hydrogen or hydrogen-in-inert derived data to likely use cases that involve bulk mixtures of hydrogen and natural gas, or hydrogen in other fuel gases (e.g., syngas)?
- Are there any cross-sector initiatives to enable widespread hydrogen usage? For example, are geologic storage solutions for combustion being considered for transportation use?
  - Storage has a huge capital cost associated with it; can we increase capacity factor of storage by diversifying the applications using the storage.
- What is the effect of weld defects on hydrogen enhanced fatigue initiation?
- What are the problems/challenges that you are seeing in regard to liquid hydrogen usage, in both metals and polymers?
- What about corrosion and corrosive environments? Is this an issue for diffusion of hydrogen?

#### **1.4.4. *Special presentation: R&D for Hydrogen Compatibility of Materials***

On Day 1, Joe Ronevich and Chris San Marchi presented Sandia's current portfolio for R&D on hydrogen compatibility of materials, and executed through its projects in Safety, Codes and Standards, and H-Mat. Slides presented can be found in SAND2020-13399PE. Chris started by reviewing Sandia's history of research conducted on hydrogen-materials interactions, including projects from the early 2000's and participation in codes and standards committees from the ASME and SAE organizations. He then explained Sandia's framework for understanding hydrogen effects on materials, which requires a combination of (i) environment (i.e., gas composition, temperature, presence of impurities), (ii) materials (i.e., composition, microstructure, defect content) and (iii) mechanics (i.e., loading) in order to activate the hydrogen embrittlement phenomenon. Chris then explained the goal of the H-Mat consortium to integrate experimental and computational methods to understand the mechanisms of material response under hydrogen exposure.

Joe discussed several of the H-Mat tasks (i.e., sub-projects) currently underway:

- Identification of high-strength ferritic steels that have improved fracture resistance over existing commercial options
- Development of atom- to engineering-scale models to predict crack nucleation and determination of how to integrate this prediction into a design strategy
- Determination of how hydrogen affects deformation and damage accumulation in austenitic stainless steels (e.g., 304L, 316L)
- Critical assessment of hydrogen effects at cryogenic temperatures
- Identification of the characteristics of polymers that contribute to hydrogen-induced damage and loss of performance

Joe also spoke of H-Mat partner projects that began in fiscal year 2020, led by collaborators at Clemson University, Colorado School of Mines, Hy-Performance Materials Testing LLC, Massachusetts

Institute of Technology & Harvard University, University of Alabama & Colorado State University, and University of Illinois at Urbana-Champaign. He also mentioned the new multi-partner project, HyBlend, with the goal of assessing the technical barriers and value proposition to blending hydrogen in natural gas pipelines.

Joe then spoke of several of the sub-projects within Sandia's work on Safety, Codes and Standards, including

- advancing test methods to evaluate the performance of welds in hydrogen,
- development of a 'universal' empirical relationship for fatigue crack growth and incorporation of this relationship into ASME Code Case 2938,
- demonstrating the opportunity for 'life extension' of components through assessment of service environment (i.e., additional life predicted due to a more realistic estimate of service pressure range).

Several topics of interest were raised during the presentation, including:

- Method(s) used by Sandia for residual stress measurement and clarification on whether/how to include residual stresses
- Differentiating welds in ferritic steels, as compared to austenitic steels
- Modifications to Code Case 2938 for low pressure hydrogen (i.e., < 40 MPa)

Regarding welding residual stresses, Sandia's focus has been to characterize the fatigue crack growth behavior inherent to the materials tested, which requires removal of the effect of residual stresses on fatigue crack growth rate data. In design and construction, those residual stresses are important and should be considered in the analysis of a given component or structure (since the residual stresses in the laboratory will be different from the residual stresses in the field). Thus, the characterization of a weld material is not synonymous with characterization of a welded component, as details of geometry/design affect the latter.

#### **1.4.5. *Special presentation: Impacts of R&D on Hydrogen Compatibility of Materials***

At the start of Day 2, Chris San Marchi and Joe Ronevich presented a summary of the impacts that Sandia has had with its R&D on hydrogen compatibility of materials. Slides presented can be found in SAND2020-13398PE. One such example is the creation of information resources for the stakeholder community. These resources include

- the current and past workshops,
- the Technical Reference on HCM (<https://www.sandia.gov/matlsTechRef/>),
- a GRANTA-based technical database for HCM (located at <https://granta-mi.sandia.gov>),
- an annual study group on materials testing and qualification for hydrogen service, and
- presentations at the ASME PVP Division Annual Conference.

One outcome from Sandia R&D has been to establish (publish) data for fatigue of pressure vessel steels, enabling ASME code-stamped vessels for hydrogen service at pressure of 1000 bar. Another has been full-scale testing of pressure vessels used for fuel cell forklift systems, examining the integrity of such tanks over an extensive number of cycles. Sandia has performed investigations on welds and heat affected zones of pipeline steels to separate the intrinsic behavior of the weld metal with regard to fatigue crack growth rate and fracture resistance from the effects that are due to residual stresses. Sandia has also performed a systematic study of the role of trace oxygen impurities and the ability to retard hydrogen-assisted fatigue by passivating hydrogen-exposed surfaces.

