Tailoring composition and deformation modes at the microstructural level for next generation low-cost high-strength austenitic stainless steels

PI: Petros Sofronis

Jessica Krogstad, Brian Somerday, James Stubbins, Elif Ertekin,

University of Illinois Urbana Champaign

Lab Partners: Sandia Livermore, Argonne, Oak Ridge

Industrial Partners: Arcelor-Mittal, Swagelok, Linde/Praxair

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AMR Project ID# IN026

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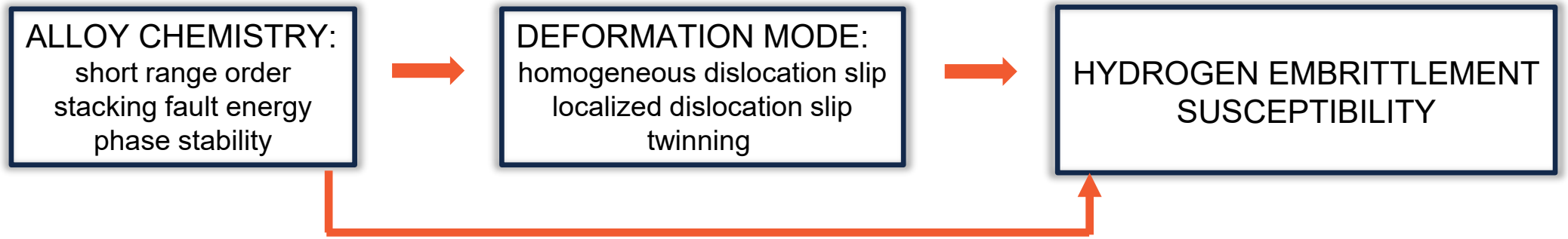
Project Goal

To enable deliberate development of cost-effective, hydrogen resistant alloys by establishing detailed relationships specific to the effects of *alloy composition*, *short-range order*, and *microsegregation* in the presence of hydrogen on the transition between homogeneous deformation and *localized plasticity* in shear bands.



Timeline & Budget

- Project Start Date: 10/01/19
- Project End Date: 09/30/23
- Total Project Budget: $2,502,247
- Total DOE Share: $2,000,000
- Total Cost Share: $502,247
- Total DOE Funds Spent*: $1,228,366
- Total Cost Share Funds Spent*: $399,414

* As of 02/07/2023

Barriers

- E. Gaseous Hydrogen Storage and Tube Trailer Delivery Costs

Partners

- Project Lead: Petros Sofronis, University of Illinois Urbana Champaign
- Jessica Krogstad, Brian Somerday, James Stubbins, Elif Ertekin
- Shelly Tang (Swagelok), Kang Xu (Praxair/Linde), Xingshuo Wen (ArcelorMittal), Chris San Marchi & Joe Ronevich (Sandia National Laboratory, Livermore), Govindarajan Muralidharan (Oak Ridge National Laboratory), Rajesh Ahluwalia (Argonne National Laboratory)

Lowering the cost of stainless steel while retaining hydrogen compatibility enables deployment of H_2 fuel technology

Hydrogen-induced degradation of austenitic steels is advanced by hydrogen enhanced localized plasticity (HELP) and is governed by the chemical composition of the alloy

- Impacts both cost and reliability of transport and storage infrastructure (E)
- Establishing a mechanistic connection between local chemistry and local deformation behavior in combination with the appropriate technoeconomic analysis will enable design of cost-effective hydrogen resistant alloys
- Enabling the deployment of hydrogen fuel technology will lower GHG emissions

Previous Year Impacts:

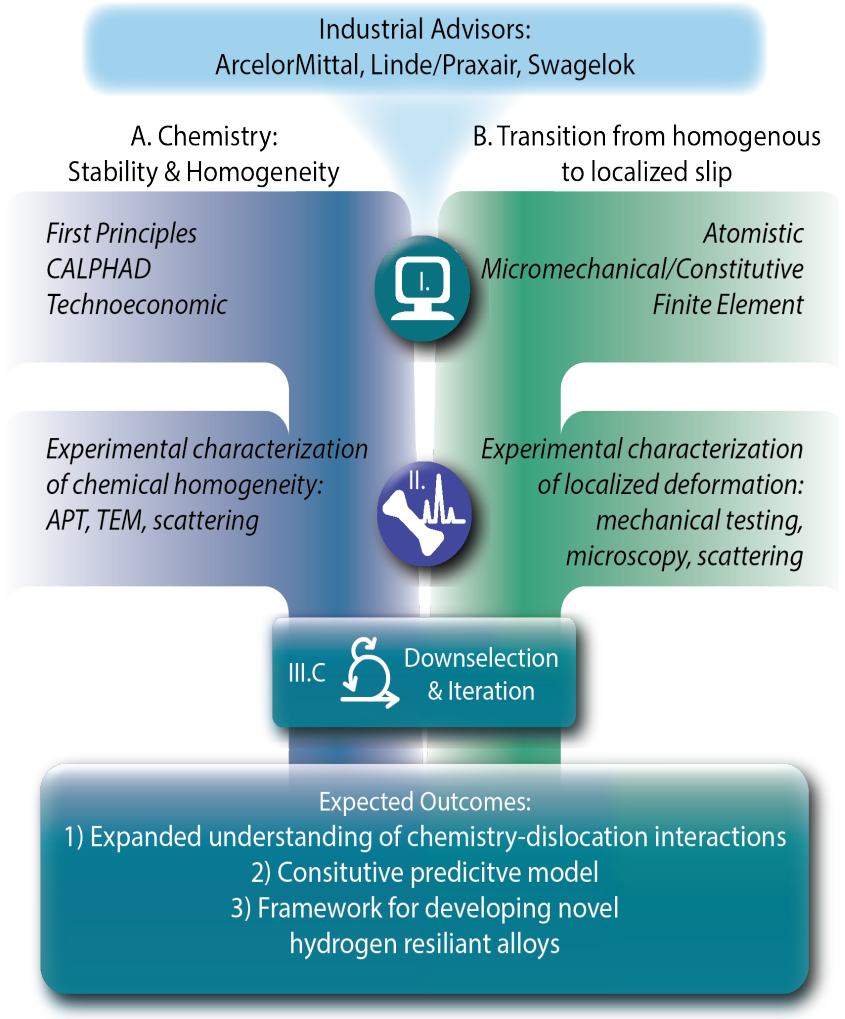
- Developed, validated and leveraged a novel characterization technique towards unique insight on the relationship between alloy chemistry, short range ordering and deformation behavior in novel, cost-effective austenitic alloys
- When this insight was integrated into continuum models, we begin to establish a mechanistic connection between local chemistry and local deformation behavior, including the transition from homogenous to localized deformation in the presence of H laying the groundwork for a broader strategy for hydrogen resistant alloy development

