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

DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting
May 7, 2024

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DOE Project Award EE0008828

Project ID IN021

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*: $1,177,945
    - Cost Share Funds Spent*: $340,851

* As of 2/28/2024

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

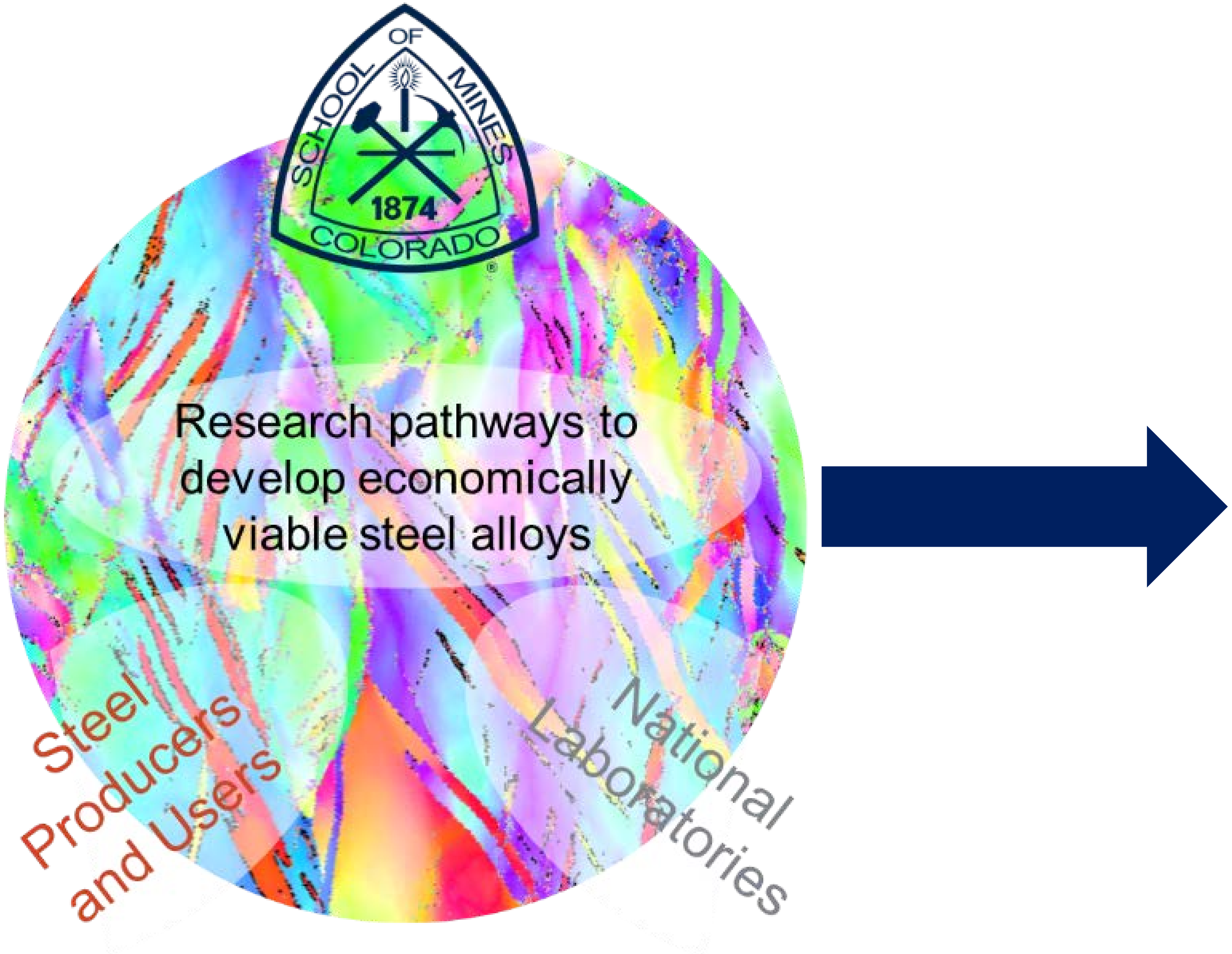
General Motors

H-Mat Consortium (Sandia National Lab)

Chevron

POSCO (cost share participant)

