Micro-mechanically guided high-throughput alloy design exploration towards metastability-induced H embrittlement resistance

PI: C. Cem Tasan, Ju Li, Bilge Yildiz (MIT), Joost J. Vlassak (Harvard)

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Project Goal

- Develop a novel high-throughput compositional and microstructural screening approach to develop new alloys with superior hydrogen embrittlement (HE)-resistance, by specifically focusing on utilization of metastability effects on toughening. This includes:
  (i) Technique development of high-throughput screening (HTS) for HE-resistance
  (ii) Discovery of new metallic materials with superior HE-resistance using the HTS techniques
  (iii) Multiscale verification of HE-resistance of the new alloys and H-barrier layers, from atomic scale to an engineering scale
Overview

Timeline

• Project Start Date: 04/01/20
• Project End Date: 03/31/23

Barriers

• Key barriers addressed in the project are:
  - Hydrogen delivery, E. Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
  - Hydrogen storage, G. Materials of construction

Budget

• Total Project Budget: $1,250,000
• Total DOE Share: $1,000,000
• Total Cost Share: $250,000
• Total DOE Funds Spent*: $468,591,09
• Total Cost Share Funds Spent*: $177,248.84

*Estimated as of 03/31/21

Partners

• Project lead: C. Cem Tasan (MIT)
• Co-PIs: Ju Li, Bilge Yildiz (MIT), Joost J. Vlassak (Harvard)
• Partner organization: ATI
Relevance

Objectives:

• Develop a novel rapid alloy design methodology for high HE-resistance, integrating micromechanical screening of composition spread island films and multi-scale verification by bulk alloy testing and atomistic simulation. The outcome can significantly accelerate new metallic material exploration process and screening of HE-resistance, which require for “Safe, Lower Cost Containment Technologies” in HFTO MYRDD.

• Explore complex-concentrated alloy (CCA) space in which phase metastability (related to deformation-induced phase transformation and mechanical twinning) can be utilized to enhance HE-resistance, using the new high-throughput alloy design methodology.

<table>
<thead>
<tr>
<th>Barrier from HFTO MYRDD</th>
<th>Impact from this project</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen delivery, E. Gaseous Hydrogen Storage and Tube Trailer Delivery Costs</td>
<td>Provide novel methods to drastically reduce the required R&amp;D period for new alloy development as well as H-related physical property screening of multiple alloys</td>
</tr>
<tr>
<td>Hydrogen storage, G. Materials of construction</td>
<td></td>
</tr>
</tbody>
</table>
Approach: Integrated high-throughput alloy design strategy

**Alloy design concept**
- Bulk alloy screening
- CALPHAD-metastability estimation
- "Binary" testing for rapid screening
- Identify trends

**Computational framework**
- ML-based Interatomic potential development
- MD-GCMC hybrid modelling of CCAs with H

**Metastability-induced HE-resistance in CCAs**

**Bulk alloy testing in high-P H₂**

**Micromechanical screening**
- Composition spread islands by co-sputtering
- Micromechanical Property screening
- Identify promising alloys from property maps

**Verification**

*new award*
Approach: Metastability control in complex-concentrated alloys

- Key focus: Enhance HE-resistance by controlling phase metastability that induces plasticity mechanism transition, which can be manipulated by composition optimization of CCAs

References:
Li et al., Nature (2016).
Approach: CALPHAD-based bulk alloy high-throughput screening

- Key focus: maximizing range of microstructures
  - Cast a small number of compositions, post-process to vary microstructures
- Adapted from other alloy design routes:
  - Rapid alloy prototyping
  - Iterative approaches based on machine learning
- Goal: explore HE dependence on phase constitution & transformations in CCAs & provide composition ranges to be explored by micro-mechanical approach in detail
Approach: *Micromechanics-based high-throughput screening*

- **Bulk alloy testing** - informed composition range selection
- **Fabrication of composition spreads** (Composition library)
- **Rapid property screening with *in situ* H-charging**
- **Identify trends from property maps, Verify in bulk scale**