Approach

Existing descriptors have been insufficient to anticipate hydrogen embrittlement in austenitic alloys

- Phase I (M1-M18): Integrated (I) computational and (II) experimental efforts aim to elucidate the contributions of (A) alloy chemistry & (B) deformation mode
- Phase II (M19-36): Downselection, evaluation & iteration

Milestone		Planned	Complete
I.2	Material Specific Costs	M12	100%
I.1	Alloy Chemisty – Atomistic Model (w/o H_2)	M15	95%
1.3	Alloy Chemistry – Atomistic Model (w/ H_2)	M18	95%
II.1	Alloy Chemistry – Characterization	M18	100%
II.2	Microstructure Characterization	M21	100%
I.4	Constitutive Model	M36	75%
III.1	GNG#1 - Downselection of 5 candidate alloys	M18	100%
III.3	GNG#2 – Downselection of 2 alloys for larger scale manufacturing & testing	M27	100%
III.4	Delivery of alloys to Sandia & UIUC	M30	0%
III.5	Quantify fatigue resistance of downselected alloys	M33	0%



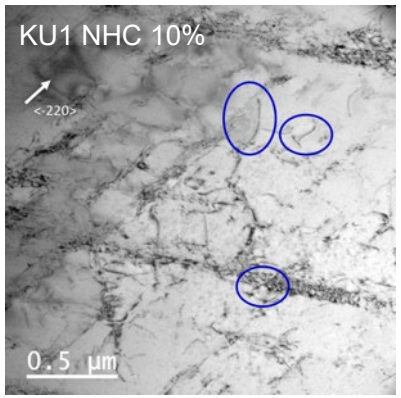
Alloy design suppresses traditional hydrogen embrittlement mechanisms to isolate contributions from nanoscale heterogenies (short range order domains)

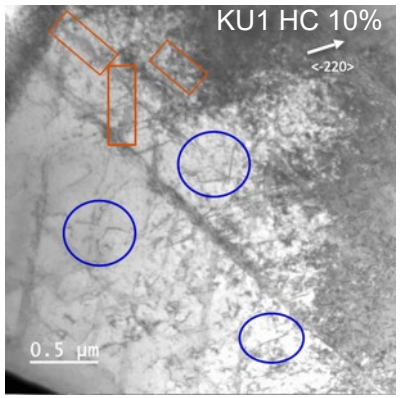
wt%	Fe	Cr	Ni	Mn	N	C	Al	Cu	Mo	Si	$$*	$$/YS
Hastealloy 22	3	22	56	0.5	0	0.01	0	0.5	13	0.08	15.12	
AISI 316L	65	17	12	<2.00	<0.1	<0.03	--	--	2.5	<0.75	4.58	0.0224
Nitronic 40 (21-6-9)	63.2	20.9	6.9	8.7	0.27	0.028	0	0	0	0	3.35	0.0100
SCF260	55.8	19.5	3.5	17.5	0.65	0.04	0	0	2	<1.00		
Basic KU1 Alloy	68.55	17	5	9	0.3	0.15	--	--	--	<1.00	2.76	0.0073
Low-Ni KU2 Alloy	67.55	17	3	9	0.3	0.15	--	3	--	<1.00	2.61	0.0071
Al-Added KU3 Alloy	65	17	5	9	--	0.3	0.7	3	--	<1.00	2.92	0.0123
High-Mn KU4 Alloy	60.4	17	--	22	0.3	0.3	--	0	--	<1.00	2.29	0.0049

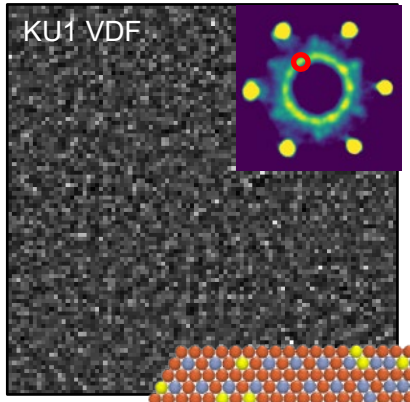
Alloy design rationale:

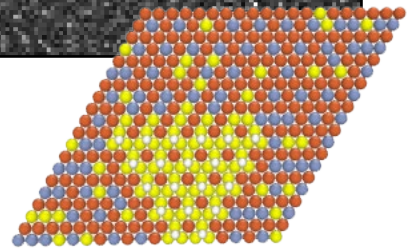
- Maintain corrosion resistance (Cr>13wt%)
- Reduce cost (Ni<6wt%)
- Single phase austenite: addition of Cu, Mn or C
- Hydrogen compatible (no deformation induced phase transformation or twinning as low at -50ºC)
  - The calculated values for M_{D30} are below -40ºC for all KU Alloys
  - Increased N content (or Al, not both) to increase SFE and suppress deformation twinning