Potential Impact



Research pathways to develop economically viable steel alloys

Steel Producers and Users

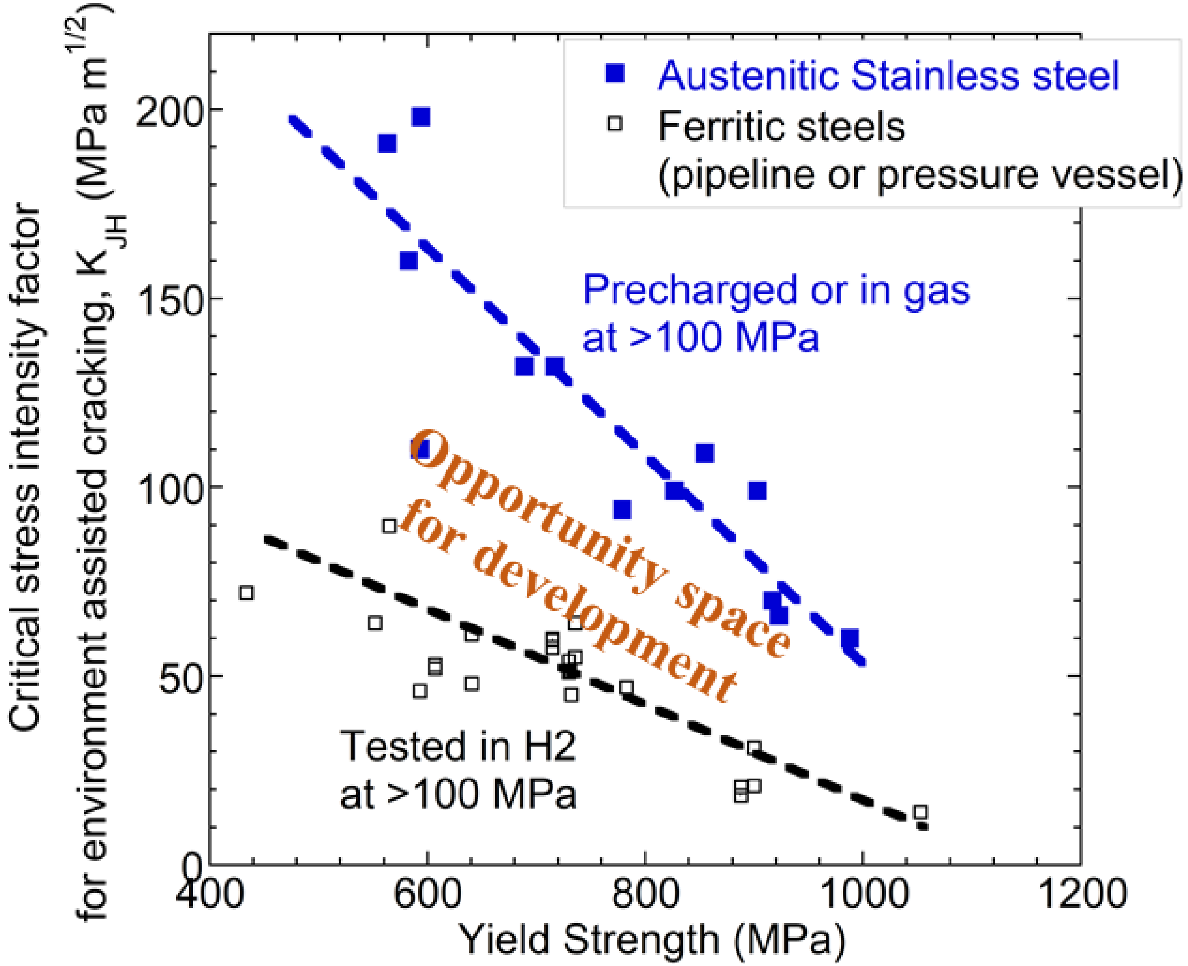
National Laboratories

U.S. produced alloys for economic competitiveness and hydrogen fueling infrastructure reliability

Approach – Safety Planning and Culture

- This project was required to submit a safety plan to HSP
  - A re-submittal was not required
  - The nature of H environments was clarified
- Safety culture applied to this project
  - For the specific labs involved in this project, each user undergoes training with personnel who manage the laboratories and are approved for use after demonstrating safe use of the pertinent equipment.
  - For new experiments, experimental apparatus designs and procedures are reviewed by the researcher, principal investigator, lab manager, and if necessary, EHS .
  - We currently inspect the glassware and seals used for solution containment upon every use. We also monitor wire sheathing on outside of the containment and applied insulation on wire that sits inside of the containment to ensure there is no improper exposure to the users and environment.

Overall Approach



Remaining Milestones:

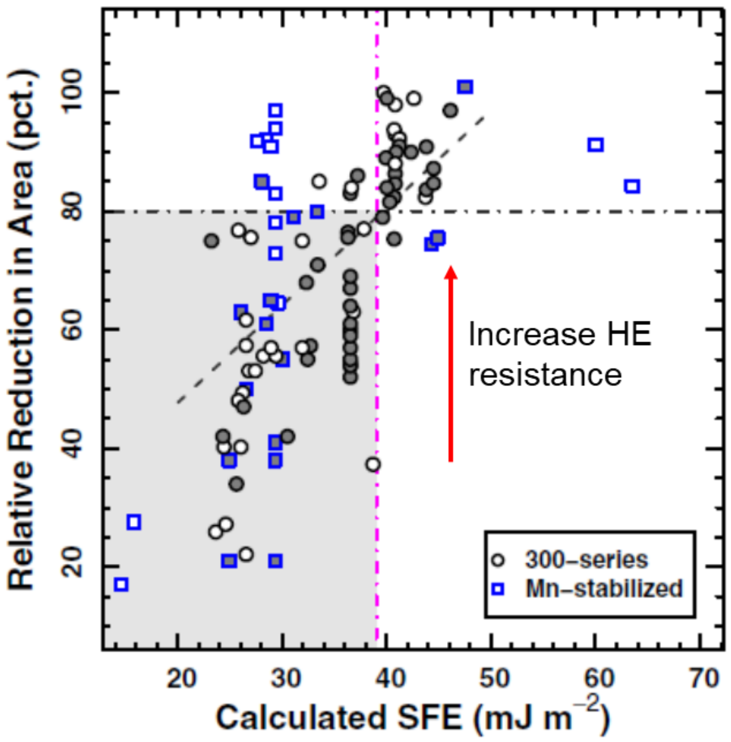
- Refined alloy conditions with enhanced combinations of strength (within the 400-800 MPa level), toughness in hydrogen, and economic viability
  - Austenitic and Duplex design approaches