- **Key focus**: Rapid property screening on composition spreads
- **Property mapping using micromechanical tests**
  - *In situ* H-charging indentation-based approach
  - Metastability mapping by H & stress-induced change
- **Goal**: explore H & deformation-induced microstructural change depending on alloy compositions and phase metastability
**Approach:** *Computational framework for complex alloys*

**Workflow of multicomponent interatomic potential development**

Deep-potential generator (DP-Gen): concurrent learning scheme

- **Systems**
  - Elemental systems and dimers
  - Binary systems
  - Ternary systems
  - Quaternary systems
  - Quinary systems

- **Compositions**
  - Thermodynamic conditions ($T$, $P$)

- **Sub-systems**
  - Phases (+SRO)
  - Structural defects

- **Iterate through each system and its sub-systems based on the DP-GEN automatic workflow.**

**Key focus:** Establish computational framework for exploring complex multicomponent alloys

**Goal:** Bridging the gap between bulk and microscale studies, mainly induced by defect structures
Technical Accomplishments and Progress*

- Research progress in the first year of the project is focused on technical development of experimental and computational methodology for high-throughput alloy design strategy, including:
  
  1. CALPHAD-based bulk alloy rapid screening for composition range confinement
  
  2. Fabrication, compositional control and post heat-treatment of composition spread islands (composition library)
  
  3. Design and fabrication of in situ H-charging + indentation setup for high-throughput property measurement
  
  4. Development of Spin-Aware Neural Network Interatomic Potential for multicomponent alloy system (confidential)

- Milestone table of the project

<table>
<thead>
<tr>
<th>Milestone #</th>
<th>Project Milestones</th>
<th>Task Completion Quarter</th>
<th>Progress Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Preparation of safety plan</td>
<td>M3, M3</td>
<td>100%</td>
</tr>
<tr>
<td>1.2</td>
<td>Confinement of alloy system &amp; composition range</td>
<td>M6, M6</td>
<td>100%</td>
</tr>
<tr>
<td>1.3</td>
<td>Compositional gradient control in film islands fabrication</td>
<td>M9, M9</td>
<td>100%</td>
</tr>
<tr>
<td>1.4</td>
<td>Micron-thick film growth and post thermal treatment</td>
<td>M12, M12</td>
<td>100%</td>
</tr>
</tbody>
</table>
Technical Accomplishments and Progress: CALPHAD-based high-throughput alloy screening

**CALPHAD: Austenite stability estimation**

Fe-xMn-10Co-10Cr  
Fe-10Mn-xCo-10Cr  
Fe-10Mn-10Co-xCr

- Exploration between med-Mn steel & FeMnCoCr CCA
- Parameters for microstructural variation:
  - $\Delta G^\gamma\rightarrow\varepsilon$ (TRIP), Co content (SFE)
  - $\alpha'$ $M_s$ and $\varepsilon$ $M_s$ temperatures (starting microstructure)
  - Require single FCC phase at high T (stabilized by Mn, Cr)

**Alloy selection and production**

<table>
<thead>
<tr>
<th>Composition (at.%)</th>
<th>$\alpha'$ $M_s$</th>
<th>$\varepsilon$ $M_s$</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 1</td>
<td>Co ~ 10, Cr ~ 6</td>
<td>174°C</td>
<td>9°C</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>Co ~ 14, Cr ~ 13</td>
<td>168°C</td>
<td>7°C</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>Co ~ 5, Cr ~ 13</td>
<td>113°C</td>
<td>113°C</td>
</tr>
</tbody>
</table>

**Binary testing: indentation cracking & phase transf.**

- Pre-H Indentation
- Post-H Indentation
- Post-Outgassing Indent.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$\alpha'$ transf?</th>
<th>Cracking?</th>
<th>$\alpha'$ transf?</th>
<th>Cracking?</th>
<th>$\alpha'$ transf?</th>
<th>Cracking?</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>3</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
</tr>
</tbody>
</table>

- Rapid screening of phase transf. and cracking responses at the limits of $\gamma$ phase metastability
Technical Accomplishments and Progress:

**Composition spread islands fabrication by co-sputtering**

**Composition control in magnetron co-sputtering**

- Parameters for enhancing compositional contrast/gradient
  - Lower Ar pressure
  - Smaller working distance
  - Smaller tilt angle

<table>
<thead>
<tr>
<th>Target material</th>
<th>Power (watt)</th>
<th>Tilt angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₄₀Mn₅₀Co₁₀</td>
<td>85</td>
<td>28.3</td>
</tr>
<tr>
<td>Fe</td>
<td>90</td>
<td>35.8</td>
</tr>
<tr>
<td>Cr</td>
<td>15</td>
<td>35.8</td>
</tr>
</tbody>
</table>

**Fabrication of individual film islands**

- Post-heat treatment of micron-thick films is essential for
  (i) removing the non-equilibrium $\alpha$-Mn phase, and
  (ii) grow the as-deposited nanocrystalline grains to micron scale

- Protective layers of HfO₂ and SiNx were applied on the alloy film and between the alloy film and substrate, in order to prevent the depletion of Mn either by evaporation or diffusion into substrate. The layers on the top can be removed by reactive etching.

**Heat treatment of fabricated composition spreads**

- Heat treatment of fabricated composition spreads:
  - 650°C (120 min)
  - 700°C (120 min)
  - 750°C (3 min)
  - 1000°C (2 min)

HfO₂

SiNx
Technical Accomplishments and Progress:

**In situ H-charging+indentation setup for high-throughput screening**

**Property mapping in pristine state (H-free)**

- Nanoindentation system (iNano, Harvard)
- In situ H-charging setup schematic diagram
  - 81 locations with 8 mm spacing
  - 5 indentations per location for avg

**In situ H-charging setup design for nanoindenter**

- An *in situ* H-charging setup for 2.5"-disk specimen (substrate size for composition spread) was developed for high-throughput screening of mechanical property change by hydrogen ingress.

- The frame compliance will be calibrated with a known reference material (e.g. Si), in order to obtain reliable indentation data.

**Modulus map**

**Hardness map**

- The as-deposited CCA film library shows strong hardness contrast, and the hard region could be related to the presence of α-Mn.
Technical Accomplishments and Progress:
Grain orientation and GB type dependence of H-distribution

**SEM/EBSD study in FeMnCoCr alloy**

- **Grain orientation and GB type dependence of H-distribution**
  - **SEM/EBSD study in FeMnCoCr alloy**
    - **Grains form 10-100% martensite**
      - H-induced ε-martensite transformation
        - Transformation progresses with increasing H content
        - Martensite forms first in fast-diffusion grains
        - Martensite forms preferentially at Σ3 boundaries

- **GCMC-MD simulation of H in binary alloy**
  - **GCMC-MD simulation of H in binary alloy**
    - 50% Ni (white) + 50% Al (black)
    - Green: FCC atoms
    - Red: Twin boundaries
    - Grey: Random grain boundaries

- **Polycrystal under H-charging**
  - $\mu_H = -2.25 \text{ eV}$

- **GBs**
  - $\sigma_{xx}$
  - $\sigma_{xy}$

- **GCMC-MD simulation of effects of grain orientation and GB types in H-distribution and atomic stress distribution (on-going)**
Collaboration and coordination

Team members and partners | Project roles
---|---
Tasan Group, MIT | Project lead, Management/coordination, Setup design, Alloy design, Experimental methodology development, Bulk alloy production
Li Group, MIT | Computational technique development, Interatomic potentials development
Yildiz Group, MIT | Surface structure and property characterization, Computational technique development,
Vlassak Group, Harvard University | Composition spread film fabrication, Heat treatment, Micromechanical testing, Experimental methodology development
ATI (Unfunded industrial partner) | Bulk alloy production, Consultant on alloy system selection, production and industrial requirements
Sandia National Lab. (H-Mat partner) | Bulk alloy testing in high-pressure hydrogen environment (planned for Year 3)
## Remaining Challenges and Barriers