Sandia has made significant contributions and demonstrated leadership in codes and standards by establishing science-based test methodologies consistent with the requirements of applications. Work at Sandia has examined both performance-based methods and design-based methods. Indeed, Sandia staff see the national laboratory role as responsible for developing and deploying foundational scientific frameworks to both establish and evaluate different methods. One such example is a performance-based method implemented in SAE J2579 for evaluation of hydrogen-assisted fatigue in metals used in high-pressure vehicle fuel systems. Another is a design-based method and the development of master design curves (published in ASME Code Case 2938) that can be used in place of hydrogen fatigue testing for SA-372 and SA-723 pressure vessel steels. Incorporation of a pressure-dependent term in those curves enable extrapolation of this design information to low pressure applications as well, although this pressure-dependent term has not been accepted into the code at the time of publication of this report. Overall, Sandia has made significant contributions to ASME Boiler and Pressure Vessel Code (Article KD-10 and Code Case 2938), ASME B31.12 code of hydrogen piping and pipelines, SAE J2579 and various CSA codes (CHMC1, CHMC2 and HPIT1).

## 2. PANEL 1: TRANSPORTATION

### 2.1. Matthias Kuntz (Robert Bosch GmbH)

A primary area of concern and focus is cost reduction of materials and components, as many of the components are already in vehicles on the road. This reduction can occur through three means:

- 1 scaling,
- 2 design changes and
- 3 use of low-cost materials.

Low-cost materials refer – for the transportation application – primarily to low-alloyed steels. Limited data are available for such steels, so one critical need is that of more data, particularly for higher-strength steels, i.e., strength  $> 1,000$  MPa. Bainitic steels are candidates for more thorough consideration.

Another question to consider is whether current tests reflect real conditions in transportation? SSRT (slow strain rate testing) and evaluation of relative reduction of area evaluate plastic deformation in the absence of intrinsic protective surfaces (i.e., parts in service may have surface coatings that impact deformation behavior, but this is not represented by laboratory specimens). Also, components are designed assuming no plastic deformation nor in-service cracking during operation. Thus, the concern is whether the results from such tests (and measured variables such as RA) are adequate, representative and useful and/or whether the limited deformation assumed in design should be considered as more representative of real conditions.

A third question to consider is the type of charging (accelerated hydrogen exposure and absorption prior to mechanical testing) and the mechanisms relevant to hydrogen transport and material deformation that result. Scientific literature has many examples of electrochemical charging and (high temperature and pressure) gaseous charging; it is not clear that same mechanisms are active as during gas exposure over long times, i.e., real conditions. Thus, it is not conclusive that electrochemical charging is an adequate substitute for long-time exposure. Also relevant to testing is the desire for short-time tests that reflect long-time behavior; the design of such tests is uncertain, i.e., how to ensure that the relationship between test time and real conditions is well-understood.

A final question to consider is how to deal with component design concepts? In particular, can a factor be determined (formulated) for fatigue that can be applied based on pressure, temperature and other known variables to compensate for yield and other more complex behavior? These questions articulate a need for hydrogen design guide that can provide prescribed safety margins to take such complexities into account.

### 2.2. Amy Ryan (Toyota Motor North America R&D)

Global sales of fuel cell vehicles necessitated government certification in each country prior to the adoption of Global Technical Regulations (GTRs). With the creation of the GTR, there is a mutual recognition such that certification in one country allowed automakers to sell in multiple countries. The GTR13 provides requirements for the integrity of compressed hydrogen motor vehicle fuel systems and include procedures on pressure cycling tests, burst tests, permeation tests and bonfire tests. However, material requirements are not included in the GTR so OEMs must adhere to the national standards of the markets in which they wish to sell.

There are several metals used in the Toyota Mirai's compressed hydrogen storage system: stainless steel 316L is used in high-pressure piping; aluminum alloy 6061 is used in the valve body, end boss and high-pressure regulator. Since there are no material requirements in the GTR, industry standards on the metals allowed to be used, and the requirements are specified country-by-country. For example, in Japan, A6061 requires Pb and Bi content of  $\leq 0.01\%$  each; 316 must satisfy RA  $\geq 75\%$  and Ni<sub>EQ</sub>  $\geq 28.5\%$ , whereas in Europe (EU), materials must meet ISO 11114-1 and 11114-4, and in the USA and Canada, no regulations are specified, leaving these decisions to manufacturers. In an attempt to harmonize requirements more closely, the GTR13 phase 2 project is looking to adopt performance-based test metrics consistent with the requirements of fuel cell vehicles, which were created by material experts and led by Sandia National Labs.

One such material that is being evaluated under these new proposed test methods is aluminum alloy 6110, already used within a vehicle's suspension arm. Toyota is investigating its potential to replace 6061 in valve body or end boss. For A6110, SSRT at room and low temperature in hydrogen shows similar strength and deformation behavior as in air, indicating a lack of a hydrogen embrittlement effect. Fatigue life tests have not yet been performed for this material but testing materials via the proposed tests allow OEMs to expand their list of available metals for high pressure hydrogen use.

While the development of harmonized, performance-based tests metrics by Sandia and others is appreciated, the desire from OEMs in the longer-term is to develop practical tests for evaluating new materials (i.e., days, not months) that are capable of being performed at commercial labs without the need for expensive, specialized equipment. There is a desire to avoid tests that cannot be done in a relatively short period of time and/or are high cost for automotive and component manufacturers due to the complexities of testing at high hydrogen pressures. Industry is seeking tests that are simple, repeatable, and practical. Furthermore, a public repository of test results from metals that have undergone the proposed SSRT and FLT would be valuable, such that OEMs can select materials knowing their performance characteristics and take advantage of testing that has already been performed. As carbon reduction remains a global effort, hydrogen applications are being broadened, from heavy-duty trucks to stationary power systems, and Toyota believes understanding material performance and selecting the right materials will be a key to their proliferation.