- Electrochemical methods that produce comparable results to gaseous hydrogen charging

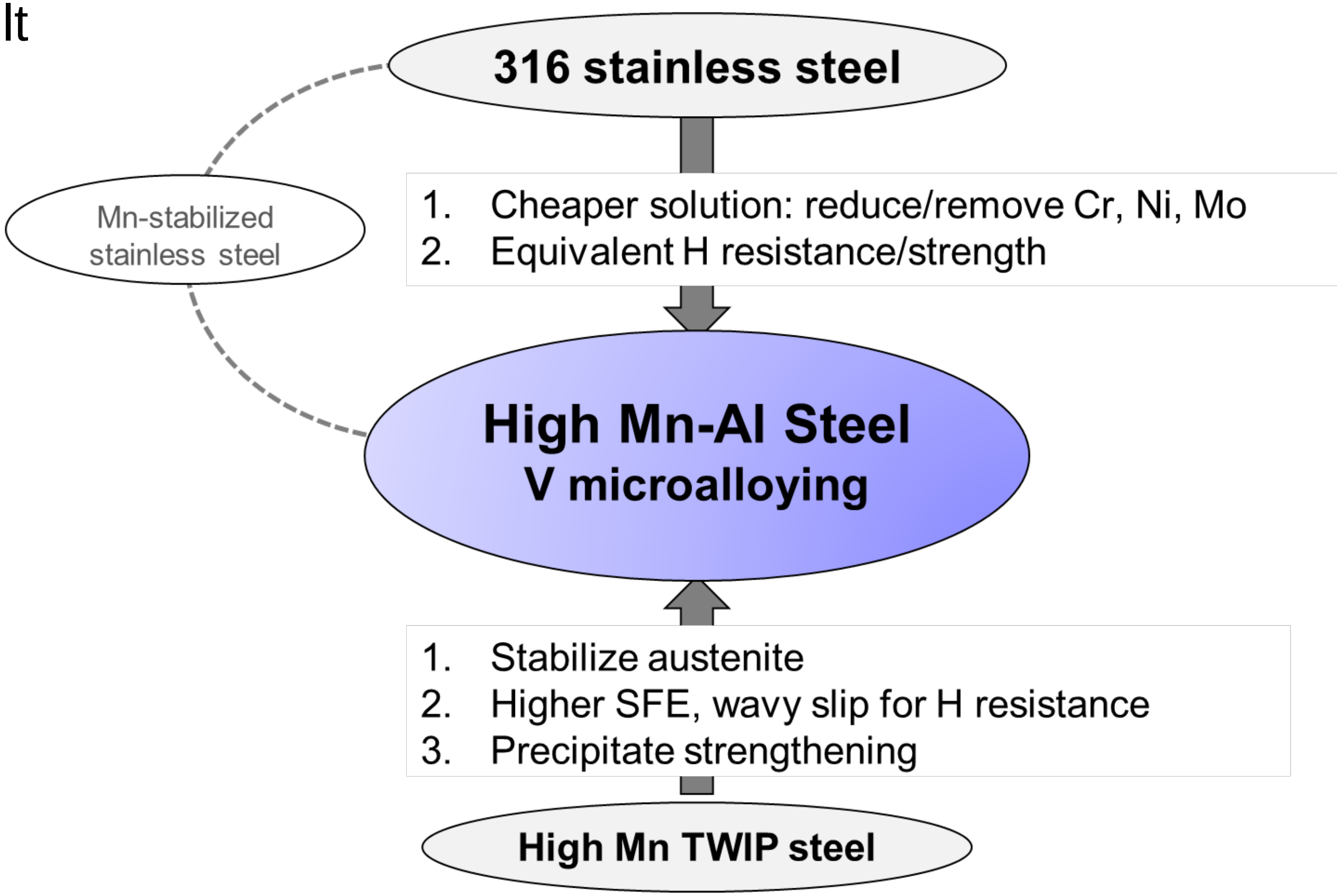
- Final Project meeting

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



316 stainless steel

Mn-stabilized stainless steel

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

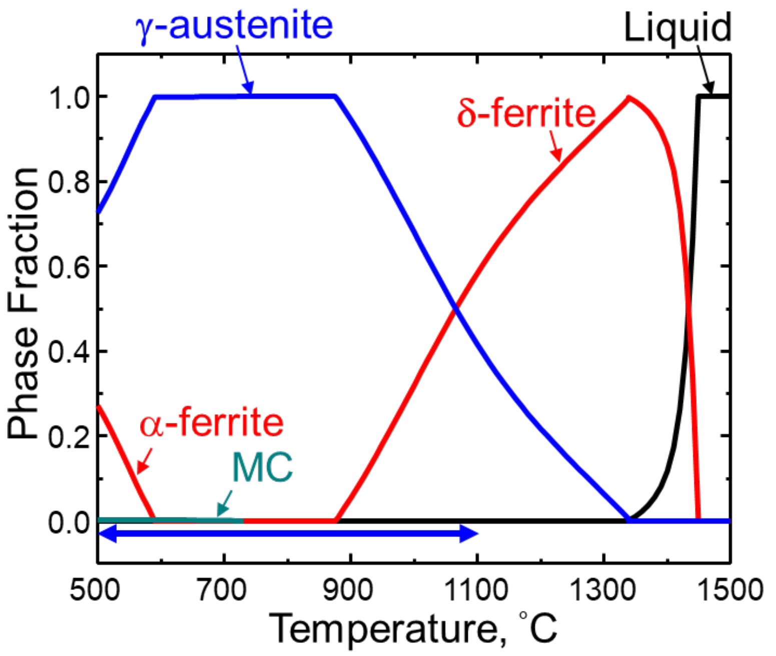
High Mn-Al Steel
V microalloying

1. Stabilize austenite
2. Higher SFE, wavy slip for H resistance
3. Precipitate strengthening

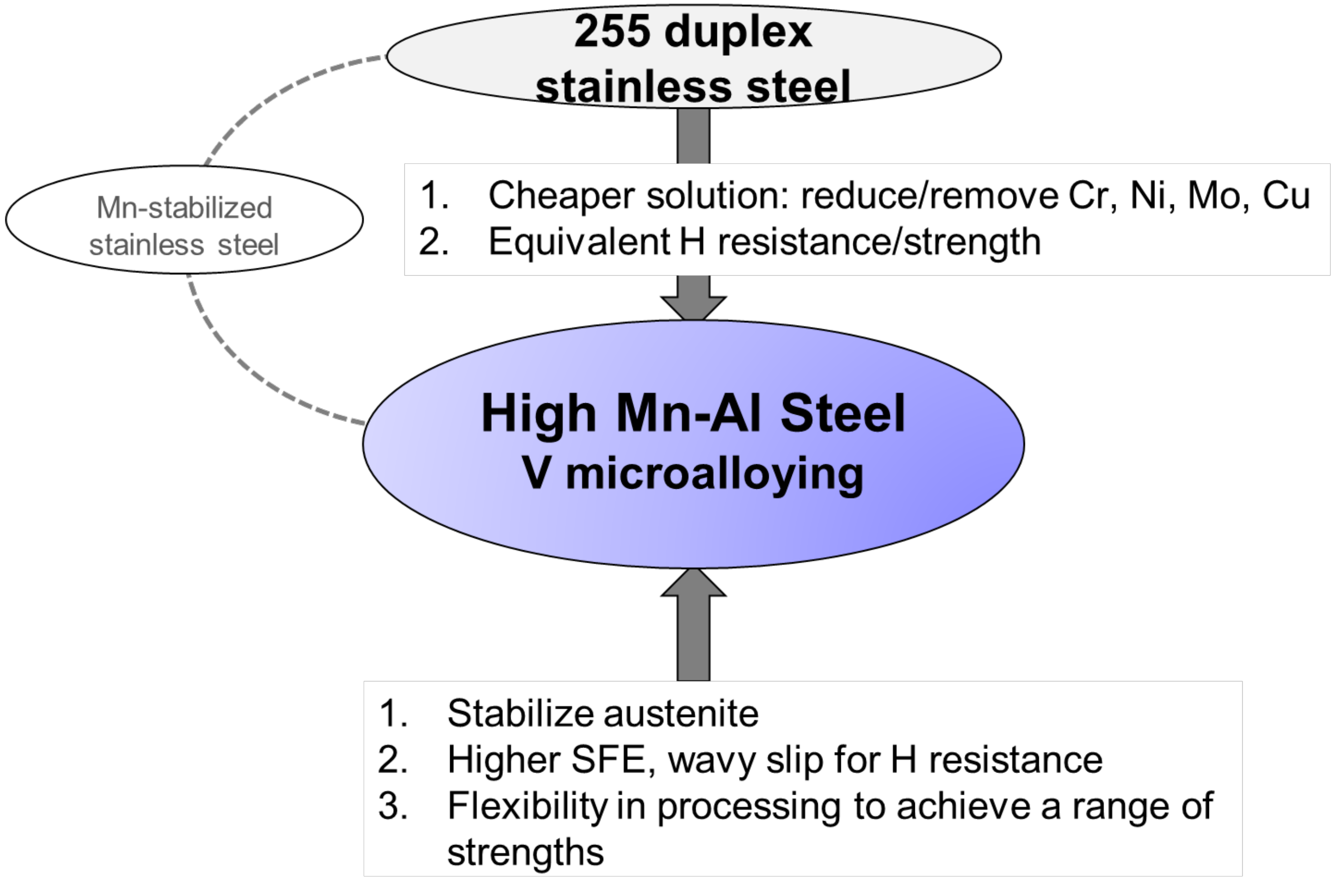