<table>
<thead>
<tr>
<th>Category</th>
<th>Remaining challenges and barriers</th>
<th>Planned resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition spread island fabrication</strong></td>
<td>Grain morphology and size control in compositional spread films</td>
<td>Optimize heat treatment conditions and analyze grain size and morphology by EBSD/XRD analysis</td>
</tr>
<tr>
<td></td>
<td>Investigation of residual stress in heat-treated films</td>
<td>Find appropriate annealing conditions for minimizing residual stress effect</td>
</tr>
<tr>
<td><strong>Micromechanics-based high-throughput screening with in situ H-charging</strong></td>
<td>Uniform H-ingress throughout the charging surface</td>
<td>Apply a buffer interlayer with high H-diffusivity and solubility to distribute H uniformly</td>
</tr>
<tr>
<td></td>
<td>Fracture toughness measurement with microscale alloy specimens</td>
<td>Binary testing using indentation cracking or pillar splitting tests, and verify with bulk alloy testing</td>
</tr>
<tr>
<td></td>
<td>Bridging micromechanical test results and bulk alloy characteristics</td>
<td>Complement effects of defects and boundaries based on computational approach and bulk testing</td>
</tr>
<tr>
<td><strong>Computational framework for multi-component alloys</strong></td>
<td>Large dataset size required for a potential as complex as FeMnCoCr-H</td>
<td>Start with a small island in composition space and sample the geometric and spin configuration subspaces</td>
</tr>
</tbody>
</table>
**Proposed Future work**

- Optimize the heat-treatment condition for composition spread islands, in order to minimize the residual stress effects and grow the nanocrystalline grains to micron scale.

- Apply the high-throughput property screening with *in situ* H-charging in heat-treated composition spread islands, for H-induced changes of hardness, elastic modulus, fracture toughness and microstructure after deformation.

- Especially for the fracture toughness evaluation in microscale, first apply the binary testing methodology using indentation cracking analysis or micropillar splitting test, and verify the results in screened compositions with cantilever bending or bulk alloy testing.

- Apply hybrid GCMC-MD simulation method with new interatomic potentials for multicomponent alloys, developed by the Spin-Aware Neural Network method.
Summary

• A CALPHAD-based bulk alloy screening approach was utilized to confine the alloy composition range in which phase metastability can be effectively manipulate, for applying the micromechanics-based approach with composition spread films.

• Fabrication techniques for composition spread films were developed, including magnetron co-sputtering, composition gradient control, film thickness control, and heat-treatment process with protective layers.

• A new in situ H-charging setup compatible with a nanoindenter system was fabricated for high-throughput screening of H-induced mechanical properties of composition spreads.

• A neural-network-based method for developing interatomic potentials for complex concentrated alloys was established, and its application to FeMnCoCr-H system will be conducted in following project years.
Technical Backup and Additional Information
Technology Transfer Activities

• In the first-year accomplishments of the project, research efforts were concentrated in developing specimen fabrication techniques and high-throughput property screening techniques. No patent application is filed in this project yet. Once the high-throughput alloy design technology is matured and novel alloy compositions with high HE-resistance are discovered, patent applications for the results will be filed.

• The project team is continuously interacting with the unfunded industrial partner, ATI. Alloy manufacturing and application experts from ATI has been joining the regular progress update meetings of the project team (quarterly) and sharing opinions on alloy system selection and industrial requirements.
This project is conducting studies about developing a novel high-throughput alloy design strategy for superior HE-resistance. The final goal of the project is the verification of the high-throughput alloy design strategy, including the confirmation of high HE-resistance of discovered alloys by comparing yield strength and fracture toughness between specimens in 100 MPa-H$_2$ condition vs. in air.

This project will contribute to the following DOE technical tasks and milestones from the “3.3. Hydrogen Storage” section of the Hydrogen and Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

**Task 1. Material Discovery**

- Perform theoretical modeling to provide guidance for materials development.
- Determine the H$_2$ storage capacity of potential storage materials and demonstrate reproducibility of their synthesis and capacity measurements

**Milestone 1.1. Material Handling:** Determine applicability of H$_2$ storage materials for material handling applications.

**Milestone 1.3. Material Handling:** Down-select H$_2$ storage materials for material handling applications.