## 2.3. Discussion

Following the panel presentations, panelists and workshop attendees participated in a discussion moderated by Charles (Will) James of Savannah River National Laboratory and Brian Kagay of Sandia National Laboratories.

### Discussion Summary:

Comments and questions were raised regarding material testing and test facilities. It was pointed out that fatigue tests detailed in SAE J2579, which are being proposed for use in UN GTR no. 13, provide an alternative to SSRT tests that use RRA as a metric. Also mentioned was that some equipment manufacturers see SAE tests as not practical, taking specialized equipment to conduct and months to execute. The desire is for the stakeholder community to have data that enables simply estimated “knock-down” factors, i.e., a design factor or safety factor to account for hydrogen’s influence on strength or other design property for a given material operating condition. It was mentioned that a DOE-sponsored effort at the Colorado School of Mines is developing accelerated test methodologies and a test bed model to provide guidance on component life based on key material parameters (for use in ASME guidelines).

Regarding test facilities, national laboratory partnership is generally best targeted toward joint R&D projects due to limited resources. In general, the national laboratories are not for hire except in circumstances where research and development questions are being investigated, and work scope aligns with DOE-designated missions. Looking globally, capabilities for high-pressure testing in hydrogen are also limited in Europe and Asia. Commercial options are limited; some types of capabilities exist at entities such as Hy-Performance Materials Testing (e.g., low-to-high temperature, up to 13 MPa pressure) and DNV GL (e.g., high temperature and exposed to harsh environments, such as hydrogen). Demand to develop high pressure capabilities that meet SAE test guidelines is uncertain and development of such capabilities takes time (~year), whereas most contracted work has a shorted time horizon (turnaround in a 3-month timespan). It was suggested that industry may need to invest in these and other commercial labs to develop capabilities for testing in hydrogen, as surrogate tests that bypass the use of high-pressure hydrogen may not reach consensus.

Another raised question was whether existing infrastructure can be leveraged and adapted for use with hydrogen rather than going through the expense of development of new materials and design & fabrication of new components? With regards to transportation and hydrogen fuel cell vehicles, i.e., equipment used within a vehicle or other mobility applications, it was commented that existing infrastructure would be inappropriate from a materials compatibility perspective. For considerations of transport of hydrogen itself, i.e., pipelines, that discussion was deferred to the Heat and Power panel.

Comments and questions were raised around larger/heavy-duty applications and the pros and cons of moving from gaseous hydrogen to liquid hydrogen (LH2). LH2 is anticipated to be the dominant fuel type for heavy-duty vehicles, including ground-based vehicles (i.e., buses, tractor-trailers), marine vessels, and locomotives. This also extends to non-vehicle uses in these application areas, e.g., maritime. Issues identified for LH2 usage include:

- temperature cycling and the effect of thermal history,

- whether alternative, unconventional materials can be used to gain a cost benefit (e.g., Nitronic steels instead of 300-series),
- storage under cryo-compressed conditions (low temperature, high pressure), and
- investment needed for liquefaction plants.

The discussion expanded to discuss alternative forms of hydrogen, i.e., hydrogen carriers such as ammonia and other liquid chemicals, to provide a solution for easier and less costly storage and transport of hydrogen. It was commented that development of hydrogen carriers is of interest to the industrial community, and there is ongoing research on such carrier materials in DOE's HyMARC, an Energy Material Network, similar to H-Mat, but focused on hydrogen storage materials and technologies.

To conclude the discussion, gaps for materials compatibility issues related to transportation were identified as:

- Understanding how hydrogen precharged materials – whether infused with hydrogen electrochemically or thermally – compares with gas-exposed materials, standardizing what testing means and determining ways to interpret and compare the results from different types of tests.
- Effects of “real” surfaces, where adsorption may be affected by coatings or other surface chemicals, as compared to pristine laboratory conditions. This includes effects of machining as well as surface treatments.
- Defect initiation: we know what happens if we have a crack, but what about components in vehicles where initiation/incubation is the larger concern, how long can cracks take to develop?
- How to translate high-frequency fatigue testing results to relevant, realistic information for long-period fatigue conditions? Does high-frequency testing produce excess conservatism?
- Very low temperature (cryogenic, LH<sub>2</sub>), high pressure behavior of materials
- Characterization of new materials (e.g., A6110)/candidate materials that can have superior performance and/or lower cost
- Needs around design factors (simple factors that account for temperature and pressure conditions in design) – engineering needs to make the science accessible, engineering tools
- Effect of hold time during stress/pressure cycling – impact on subcritical crack growth rate or creep effects that decrease crack growth rate – dependent on material system and environmental conditions.
- Consideration of low-density materials and their compatibility with hydrogen environments.
- There are limited data due to the cost of cycling and the manufacturability of type III hydrogen vessels (thin-walled metal liners), especially for cryogenic service. Questions remain about autofrettage, joining dissimilar metals, and combined thermal and pressure fatigue.
- Look farther out and develop active/adaptive/self-healing materials to combat damage (i.e., crack formation). New project by Clemson University on self-healing hoses through H-Mat is one example.
- Understanding the intersection of material manufacturability and its compatibility with hydrogen. This includes easier methods for testing or predicting the performance of welds.