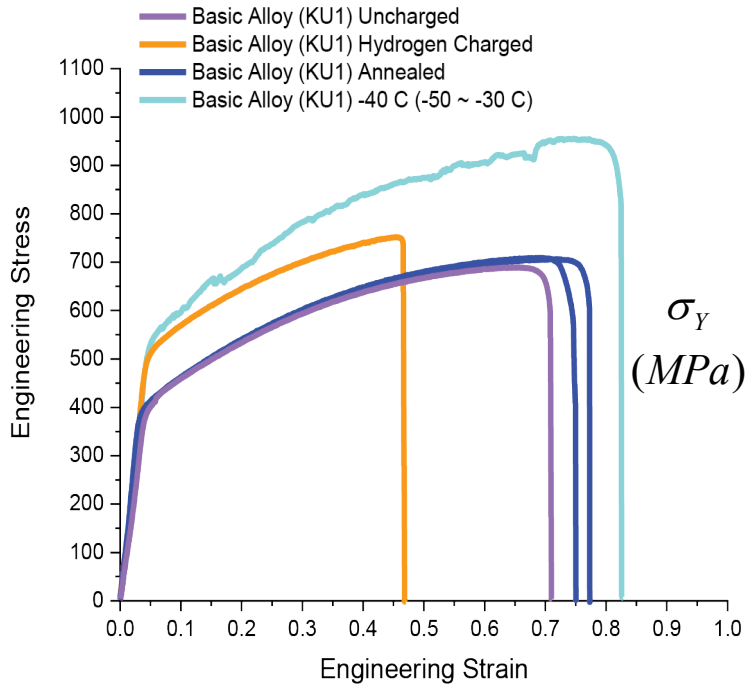
Approach:
Understanding intrinsic contributions to HELP in model or commercial alloys



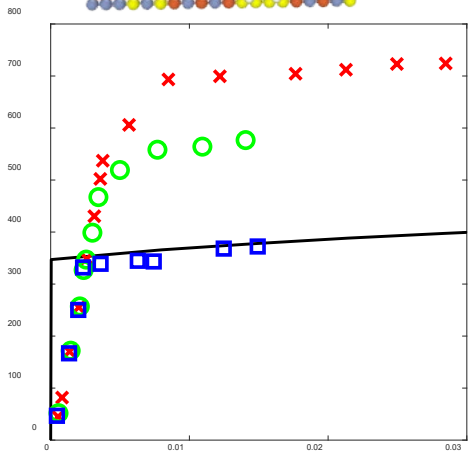








σ_Y (MPa)



ε^p

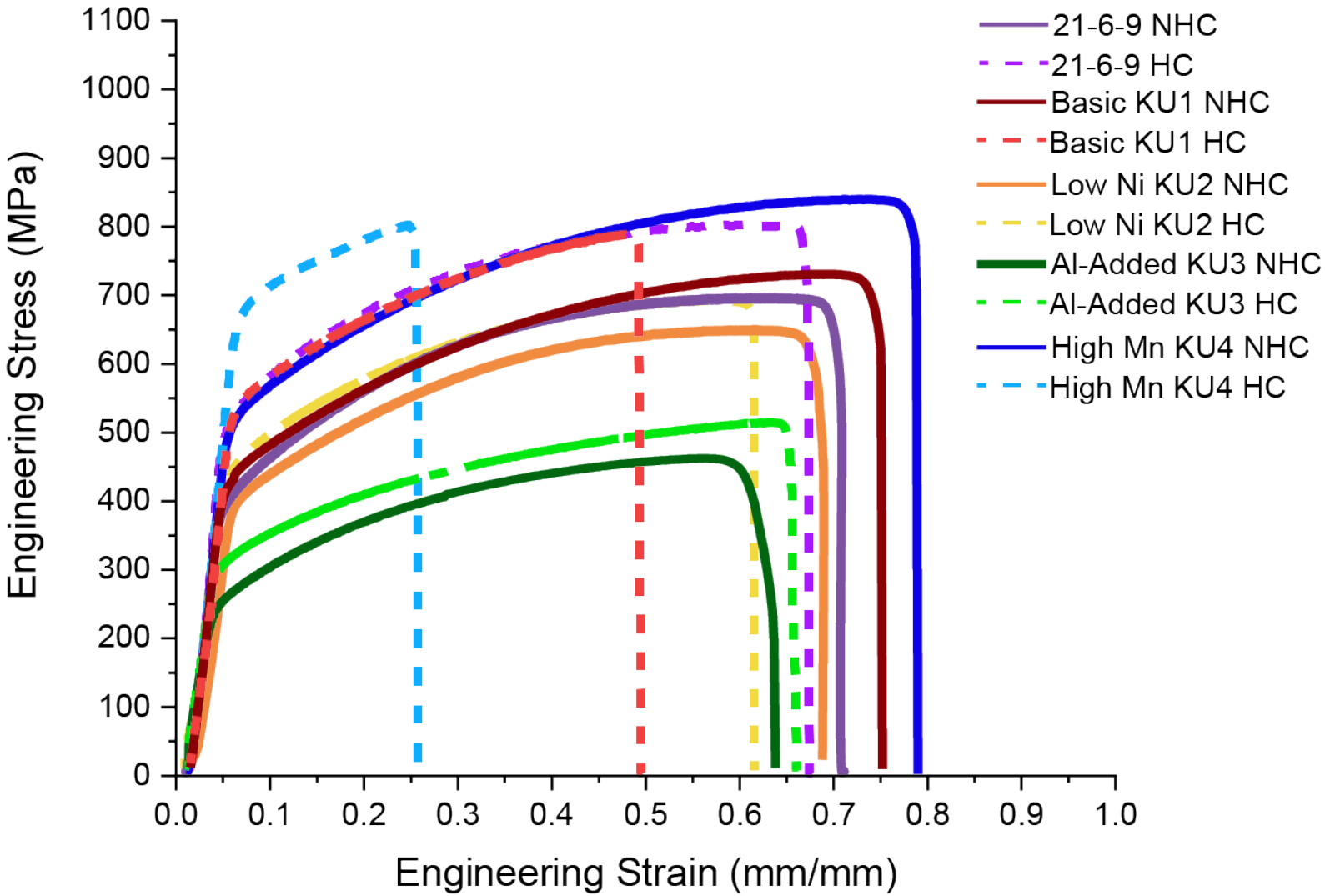
What are the consequences of nanoscale heterogeneities for deformation in the presence of hydrogen?