High Mn TWIP steel

Approach – Ferrite-Austenite Microstructures

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



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



255 duplex stainless steel

Mn-stabilized stainless steel

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

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)

	Fe	Cr	Ni	Mo	Cu	Mn	Si	C	N	Ti	Nb	SFE (mJ/m^2)
255 Duplex Stainless Steel	Bal.	25.9	6.21	3.28	1.56	0.87	0.38	0.018	0.16	-	-	
316L Austenitic Stainless Steel	Bal.	17.57	12.97	2.71	0.22	1.25	0.59	0.017	0.048	0.002	0.03	~ 40

High Mn Austenitic Steel Compositions (wt pct) – produced by POSCO

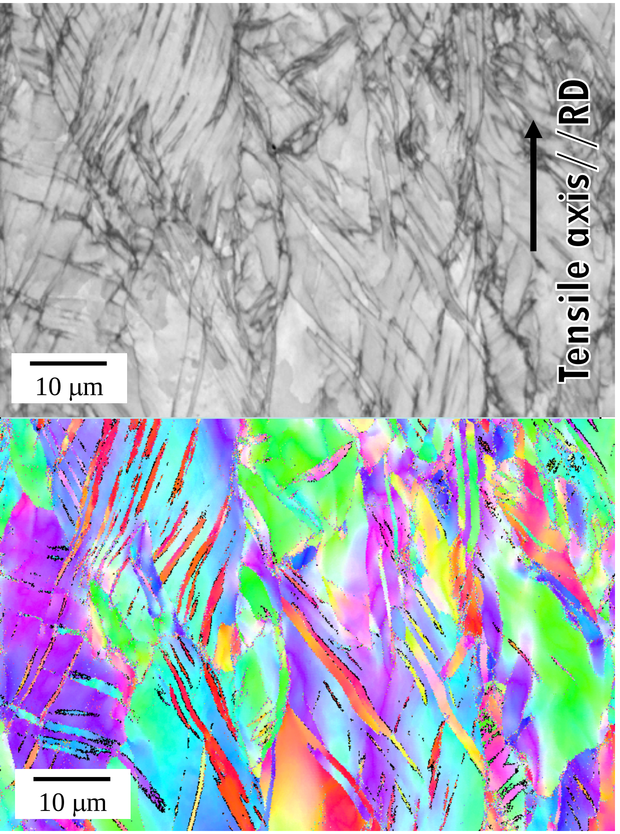
Alloy	Fe	C	Mn	Cr	Al	Ni	SFE (mJ/m^2)
LSFE (POSCO alloy)	Bal.	0.24	30.0	2.73	-	-	28.9
HSFE (POSCO alloy)	Bal.	0.25	30.4	2.71	1.75	3.0	49.0

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

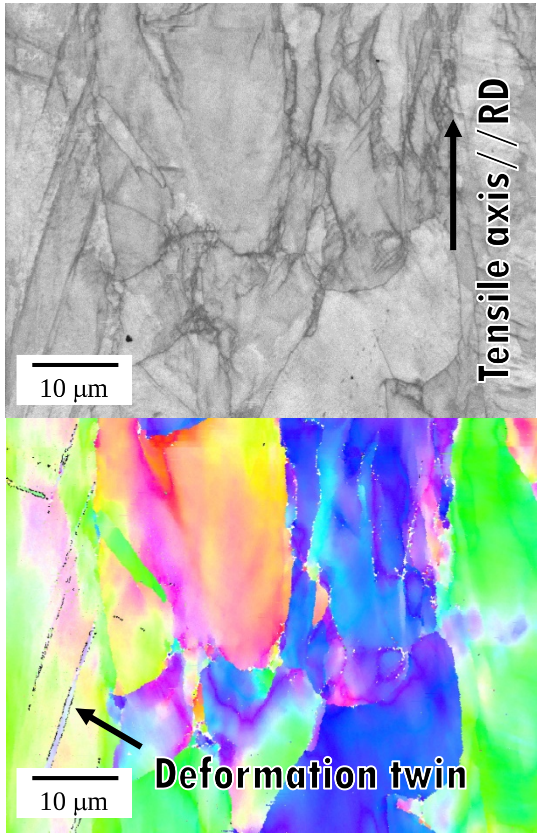
	Fe	C	Mn	Al	Ni	V	S
Duplex (2021)	Bal.	0.115	20.9	5.81	-	0.102	0.0137
Duplex (New)	Bal.	0.148	20.3	~6.3	-	0.108	0.0024
Austenitic	Bal.	0.262	29.6	1.66	2.87	0.243	0.00996