- Improvements to CHMC1/CHMC2 that may be needed to address pressure regime concerns.

A survey was conducted regarding the most common topics that were noted in the discussion above, with participants asked to vote for the top 3 topics of importance from their perspective. Voting results are provided in Table 1. Due to the nature of a virtual meeting, an active brainstorming exercise was not attempted. The topics in Table 1 were identified by the organizers.

**Table 1: Survey results for topics on hydrogen use in Transportation**

<i>Topic</i>	<i>Votes</i>
Common database of materials properties	17
Materials properties in cryogenic hydrogen	16
Similitude of different environments (electrochemical vs precharging vs in-gas) and transferability of test results	13
Performance of welds (austenitic on vehicles and for refueling station piping)	10
Master curve development for fatigue life (analog of ASME CC)	9
Guidance on knockdown factors for design	8
Performance of soft materials (polymers for sealing and other applications)	7
Guidance on pressure (to facilitate testing)	7
Reduce cost and access to testing	7
Composites for cryogenic applications	2
Self-healing materials	2

### **3. PANEL 2: HEATING AND POWER**

#### **3.1. John Scheibel and Jonathan Parker (Electric Power Research Institute)**

The Low-Carbon Resources Initiative (LCRI) is a five-year, focused R&D commitment to develop the pathways to advance low-carbon technologies for large-scale deployment. Its goal is to enable a risk-informed understanding of options and technologies that enable decarbonization through global partnerships and demonstrations, as well as applied engineering. LCRI brings together a host of industry stakeholders and sponsors. LCRI is organized through a number of technical sub-committees, including one on power generation. Research focus areas include materials properties, fabrication technologies, long-term degradation during service, repair methodologies, life management and technology transfer.

Within power generation, gas turbines are long-lived technologies that are still in operation today and underpin the reliability of electricity delivery systems. A range of materials are used in turbines for power generation, including equiaxed, directionally solidified, and single crystal nickel alloys and ceramic matrix composites. The impact of hydrogen is unknown for these materials and equipment. LCRI is looking at long duration, i.e., 4-5 years under high temperature and high moisture conditions induced by steam injection. Current work has been in advanced methods such as additive manufacturing. Turbine blades often have thermal barrier coatings that exhibit failure by delamination due to heat loading. Also of concern is thermomechanical fatigue, a phenomenon observed by gas turbine operators.

As we move from natural gas to hydrogen, potential impacts and areas of concern include:

- New combustion designs shift heat loads causing localized overheating and more cyclic driven damage
- Higher moisture content gas increases heat transfer rates resulting in accelerated creep damage
- OEMs are anticipated to recommend reduced Turbine Inlet Temperature, effectively derating MW output
- Possible maintenance factor adjustments impacting operating interval
- Possible secondary impacts on thermal barrier coatings (TBC), such as debonding, due to combination of hydrogen and heat loading
- Extensive use of OEM proprietary alloys and service agreements with no code oversight
- Durability of turbines due to impurities
- Secondary impacts on thermal barrier coatings, e.g., debonding.
- In-service/long-term degradation
- Thermomechanical fatigue

### **3.2. Kang Xu (Linde)**

Of concern are “non-compatible” materials, i.e., high specific strength (ratio of yield strength to density) materials used in applications such as turbomachinery that are known to have significant compatibility issues with hydrogen, for example Ti-based alloys. While some anecdotal information exists regarding use of such materials in cryogenic hydrogen, further research is needed to identify better potential alloys, to identify impurities that inhibit the hydrogen embrittlement effect in Ti alloys, to define safe operating windows and boundary conditions for use of such metals in hydrogen, and to develop mitigation methods for safe use of these metals in hydrogen.

Regarding conventional materials used in industrial gas operations (e.g., austenitic stainless steels), there are subtleties that can improve reliability and improve fabrication cost of equipment. One example includes cold working, where improved properties can be achieved through techniques such as manufacturing of cold stretched vessels and enhanced fatigue strengths through severely cold worked 301-type stainless steel. Cold stretched stainless steel for cryogenic use is necessary but ASME doesn't allow cold worked in its standards. Research is needed to quantify the correlation between the amount of cold work and material property degradation due to hydrogen exposure. Other common materials of interest for cryogenic uses include stainless steel castings, precipitation hardening alloys, high-nickel alloys (e.g., Inconel, Hastelloy). Research is also needed to expand the service condition of these, and other materials already used by industry, as these alloys exhibit satisfactory performance at low pressure, but performance at high pressure is uncertain.

There are two approaches for fatigue design in industry: (1) a fracture mechanics approach (i.e., ASME BPVC VIII.3.KD-10 and Code Case 2938), where fatigue crack growth rate  $da/dN$  is utilized in design, and (2) a fatigue life design method (e.g., BPVC VIII.2 and VIII.3.KD-3) where stress-life (S-N) curves are used in design. The fracture mechanics approach tends to underpredict fatigue life by a significant margin (overly conservative) and more data are needed to improve its fidelity. The fatigue life design method has been successfully implemented for hydrogen cyclic vessels exposed to lower stresses but has built-in conservatisms in its design curves. Research is needed to bridge these two approaches, specifically to understand the processes of crack nucleation and initiation, to take initiation life into account to reduce unnecessary conservatisms, and to identify the limits of the fatigue life design by comparing the S-N curves in hydrogen and air.