- Microstructural characterization of model austentic steels via electron microscopy and diffraction
- Atomistic simulation of short range ordering behavior with and without hydrogen
- Experimental mechanical testing and characterization of dislocation-microstructure interactions
- Development of a microstructurally-informed constitutive model
- Technoeconomic analysis

Short range order can describe any deviation from a random solid solution, including clustering or ordering

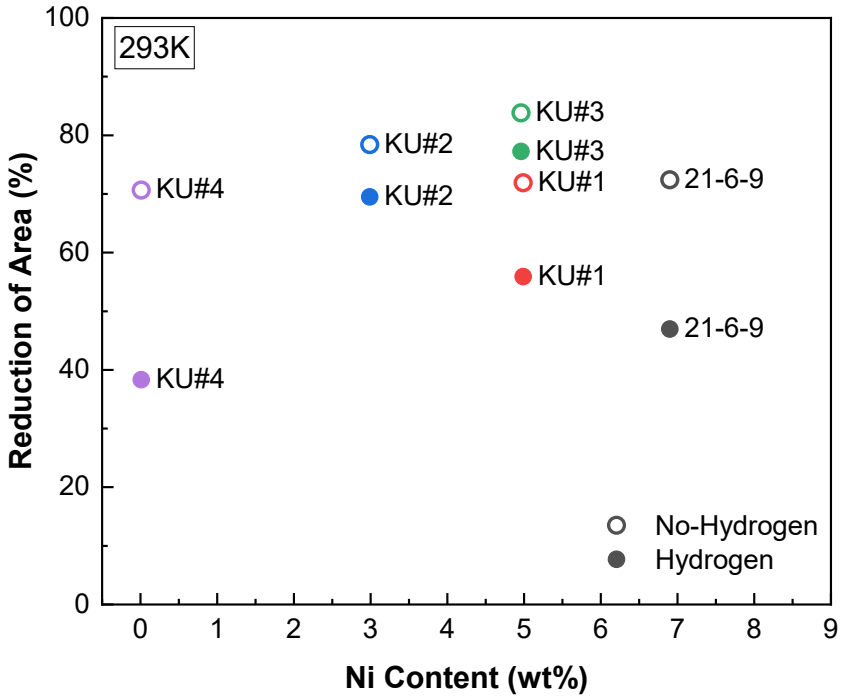
Overview of mechanical behavior

- Basic (KU1) and High-Mn (KU4) alloys exhibited the greatest ductility losses upon H-charging
- Basic (KU1), Low Ni (KU2) and 21-6-9 alloys had similar yield strength in the uncharged state (330-370MPa); Yield strength of Al-Added (KU3) is comparable to 316L (solution treated)
- All alloys exhibited some increase in strength and ductility at lower temperature (microstructural analysis of low temperature specimens is still underway)
- All tensile tests were performed to failure and 10%strain for dislocation analysis