Accomplishments: Austenitic Alloy H-Embrittlement Resistance

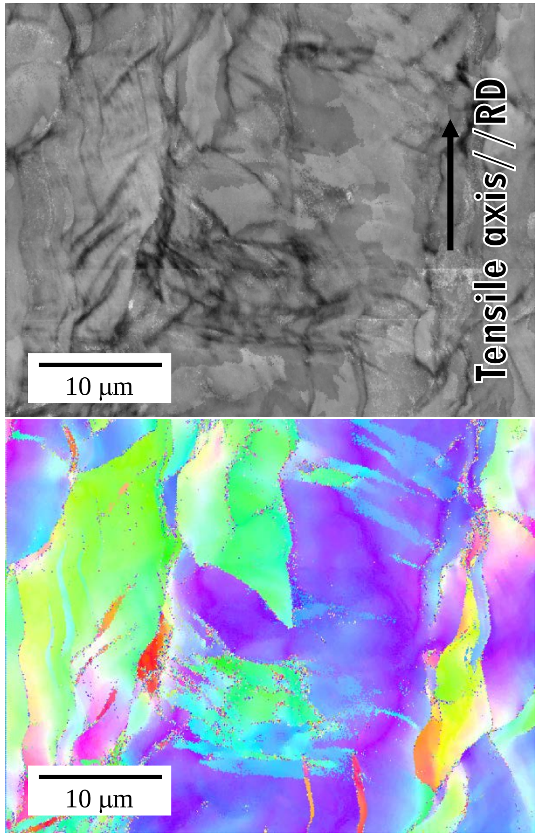
LSFE, Deformed in air



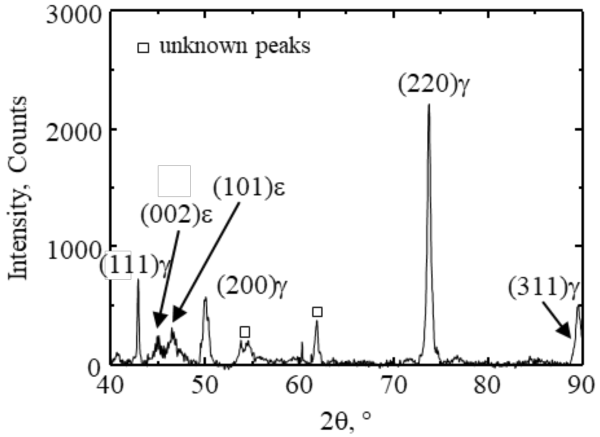
HSFE, Deformed in air



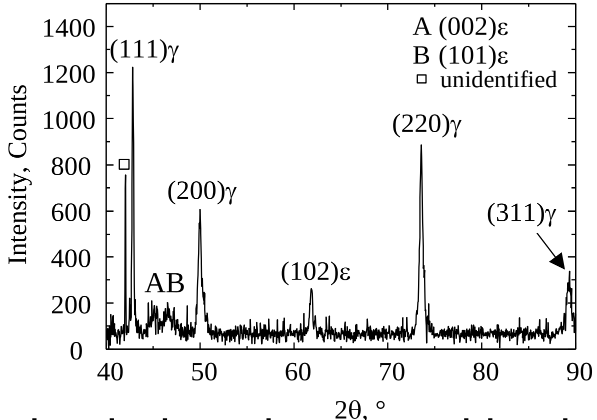
V-microalloyed, Deformed in air



LSFE



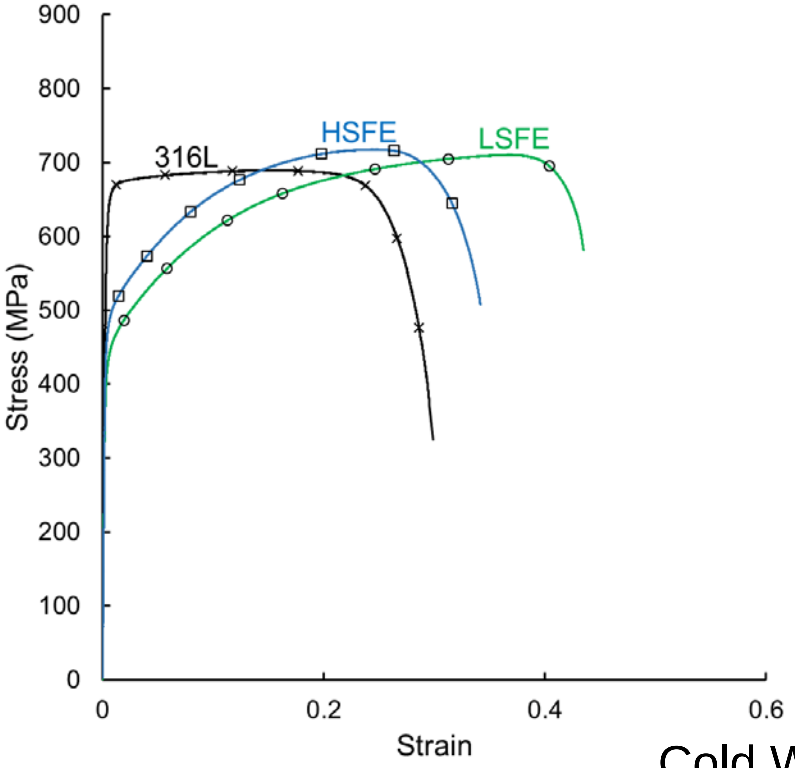
Designed V-Microalloyed