Additional materials challenges exist in hydrogen production, such as metal dusting and high temperature hydrogen attack (HTHA). Metal dusting is a carburization process that occurs in alloys at elevated temperatures; no engineering materials are truly resistant, and it represents a strong bottleneck in process design. Coating technology has been used to address this phenomenon, but it has its own limitations. For HTHA, research is needed to establish a correlation between materials – including welds – hydrogen pressure and temperature.

### **3.3. Hemanth Satis (TC Energy, PCRI)**

The Pipeline Research Council International (PCRI) is a consortium of pipeline companies where design committees are formed, and resources are combined to address identified research areas.

Injection of hydrogen into natural gas pipeline systems is being considered to reduce carbon intensity. Several areas of interest and challenges that need to be addressed to support this injection are:

- The effect of hydrogen on materials used in pipelines, gas turbines, gas engines and turbomachinery. This is of particular concern for legacy pipelines and vintage materials where construction dates back to the 1940's.
- The effect of hydrogen on soft materials used in seals and other components.
- Determining the long-term effects of hydrogen injection.
- Determining how hydrogen affects safety with respect to area classification? When hydrogen comes into other class equipment, does it change their classification?
- Hydrogen 'leakage' into electrical equipment: are there material-specific effects?

### **3.4. Discussion**

Following the panel presentations, panelists and workshop attendees participated in a discussion moderated by Zhili Feng of Oak Ridge National Laboratory and Joe Ronevich of Sandia National Laboratories.

#### **Discussion Summary:**

Understanding how hydrogen interacts with the large assortment of both conventional and proprietary materials used in heating and power systems is needed. This applies to Ni-based alloys, Ti-based alloys, the use of thermal barrier coatings (TBCs), other high strength alloys, lightweight aluminum alloys, Co-based steels, and high-strength austenitic stainless steels (e.g., Nitronic-50, also called XM-19). High temperature material compatibility with hydrogen is of interest. Machinery operators have a good understanding of what materials they're using but are in need of data and understanding for their interaction with hydrogen over the long-term. This understanding is critical; for example, in Ti alloys, hydride formation can lead to catastrophic embrittlement when the alloys are exposed to hydrogen and stress, resulting in unacceptably high risks for use of common Ti-alloys in hydrogen service. However, there may be a 'window' of alloy content and service conditions in which hydride formation would not necessarily occur and some Ti-alloys could be utilized. More broadly, high-strength alloys are needed, and materials discovery research should be pursued to identify new alloys, including alternative steels, compatible with hydrogen.

Specific questions and concerns exist around how hydrogen enters a material, i.e., the mechanisms of adsorption, as well as its behavior at both surfaces and interfaces including cooling holes and other features. This is particularly relevant for precipitation-hardened alloys where multiple phases exist, and the rates of hydrogen adsorption and diffusion may vary. This latter issue is also especially relevant when TBCs are used. Research is also needed for soft materials used in seals, gaskets and other components, e.g., explosive decompression of O-rings.

While some of these materials offer unique functionality needed for heating and power equipment, certification of them in hydrogen environments – or the development of variants suitable for such environments – may introduce new costs that make conventional choices (e.g., 316L) cheaper in the short-term. Repurposing the entire gas distribution system dedicated to hydrogen technology may cost trillions of dollars; therefore, reusing the current gas line infrastructure can be of great value.

Interaction with hydrogen also leads to more general consideration of the corrosion resistance of materials when multiple conditions are present, i.e., impurities due to a heterogeneous gas environment, high temperature, and high pressure. The combined effect of corrosion (due to the purposeful environment exposed to the material) and impurities also needs to be studied, as does mitigation strategies such as cathodic protection. The creation of a database with this corrosion and impurity information would be of great value, i.e., a resource where the reduction in life due to hydrogen exposure and other factors (i.e., corrosion) is quantified.

More information is needed regarding the loading and boundary conditions that heating and power applications place on materials exposed to corrosive and hydrogen environments. It is not clear how to define the most relevant tests that reflect in-service conditions, whether multiaxial stress evaluation is needed, or if the boundary conditions are understood properly? In the pipeline application both fatigue and fracture are important, but is one dominant over the other? One such concern was raised for fatigue/cyclic testing where the frequency of 1 Hz has been used to optimize testing efficiency, whereas real applications may involve lower frequencies of loading. It was suggested that to study the response at very low frequencies and see if at low frequencies the fatigue crack growth rate would decrease and whether creep effects might be more relevant. Also relevant to such understanding is the use and reliability of non-destructive evaluation (NDE) techniques for inspection. The fidelity of such methods may be uncertain and other methods to assess the current condition of the vintage components need to be established.

A survey was conducted regarding the most common topics that were noted in the discussion above, with participants asked to vote for the top 3 topics of importance from their perspective. Voting results are provided in Table 2. Due to the nature of a virtual meeting, an active brainstorming exercise was not attempted. The topics in Table 2 were identified by the organizers.