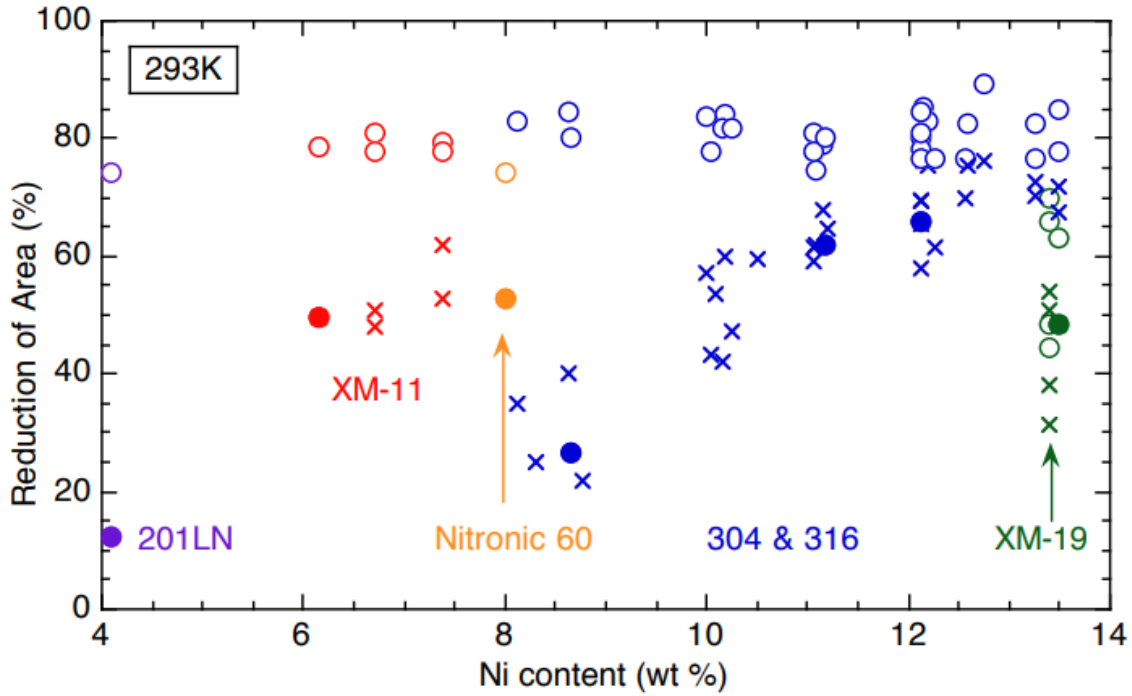


Comparison to Commercial Alloys via RA (uniaxial tension)

At lower Ni content our alloys maintain appreciable tensile ductility in the presence of hydrogen



Present work.

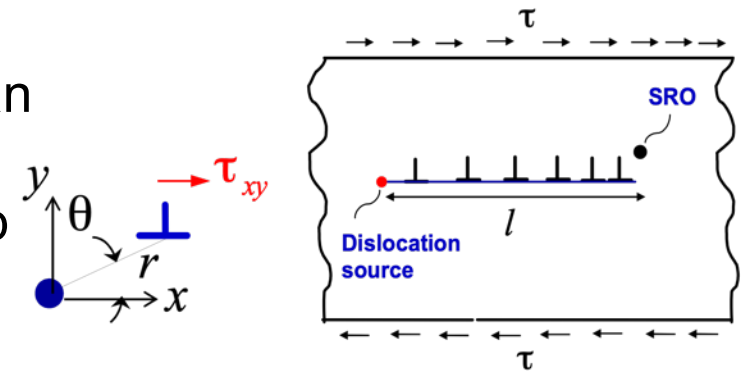


(5) San Marchi, C. Hydrogen Embrittlement of Stainless Steels and Their Welds. *Gaseous Hydrog. Embrittlement Mater. Energy Technol. Probl. its Characterisation Eff. Part. Alloy Classes* 2012, 592–623. https://doi.org/10.1533/9780857093899.3.592. (figure 16.2)

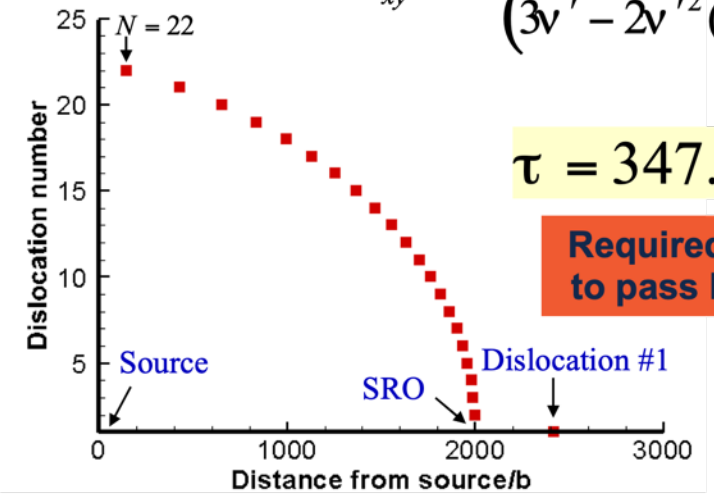
How do we explain these differences in deformation behavior, especially in the presence of hydrogen?

- Differences in chemistry may give rise to highly localized, nanoscale heterogeneities, such as short range order (SRO) domains
- Dislocations can interact with these SRO domains—a process that can be dramatically modified by the presence of hydrogen around the dislocation or the SRO domain, as our continuum models have begun to reveal

Moving dislocations interact with SRO stress fields that can induce pile-up formation along slip bands



$$\tau_{xy} = -\frac{\nu' E' E \varepsilon^T}{\left(3\nu' - 2\nu'^2(1+\nu) + E'\right)}\left(\frac{r_0}{r}\right)^2 \sin 2\theta$$



$\tau = 347.5$ MPa

Required stress to pass by SRO

So what exactly do we mean by SRO and how do we study it?

