Microstructural Engineering and Accelerated Test Method Development to Achieve Low Cost, High Performance Solutions for Hydrogen Storage and Delivery

DOE Hydrogen Program
2023 Annual Merit Review and Peer Evaluation Meeting

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DOE Project Award EE0008828

Project ID IN021

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Project Goals

- Develop lower cost steel alloys with high performance, through novel microstructural design, for use in hydrogen refueling infrastructure to accelerate implementation of hydrogen fueling infrastructure.
- Develop and validate accelerated test methods to efficiently evaluate variations in alloy and microstructure design to enable broader accessibility and lower cost testing in hydrogen environments.
Overview

Timeline and Budget
• Project Start Date: February 1, 2020
• Project End Date: May 31, 2024
• Total Project Budget: $1,804,560
  • Total Recipient Share: $360,912
  • Total Federal Share: $1,443,648
  • Total DOE Funds Spent*: $963,188
  • Cost Share Funds Spent*: $254,069
* As of 12/31/2022

Barriers – Hydrogen Delivery
• Hydrogen delivery infrastructure costs and reliability

Partners
Project Lead: Colorado School of Mines
Los Alamos National Laboratory
National Renewable Energy Laboratory
WireTough
U.S. Steel
General Motors
H-Mat Consortium (Sandia National Lab)
Chevron
POSCO (cost share participant)
U.S. produced alloys for economic competitiveness and hydrogen fueling infrastructure reliability
Overall Approach

• Develop lower cost austenitic alloys that meet or exceed the hydrogen embrittlement performance of austenitic steels

• Develop lower cost ferrite-austenite alloys that have intermediate hydrogen embrittlement performance between austenitic stainless steels and lower alloy ferritic steels
Approach – Low Cost Austenitic Alloys

- Replace Ni with lower cost Mn to produce lower cost austenitic alloys (lower hydrogen diffusion)
- Utilize alloying approaches to achieve deformation mechanisms (through changes in stacking fault energy) known to be beneficial for hydrogen resistance.

Gibbs et al., JOM, 2020
Approach – Ferrite-Austenite Microstructures

- Produce lower cost high Mn duplex alloys
- Microstructure morphology can potentially be altered through thermomechanical processing to change HE resistance

![Phase Fraction vs Temperature Diagram](image)

- Fe-0.115C-20.9Mn-5.81Al-0.1V (wt %)

255 duplex stainless steel

1. Cheaper solution: reduce/remove Cr, Ni, Mo, Cu
2. Equivalent H resistance/strength

Mn-stabilized stainless steel

High Mn-Al Steel V microalloying

1. Stabilize austenite
2. Higher SFE, wavy slip for H resistance
3. Flexibility in processing to achieve a range of strengths
## Approach – Alloy Compositions

### BASELINE: Stainless Steel Compositions (wt pct)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>Ti</th>
<th>Nb</th>
<th>SFE (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>255 Duplex Stainless Steel</td>
<td>Bal.</td>
<td>25.9</td>
<td>6.21</td>
<td>3.28</td>
<td>1.56</td>
<td>0.87</td>
<td>0.38</td>
<td>0.018</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
<td>255</td>
</tr>
<tr>
<td>316L Austenitic Stainless Steel</td>
<td>Bal.</td>
<td>17.57</td>
<td>12.97</td>
<td>2.71</td>
<td>0.22</td>
<td>1.25</td>
<td>0.59</td>
<td>0.017</td>
<td>0.048</td>
<td>0.002</td>
<td>0.03</td>
<td>316L</td>
</tr>
</tbody>
</table>

### High Mn Austenitic Steel Compositions (wt pct)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Cr</th>
<th>Al</th>
<th>Ni</th>
<th>SFE (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1 (POSCO alloy)</td>
<td>Bal.</td>
<td>0.24</td>
<td>30.0</td>
<td>2.73</td>
<td>-</td>
<td>-</td>
<td>28.9</td>
</tr>
<tr>
<td>H2 (POSCO alloy)</td>
<td>Bal.</td>
<td>0.25</td>
<td>30.4</td>
<td>2.71</td>
<td>1.75</td>
<td>3.0</td>
<td>49.0</td>
</tr>
</tbody>
</table>

### V-Microalloyed High Mn Alloys (Designed Alloys) – produced by U.S. Steel

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Al</th>
<th>Ni</th>
<th>V</th>
<th>S</th>
<th>SFE (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duplex</td>
<td>Bal.</td>
<td>0.115</td>
<td>20.9</td>
<td>5.81</td>
<td>-</td>
<td>0.102</td>
<td>0.0137</td>
<td>47.3</td>
</tr>
<tr>
<td>Austenitic</td>
<td>Bal.</td>
<td>0.262</td>
<td>29.6</td>
<td>1.66</td>
<td>2.87</td>
<td>0.243</td>
<td>0.00996</td>
<td>47.3</td>
</tr>
</tbody>
</table>
Accomplishments: Austenitic Alloy H-Embrittlement Resistance

Alloy design influences deformation mechanisms related to HE resistance

Deformation induced martensitic phase transformation in H1 and designed alloy
Accomplishments: Austenitic Alloy H-Embrittlement Resistance

Cold working and aging can be tailored for strengthening

Alloy Design + Thermomechanical Processing resulted in comparable strength and HE performance to baseline 316L stainless
Accomplishments: Duplex Alloy H-Embrittlement Resistance

255 Duplex Design and Thermomechanical Processing affects phase fraction and morphology

High Mn Designed Alloy

EBSD
- Austenite grain size 7.1 µm
- Ferrite grain size 5.5 µm

XRD
- Austenite fraction 49 %
- Ferrite fraction 51 %

EBSD
- Austenite GS 4.0 µm
- Ferrite GS 4.4 µm

XRD
- Austenite fraction 63 %
- Ferrite fraction 37 %

Alloy design and thermomechanical processing affects phase fraction and morphology
**Accomplishments:** Duplex Alloy H-Embrittlement Resistance

Cold working and aging can be tailored for strengthening.