**Table 2: Survey results for topics on hydrogen use in Heating and Power**

<i>Topic</i>	<i>Votes</i>
Performance of high-strength alloys in combustion/burner (e.g., nickel alloys)	12
Performance of welds	11
Impurities: degrading (e.g., hydrogen sulfide)	11
Corrosion effects and synergy with hydrogen	10
Stress hold in fatigue	9
Fatigue frequency, transferability to very low frequency	9
Materials in geologic storage and other large-scale storage methods	7
High-temperature effects (HTHA)	6
Impurities: beneficial (e.g., oxygen, carbon monoxide)	4
Performance of polymer distribution piping	4
Non-pressure boundary, functional alloys (not responsible for pressure containment)	3
Moderate temperature excursions due to gas compression	2

## 4. PANEL 3: INDUSTRIAL USES FOR HYDROGEN

### 4.1. Anders Werme (ArcelorMittal)

Several routes exist for steelmaking including (i) the use of iron ore within a blast furnace (most common) with Coke that emits 2 tons of CO<sub>2</sub> per ton of steel produced, (ii) the use of iron ore within a direct reduction furnace with reformed syngas that emits 1.2 tons of CO<sub>2</sub> per ton of steel produced, and (iii) the reduction of scrap within an electric arc furnace that emits 0.4 tons of CO<sub>2</sub> per ton of steel produced. Hydrogen can possibly reduce the carbon load for blast furnace use by 20%; for direct reduction furnace, hydrogen can enable carbon-free (100% H<sub>2</sub>) steel production. Hydrogen can also be used for heat treatments necessary to tailor steel properties. To use hydrogen in these technologies, the leveled price needs to be around \$1.5/kg-H<sub>2</sub>. Higher prices can be competitive if CO<sub>2</sub> emissions are taxed, as is being done in Europe and other places. As steel production is continuous, a significant volume of stored hydrogen (i.e., large storage facility) is needed to ensure no expensive interruptions occur.

Regarding answers to posed framing questions:

- What applications suffer from a lack of materials options for hydrogen use? Are there materials that could be suitable that haven't been considered or evaluated?
  - No immediate lack of materials has been identified for hydrogen use in the steel industry. For low pressures and temperatures ranging from ambient to 900°C temperatures, we mostly foresee use of carbon steels (at lower temperatures) and stainless steels (at higher temperatures). Cost optimization/minimization of the required materials will promote hydrogen use. Since the steel industry can accept "low pressure hydrogen", this can become a cost advantage in choosing method and materials for storage of the hydrogen, such as low-pressure caverns (possibly lined), pressurized storage (different pressures), or in different compounds, etc. Liquefaction seems too costly. It is a lot about cost minimization.
- How could materials that are already used in hydrogen be improved or better characterized?
  - By more testing! Also, further characterization of modern cost optimized steels (carbon, alloy and stainless) for use at different hydrogen (partial) pressures and temperatures.
- Where does industry lack understanding of the required metrics for materials selection in hydrogen environments?
  - As a hydrogen industrial consumer: protocols for safe handling of hydrogen at industrial sites are already in place. Widespread use in the energy system still needs further development of safety procedures and public awareness.
  - As steel supplier for the hydrogen energy system, we are reviewing regulation and adapting our procedures to validate steel to the specific requirements, such as ASME code requirements for pipeline and pressure vessel materials. However, most available specifications are considered too conservative and are under review in different standardization working groups. It is important for the extended use of hydrogen in the energy system that new specifications guarantee safe implementation while ensuring optimized cost. Prequalification of use of certain alloys in hydrogen is needed.

- What are the largest hurdles (cost, manufacturability, supply chain reliability, performance etc.) to materials selection for hydrogen service?
  - Cost minimization will always be advantageous for the adoption of hydrogen applications. While some challenges remain regarding manufacturability/production of materials, they can likely be solved. Supply chain reliability is a little bit like the “chicken and egg story”; if demand exists, it will likely be solved over time.
- What standards, test methods, performance metrics and design requirements are missing to support broader implementation of hydrogen technologies?
  - Steel producers are contemplating how steel grades should be acknowledged as “hydrogen compatible” for the different applications. Likely some pre-qualification processes (as used for other applications) need to be developed and agreed. It will be very difficult and cost counter-productive to test every single sheet/plate/tube produced!
- Are there material advances necessary to enable broader use of cryogenic hydrogen?
  - For wider use, further research could be valuable on (i) cryogenic applications - optimized stainless and even high-Mn austenitic steels; and (ii) cryo-compressed applications - cost saving high strength Ni-alloyed grades.
- Are there open questions about joining and welding of materials for use in hydrogen?
  - As for carbon steel in general: Yes, there are! There may be a reluctance from end-users/EPC's to use welded solutions (for pipes and vessels). It might be worth to reconsider this to become more cost competitive. Probably cost savings could be achieved if welded products could be proven to be acceptable – SAW, HFI/ERW, etc. Regarding welding of cryogenic alloy steels, work remains to find suitable technologies which maintain the properties of the base metal at the same time as those are cost efficient (especially for non stainless grades like Ni-alloyed and High-Mn steels).