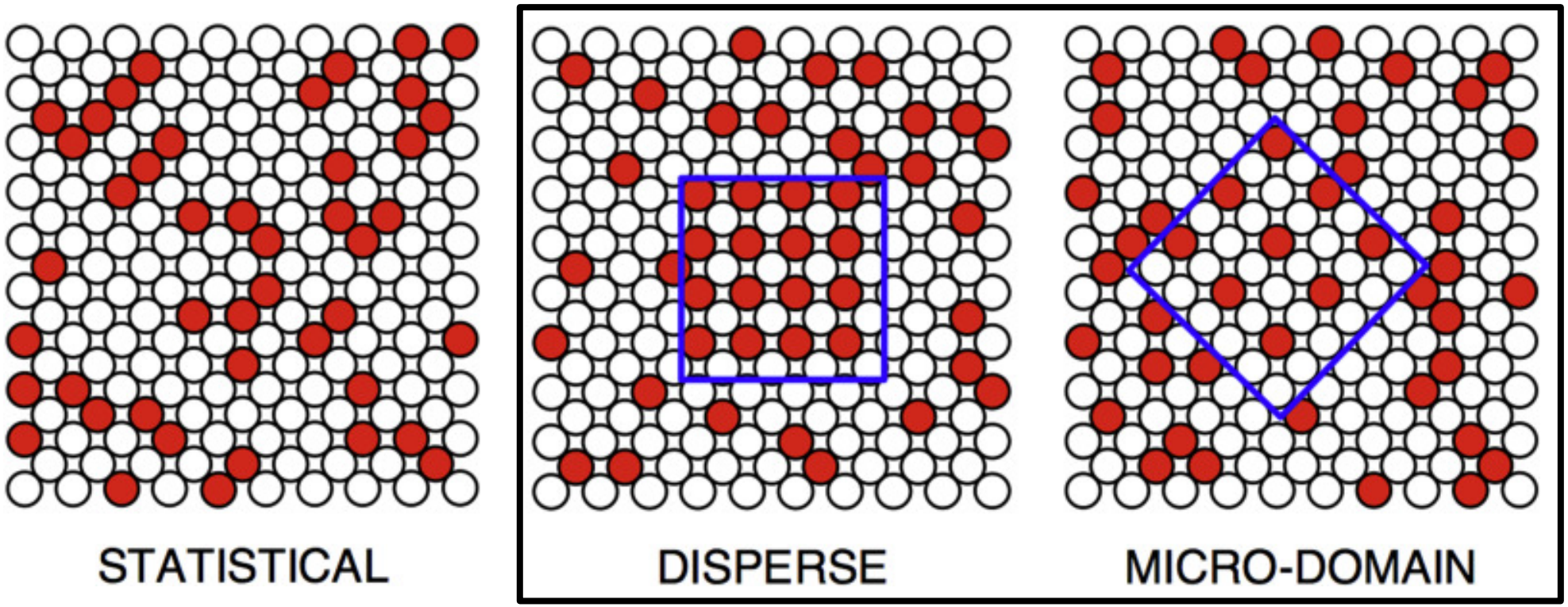
SRO in crystalline materials can be categorized into homogeneous SRO or heterogeneous SRO, and require different techniques for characterization

Homogeneous SRO

Tendency of likewise nearest neighbor pairs throughout the material

Heterogeneous SRO

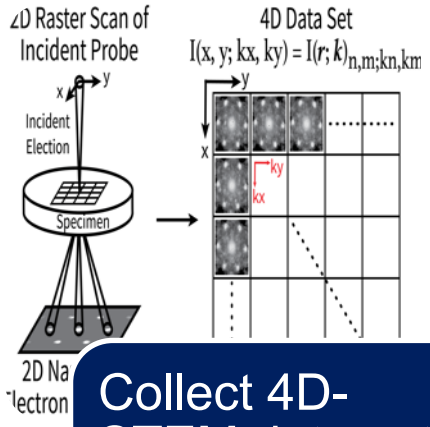
Nano-meter scale ordering/clustering domains embedded with random matrix



Owen, L. R., et al. "A new approach to the analysis of short-range order in alloys using total scattering." Acta Materialia 115 (2016): 155-166.

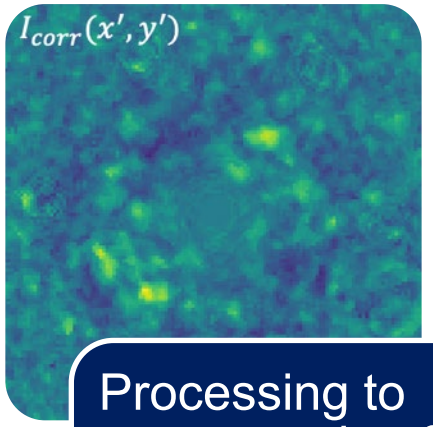
Making connections to nanoscale microstructural features: microscopy & modeling