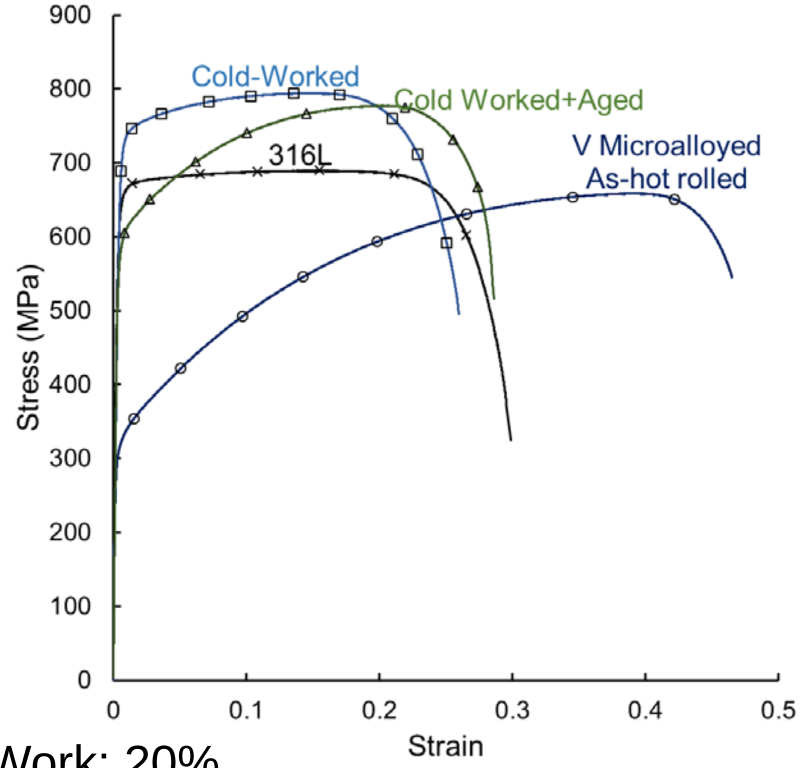


Alloy design influences deformation mechanisms (e.g. planar slip mechanisms) related to HE resistance

Deformation induced martensitic phase transformation in H1 and designed alloy

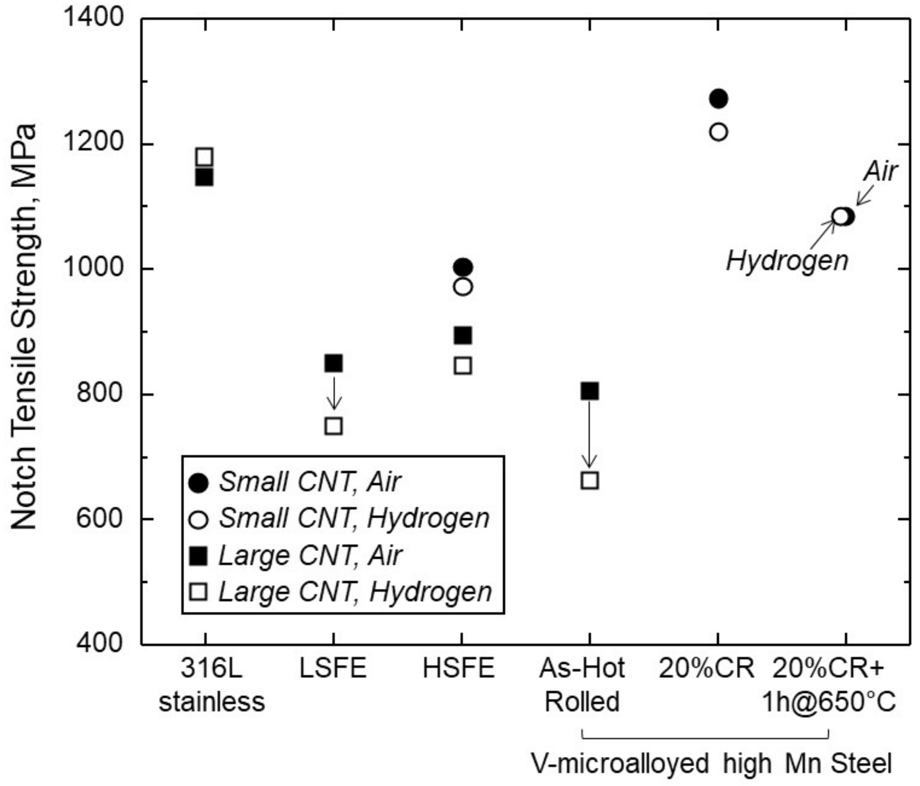
Accomplishments: Austenitic Alloy H-Embrittlement Resistance