## 4.2. Gerhard Schiroky (Swagelok)

Regarding answers to framing questions:

- What applications suffer from a lack of materials options for hydrogen use? Are there materials that could be suitable that have not been considered or evaluated?
  - Most customers are satisfied with the use of 316/316L stainless steel in their equipment that interfaces with hydrogen, containing 10 – 14% Ni per ASTM standard specifications. Few customers require a higher minimum Ni content than 10% and have special requirements for mechanical properties of cold-drawn bar and tubing. In Japan, the Ni equivalent (Ni<sub>eq</sub>) for stainless steel alloys is 28.5% min. In China, requirements on minimum Ni equivalent composition are still to be determined. Some internal valve components must be produced from alloys with high yield and tensile strength, including stems in ball and needle valves, Belleville springs in valves with live-loaded seats and seals, helical springs in check valves, and diaphragms in pressure regulators. Customers do not specify alloys for these components

- Issues exist such as
  - globally varying preferences for 316/316L composition that have led to supply chain inefficiencies,
  - convoluted hoses and helical springs are not readily available from 316/316L with elevated nickel content,
  - annealed 316/316L has relatively low yield and tensile strength and introduces limitations for construction of high-pressure fluid system components,
  - while cold-drawn 316/316L bar has higher strength, forgings for elbow and tees have the lower mechanical properties of annealed material, welding of cold-drawn tubing reduces strength,
  - limited information exists for hydrogen compatibility of high-strength alloys which are used to make internal valve components, in addition understanding their performance at cryogenic temperatures, and
  - lack of performance data for elastomers in high-pressure hydrogen.
- Opportunities to address these issues are as follows:
  - Establish a more quantitative differentiation of the performance of 316/316L with Ni content between 10 and 14%, and determine whether high Ni content or high  $Ni_{EQ}$  provides a significant advantage.
  - Evaluate the performance of materials with higher strength than 316/316L, such as 6-moly superaustenitic stainless steel (50% higher YS than annealed 316/316L; nitrogen  $\sim 0.20\%$ ) or Nitronic 50 (XM-19; UNS S20910; nitrogen  $\sim 0.30\%$ ).
  - Evaluate performance of high strength materials for internal valve components, such as highly cold-worked Nitronic 50, Co-Ni alloys (Elgiloy, MP35N) and Ni-alloys (cold-worked C-276, X-750)
  - Characterize performance of elastomers under cyclic pressure conditions and “low” temperature.
- How could materials that are already used in hydrogen be improved or better characterized?
  - Performance data are available for 316/316L stainless steel. Hydrogen increases mechanical properties (unless material is excessively cold worked) but causes major reduction of fatigue life (notched tensile samples). Actual fluid system components can experience fatigue failure during pressure cycling. Highest risk is for bodies with locations of high stress concentrations.
  - An opportunity would be to apply Sandia’s fatigue-life curves to pressure-cycled bodies and determine fatigue-life curve for pressure cycling in hydrogen using Sandia’s notched tensile fatigue-life curves in air and hydrogen.
- Are there materials advances necessary to enable broader use of cryogenic hydrogen?
  - It is generally understood that 316/316L performs well at cryogenic temperatures, but some disagreements on performance appear to exist. Less performance data exists for other alloys.
  - Opportunities to address this concern include:
    - Perform additional experiments to close knowledge gaps regarding 316/316L, examining a lower/larger range of temperatures.

- Generate data to allow for cryogenic use of Nitronic 50 in ASME-certified applications as existing data are limited.

### **4.3. Neeraj Thirumalai (ExxonMobil)**

Focus is on repurposing life of existing (natural gas) infrastructure. Blending of hydrogen in natural gas streams is of large interest. 50% of pipelines were built during or before the 1970's and may not be suitable for hydrogen service in all conditions. Of concern for vintage pipes are seam welds (low frequency [LF] electric resistance welds [ERW]) as older pipes with these welds have experienced failures even with normal use. One research challenge is to test vintage materials and understand fracture and failure modes in these materials.

Another challenge pertains to high temperature hydrogen attack (HTHA). There are few scientific studies of HHTA since 1980's, specifically on volumetric damage and crack-induced failure in relation to HHTA. Nelson curves have come under scrutiny recently. Fundamental understanding is needed on the micromechanisms of damage evolution.

A third challenge is to gain an understanding of sub-critical crack growth in the presence of hydrogen. Two conditions are relevant here: (1) Cr-Mo steels that have experienced "in service" hydrogen charging and role of hydrogen and cracks – and crack initiation – during cool-down, and (2) "sour water" gas vessels where both hydrogen and hydrogen sulfide are present and there is a lack of understanding of how fast flaws grow in these vessels. Relationship between cathodic protection, which introduces hydrogen externally, and the presence of internal hydrogen is also of importance to predict failure within a pipe.

Finally, more research is needed regarding NDE as life extension of components requires knowledge of both material properties AND the detection of existing damage/flaws. Microcracking damage may evolve, and there is need to know how to detect defects early and correlate damage to material properties. Also, systematic ways to measure residual stresses by non-destructive methods are needed.

### **4.4. Discussion**

Following the panel presentations, panelists and workshop attendees participated in a discussion moderated by Kevin Simmons of Pacific Northwest National Laboratory and Chris San Marchi of Sandia National Laboratories.

#### **Discussion Summary:**

In situ coating techniques for repair coatings are of interest for use as hydrogen barrier coatings to enable hydrogen blending in legacy pipelines. Concern does exist as to the reliability of such coatings. Whether they can help is a question worth exploring. The ARPA-E REPAIR program is including hydrogen permeation testing as part of the program. There are potential metal coatings that can be applied, for example aluminum. These could be significantly better than polymer-based coatings from a hydrogen perspective. ULC Robotics has a cold spray program currently for pipeline repair.

Regarding use of aluminum components, thread strength is of concern in meeting code requirements for service in hydrogen. In the end, the emphasis is a low-cost product, which may not necessarily equate to a low-cost material. Not much demand for aluminum fittings at this time.