Alloy Design + Thermomechanical Processing resulted in comparable strength and *better HE performance* than baseline 255 Duplex stainless.
Accomplishments: Neutron scattering assessment of deformation mechanisms

High Mn Austenitic
LANSCE measurements indicate alloying and H effects on stacking fault formation

High Mn Duplex
LANSCE measurements indicate H effects on stress partitioning between ferrite and austenite phases
**Accomplishments:** Fatigue Crack Growth Modeling

- Fatigue crack growth modeling accounts for accelerated fatigue crack growth rates in hydrogen and also can also account for residual stresses associated with autofrettaging of pressure vessels.

\[ X_{tr} \text{ = Region in which the hydrogen concentration is high and due to localized plasticity, } C_T, \text{ (Hydrogen trapping)} \]

\[ C_L \ll C_T \]

Pressure vessel simulation
**Accomplishments:** Technoeconomic Analysis

**Estimated liquid steel prices**
- 316 SS: $6,658/ton

**New alloys**
- Med. Mn Duplex: $1,824/ton
- High Mn Austenitic: $2,769/ton

Important to consider additional cost assumptions!
Responses to 2021 Review Comments

• “This project needs to...speed the testing”
  ➢ We have met all of our original milestones with respect to testing and the Go/No Go criterion
• “It is not clear that activities associated with...LANL and WireTough Cylinders align with project goals.”
  ➢ LANL is providing hydrogen permeation testing, which will provide an informative assessment whether H-transport properties vary between the designed alloys and currently available commercial alloys. H-transport is critical to evaluate as it plays a major role in H-embrittlement.
  ➢ WireTough is providing an assessment of fatigue crack growth rate testing, which is one of the critical and limiting properties of steels used in hydrogen infrastructure. The models being developed can utilize material parameters to predict fatigue crack growth in the presence of hydrogen and thus are flexible to predict behavior of austenitic steels (e.g. this study) or steels used for liner applications.
• “Improvements to electrochemical/hydrogen charging evaluation approaches are recommended.”
  ➢ We have established electrochemical hydrogen charging conditions that match results gaseous pre-charging and in-situ charging. These results will facilitate comparisons between results from these two techniques in the current study, but dedicated future work taking into account fundamentals of electrochemistry should be performed to expand the correlation in a more general way. As the reviewers suggest, this future effort is outside of the scope of this study.
## Collaboration and Coordination

<table>
<thead>
<tr>
<th>Organization</th>
<th>Relationship</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colorado School of Mines</td>
<td>Prime</td>
<td>Project lead, management and coordination, hydrogen embrittlement testing, alloy design</td>
</tr>
<tr>
<td>Los Alamos National Lab</td>
<td>Sub-recipient</td>
<td>Hydrogen transport and in-situ experiments</td>
</tr>
<tr>
<td>National Renewable Energy Lab</td>
<td>Sub-recipient</td>
<td>Market transformation analysis</td>
</tr>
<tr>
<td>WireTough</td>
<td>Sub-recipient, cost share</td>
<td>Test bed methodology development, market transformation plan</td>
</tr>
<tr>
<td>U.S. Steel</td>
<td>Cost share</td>
<td>Produce designed alloys, input on alloy feasibility</td>
</tr>
<tr>
<td>POSCO</td>
<td>Cost share</td>
<td>Provide initial materials for assessment</td>
</tr>
<tr>
<td>General Motors</td>
<td>Non-funded collaborator</td>
<td>Provide input on hydrogen vehicle market</td>
</tr>
<tr>
<td>Chevron</td>
<td>Non-funded collaborator</td>
<td>Provide input on hydrogen transport and storage</td>
</tr>
<tr>
<td>H-Mat (Sandia National Lab)</td>
<td>Funded partner</td>
<td>Testing in gaseous hydrogen, input on relevant metrics and previous work</td>
</tr>
</tbody>
</table>
Remaining Challenges and Barriers

• Further enhancement of strength and H-embrittlement performance of designed alloys
• Advanced characterization to link alloy and deformation characteristics to H-embrittlement
• Correlating electrochemical H-charging experiments to gaseous H-charging experiments
• Assessment of next steps to implement alloy solutions
Proposed Future Work
Based on Project Year (6/1/23 – 5/31/24)

Any proposed future work is subject to change based on funding levels

• Remainder of FY 2022
  – Explore microstructure evolution and properties from thermomechanical processing of designed medium Mn duplex alloy

• FY 2023
  – Correlate gaseous H-charging toughness results to electrochemical charging results
  – Utilize LANSCE capabilities to link alloying effect on deformation mechanisms to H-embrittlement
  – Market transformation analysis
  – Identify most promising alloy and process conditions based on strength, hydrogen embrittlement resistance, and cost
Summary

- Mn alloy design approaches can be used in conjunction with thermomechanical processing to achieve comparable HE resistance to stainless steels.

- Preliminary technoeconomic analysis indicates economic viability of designed alloys.
  - Critical aspects still need to be evaluated.

- The collaboration between Mines and industry and laboratory partners is meant to facilitate further development and implementation of these strategies for hydrogen fueling infrastructure applications.