Brief overview of our novel method for characterizing heterogeneous SRO

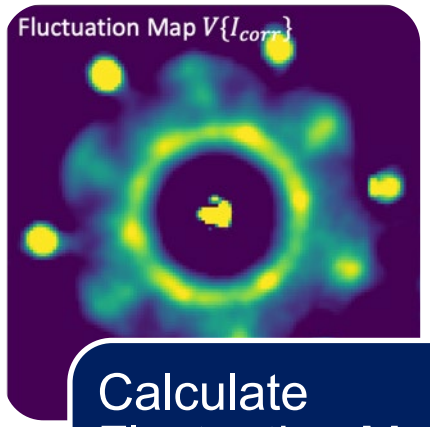


Collect 4D-STEM data set

- 200nm x 200nm arrays of NBED
- 1nm step size

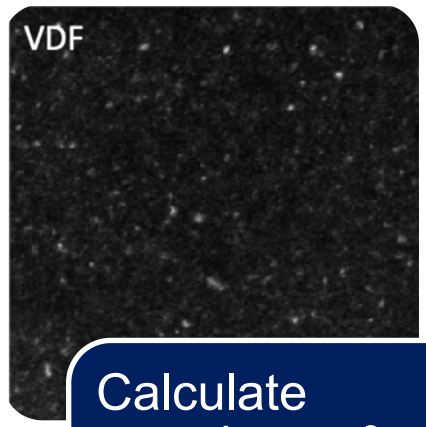


Processing to remove noise & background



Calculate Fluctuation Map

- Just normalized variance
- Localized signal only

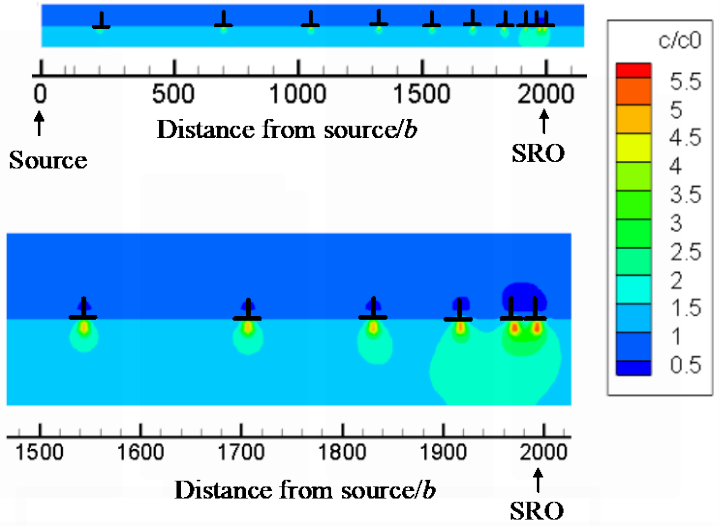


Calculate covariance & create virtual dark field images

- We can now quantify SRO domain size and spatial distribution, and are making significant progress towards understanding the unique structures of these SRO populations (some alloys show evidence of more than one type of SRO structure)
- Insight from atomistic modeling efforts continues to provide guidance on the interpretation of these data, which are primed to inform the evolving continuum models

Failure through hydrogen-induced shear localization: Linking the macroscale to microscale through atomistic modeling

H concentration: 10^{-4} H/Fe



Dynamic pile up formation and hydrogen atmospheres

- **Atomistics**

Hydrogen and composition dictate dislocation emission threshold stress, friction stress, SRO misfit strains, lattice misfit parameters, dislocation velocities

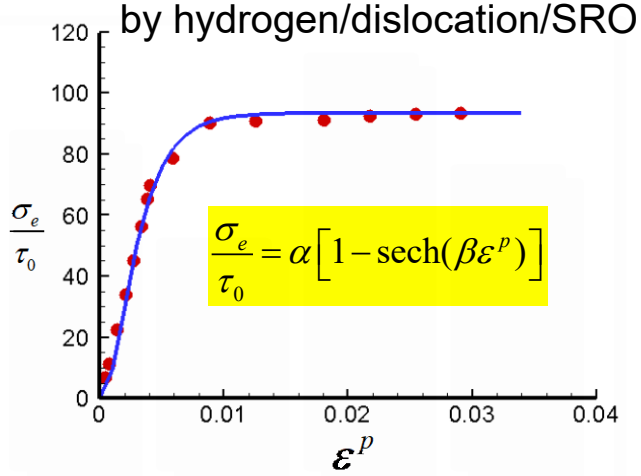
- **Micromechanics**

Modeling and simulation of dynamic pile-up formation against SRO domains yields the stress-strain relationship characterizing the localized shear band

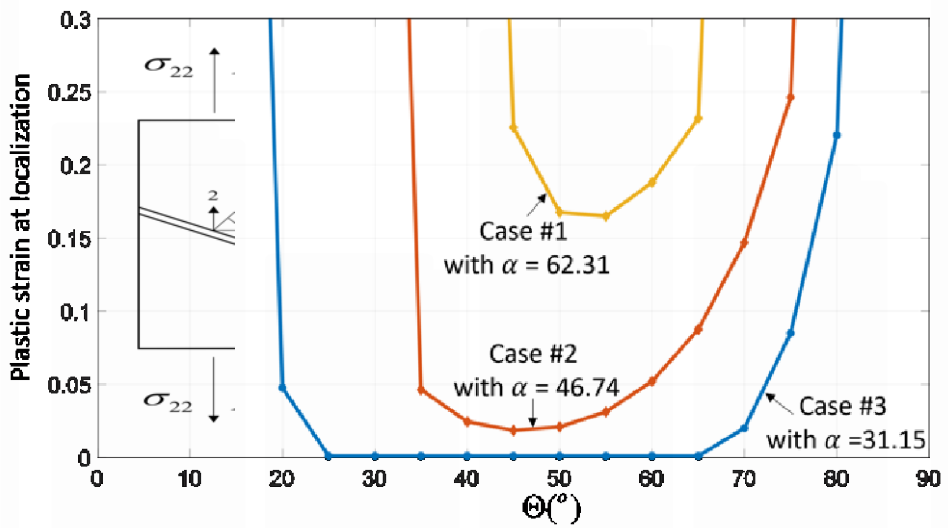
- **Continuum**

Predict the level of macroscopic loads at which the homogenous macroscopic deformation can be compatible with localized shear banding, **which defines the onset of failure**

Localized shear banding response dictated by hydrogen/dislocation/SRO interactions



Predicting the onset of stress-localization as a function of SRO strength



Highly practical advances in alloy development and fundamental understanding/prediction of hydrogen embrittlement in austenitic steels

- We developed novel austenitic alloys that have demonstrably different hydrogen tolerance under uniaxial tension, including improvements in cost/kg
  - Alone, these empirical observations are sufficient to further guide alloy development, but…
- Our advances in experimental characterization methodology (via Fluctuation Electron Microscopy) combined with the advancing continuum tools, we are also on the precipice of understanding the fundamental relationships between austenitic alloy compositions and hydrogen tolerance, for example…
- With the continuum tools that we have developed to this point, we can model how SRO domains could facilitate localized plasticity and accelerate hydrogen embrittlement
  - Further advances in our experimental characterization of SRO behavior informed by improving atomistic models will expand the utility of these continuum models and allow for specific tuning to the alloy compositions of interest

Go-no-go Milestone III.3

The local, small-scale observations in Subtasks III.C.3 and III.C.4 will be used to down-select two alloys to manufacture in larger heats (~50 lbs). These larger heats will enable more relevant mechanical testing configurations to be implemented. Selection will be made based on a ranking scheme assuming the criteria for the original downselection (phase stability, $\Delta G_{\gamma/\alpha}$ <-2100 J/mol, MD_{30}<-40ºC and SRO strength) are realized and the uncharged tensile properties meet or exceed the identified targets for Task III.C (σ_y >515 MPa, %RA>65%).