Regarding Nitronic alloys, there is some Nitronic 50 toughness data at cryogenic temperatures in literature, but more is needed. Currently, the ASME code limits the allowable service temperature of Nitronic 50 (-25F in B31.3). There is an existing code case within B31.12 for the use of Nitronic alloys at cryogenic temperature. There are plans to review performance factors in B31.12 for these alloys; there is some significant conservatism, which could potentially be relaxed in the code. For Nitronic 50, the “Z-phase” – Nb-Cr-N-based plates – can form under some manufacturing conditions. There are concerns that this may reduce fracture toughness, as reported in previous work. Z-phase can also have a strong strengthening effect in some systems. ORNL developed high strength cast CF8C-Plus with high Mn and N similar to Nitronic and did not have problem with Z phase.

A lot of activities around code B31.12 are currently in progress, including review of the design factors for hydrogen pipelines. Long-term goal should be to increase the design envelope. Current issue is also injecting hydrogen at low concentrations into existing high-design-factor pipelines; reducing design factor to retrospectively meet ASME B31.12 would be expensive and prohibitive. ASME B31.12 also imposes weld hardness limits. There is an interest to have research that relates weld hardness to hydrogen embrittlement and if possible, relaxing these requirements as they cannot be applied retrospectively. There is also the question of how critical flaw size changes with the introduction of hydrogen into legacy natural gas infrastructure and how that should be factored into risk management programs. This is addressed by measuring fracture properties in relevant environments. Pipeline design also requires a consideration of fracture *arrest* conditions. There may be a scarcity of knowledge about fracture propagation speeds in a material being used in hydrogen service, which adds a lot of uncertainty in design for fracture arrest.

Another raised issue is the influence of the epoxy layer on hydrogen uptake in existing natural gas pipelines. Some diffusion of hydrogen will occur, but not a major concern. Also, soft components are key parts of regulators/relief valves, critical for pressure control. There are also other materials that may have to be assessed, e.g., titanium coated ultrasonic sensors for flow measurement. The permeability of hydrogen through electrical conduit seals is also a materials issue to address, but pipe and control components are by far the biggest concerns from an integrity and control perspective. There is also interest in learning more about the use of, challenges with, and current research in plastics/polymers for hydrogen seals, tubing, components, etc. Some workshop participants would value a follow-on forum to deep dive into this topic.

Defect detection was also discussed. NDE rarely finds all the defects, all the time. Designs need to be damage tolerant as the risk is too large to rely entirely on detection. That said, challenges exist in continued use of equipment over long times and verification of remaining lifetime for a given component. Probabilistic approaches need to be used in conjunction with NDE findings to provide more reliable predictions. Probabilistic approaches are not currently employed in the U.S., but they are used in Canada.

A survey was conducted regarding the most common topics that were noted in the discussion above, with participants asked to vote for the top 3 topics of importance from their perspective. Voting results are provided in Table 3. Due to the nature of a virtual meeting, an active brainstorming exercise was not attempted. The topics in Table 3 were identified by the organizers.

**Table 3: Survey results for topics on hydrogen use in Industrial Processes**

<i>Topic</i>	<i>Votes</i>
Fatigue life assessments and design methods with hydrogen	17
Performance of high-strength pressure-containing alloys	16
Hydrogen-induced crack initiation/nucleation	15
Performance of welded components	12
Hydrogen in high-temperature environments	7
Existing infrastructure in high-temperature heating applications (e.g., steelmaking, glassmaking, etc.)	6
Long-term hydrogen storage for emergency/backup power	6
Existing infrastructure in industrial settings for managing gases (i.e., replacement for natural gas)	5
Residual hydrogen in steel due to hydrogen-steelmaking	1

## **5. SUMMARY OF PRIORITIES FOR HYDROGEN COMPATIBLE MATERIALS R&D**

This two-day event included informed panel presentations and rich discussion from the participants and panelists. As the discussion summaries show, both high-level and detailed elaboration of industrial usages, practices and needs were shared. While the voting topics did not incorporate every aspect of the discussions, the survey results provide a snapshot of some of the high priority topics for hydrogen compatible materials research and development. The top priorities from the real-time survey of the participants within each topic are:

### **Transportation**

1. Establishment and population of a common database of materials properties
2. Data on material properties in cryogenic hydrogen
3. Understanding similitude of different environments (i.e., electrochemical vs precharging vs in-gas) and transferability of test results
4. Characterizing the performance of welds

### **Heating and Power**

1. Characterizing the performance of high-strength alloys in combustion/burner equipment (e.g., nickel alloys)
2. Assessing the effect of degrading impurities (e.g., hydrogen sulfide)
3. Assessing corrosion effects and the synergy of such effects with hydrogen
4. Stress hold in fatigue; Fatigue frequency and transferability to very low frequency

### **Industrial Uses for Hydrogen**

1. Fatigue life assessments and design methods with hydrogen
2. Characterizing the performance of high-strength, pressure-containing alloys
3. Understanding hydrogen-induced crack initiation/nucleation
4. Characterizing the effect of hydrogen in high-temperature environments

For this list, the top 4 topics were taken from the surveys for each of the panel sessions. In addition, we removed duplication in our surveys, noting that welds were a priority in all three panel themes, but only listed about in the transportation theme. Future national lab research should reflect at least some of these areas, as well as other topics described in this report and determined from follow-on discussion with industry partners.

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