- *Target metrics are contingent upon advice from industrial partners*
  - *Both Swagelok and Linde partners have advised that σ_y >515 MPa does not satisfy their qualifications as high strength and as a result, suggest that we emphasize other metrics more consistent with hydrogen embrittlement performance*

Downselection Strategies Considered

Option #1

Low-Ni (KU2) & Al-Added KU3

- Minimum hydrogen embrittlement under uniaxial tension
- Limited evidence of SRO, especially in KU2
- Yield strength is comparable to existing commercial alloys (21-6-9 and 316L)
- Consider efforts to reduce wt%C

Option #2

Low-Ni (KU2) & High-Mn (KU4)

- KU4 has the highest yield strength, but also the greatest degree of embrittlement under tension
- Uniaxial tension is not always sufficient to assess embrittlement
- Industrial partners are interested in this compositions based on broader trends

Option #3

Basic (KU1) & Low-Ni (KU2)

- Stronger SRO presence in KU1 makes this comparison a route to better understand the mechanistic contributions of SRO to hydrogen embrittlement
- But given its similarity to 21-6-9, KU1 is commercially less viable due to increased embrittlement
- Similar goals could be met by continuing to carry 21-6-9 into the next phase

Accomplishments & Progress: Responses to Previous Year Reviewers' Comments

AMR 2021 Comment	Response
The first year focused too much on the limited scope of work and should have focused more on alloy development.	As represented in the presentation, alloys with tailored compositions developed by Kyushu University were the focus of work in the second year
Establishing a mechanistic connection between local chemistry and local deformation behavior, in combination with the appropriate technoeconomic analysis, will enable the design of cost-effective hydrogen-resistant alloys that will have impacts on both the cost and reliability of hydrogen infrastructure. A key to realizing the potential impact will be how well the knowledge/technology can be transferred to stakeholders. This was not well-described during the review.	The stakeholders Swagelok and Praxair are active partners and participate in project meetings
There is concern that, if the atomistic and continuum-level models cannot be validated by use of measurements, the work will not have the impact desired. Considerable time and effort should be expended, sooner rather than later, on determining an appropriate measurement technique to validate the modeling results.	The continuum and atomistic models that are linked judiciously are being developed based on the microstructural observations of i) the SRO lattice structure and the effect of hydrogen on the lattice and modulus mismatch with the surrounding matrix; ii) potential effect of hydrogen on destruction of the SRO domains. The synthesized model will give a design tool that can help associate the level of macroscopic loads with the onset of shear localization, which is the ultimate validation, and which can be conducted with laboratory test-pieces.
The project should look at the effect of cold work on the alloy and properties with different elemental additions and the effect of nitrogen on alloys and precipitates.	Three of the four alloys with tailored compositions developed by Kyushu University contain nitrogen. Examining the effect of cold work would indeed be valuable, since this may be the primary pathway to increasing strength and partner ORNL is helping us realize this.

Collaboration & Coordination

Partner	Project Role
University of Illinois Urbana Champaign	Project lead, management & coordination*; Sofronis (PI) & Ertekin*: Continuum & atomistic modeling; *Krogstad & Stubbins*: Microstructural characterization & mechanical testing; *Stubbins*: Technoeconomic analysis; *Somerday*: Alloy design & project oversight
Xingshuo Wen, Arcelor Mittal	Key partner: Advising on alloy development and custom alloy production
Shelly Tang, Swagelok	Key partner: Advising on application specific requirements, technoeconomic analysis, alloy development and joining
Kang Xu, Linde/Praxair	Key partner: Advising on application specific requirements, technoeconomic analysis, mechanical testing and joining
Chris San Marchi & Joe Ronevich, Sandia Livermore	H-Mat partner: H-permeation & diffusion labs, mechanical testing, advising on code & standards in alloy development
Govindarajan Muralidharan, Oak Ridge	H-Mat partner: Alloy development & processing
Toshihiro Tsuchiyma & Masanobu Kubota, Kyushu University	International partner (unfunded): custom alloy development and production, specific experience with low-Ni austenitic steels

Remaining Challenges & Barriers

Outstanding scientific questions

1. Do ordered domains or compositional clusters promote a deformation mode that is implicated in degrading hydrogen embrittlement resistance?
2. How are cluster-modified deformation modes affected by hydrogen?

Challenges

1. Unclear whether observed hydrogen resilience will persist under cyclic loading conditions
2. Proposed solutions include
    1. Larger scale production of downselected alloys
    2. Fatigue testing in collaboration with H-Mat partners

Steps towards final milestones and overall project objectives

1) Scale up at both ORNL & Kyushu University (Milestone III.4)
2) Larger specimen tension testing at ORNL, UIUC and Sandia
3) Fatigue testing with H-Mat partners at Sandia (Milestone III.5)
4) Refinement of continuum model based on fatigue data (Milestone I.4, Expected Outcome #2)
5) System-level feasibility and cost savings analysis of the identified alloys
6) Summarize and report upon established mechanistic connection between local chemistry and local deformation behavior (Expected Outcomes #1 & #3)

Summary

Key points:

1. We developed novel austenitic alloys that have demonstrably different hydrogen tolerance under uniaxial tension, including improvements in cost/kg
2. We have integrated computational methods across length scales with experimental microstructural observations to understand the consequences of SRO on alloy microstructure, stability, dislocation mobility and hydrogen interactions
3. Solicited input from industrial partners for final downselection

Steps towards future milestones:

1. Scale up of downselected alloys and performance of more advanced deformation experiments
2. Input and refinement of predictive continuum models that will ultimately be leveraged to design cost effective hydrogen resilient austenitic alloys