Cold Work: 20%
Aging T: 650 °C

Alloying and cold working/ aging can be tailored for strengthening

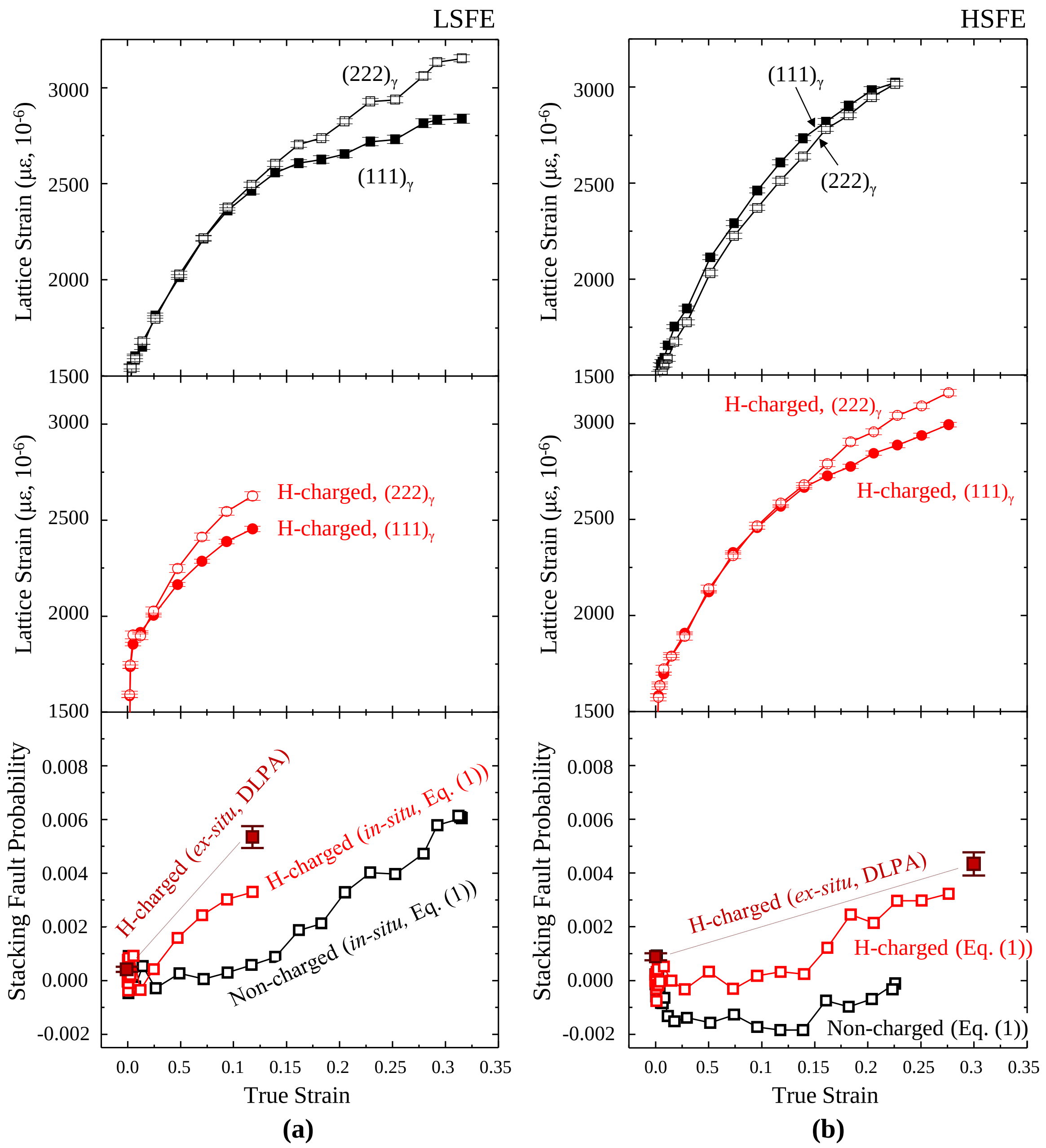


Alloy Design + Thermomechanical Processing resulted in comparable strength and HE performance to baseline 316L stainless

Accomplishments: Neutron Diffraction of Austenitic Alloys

Non-charged

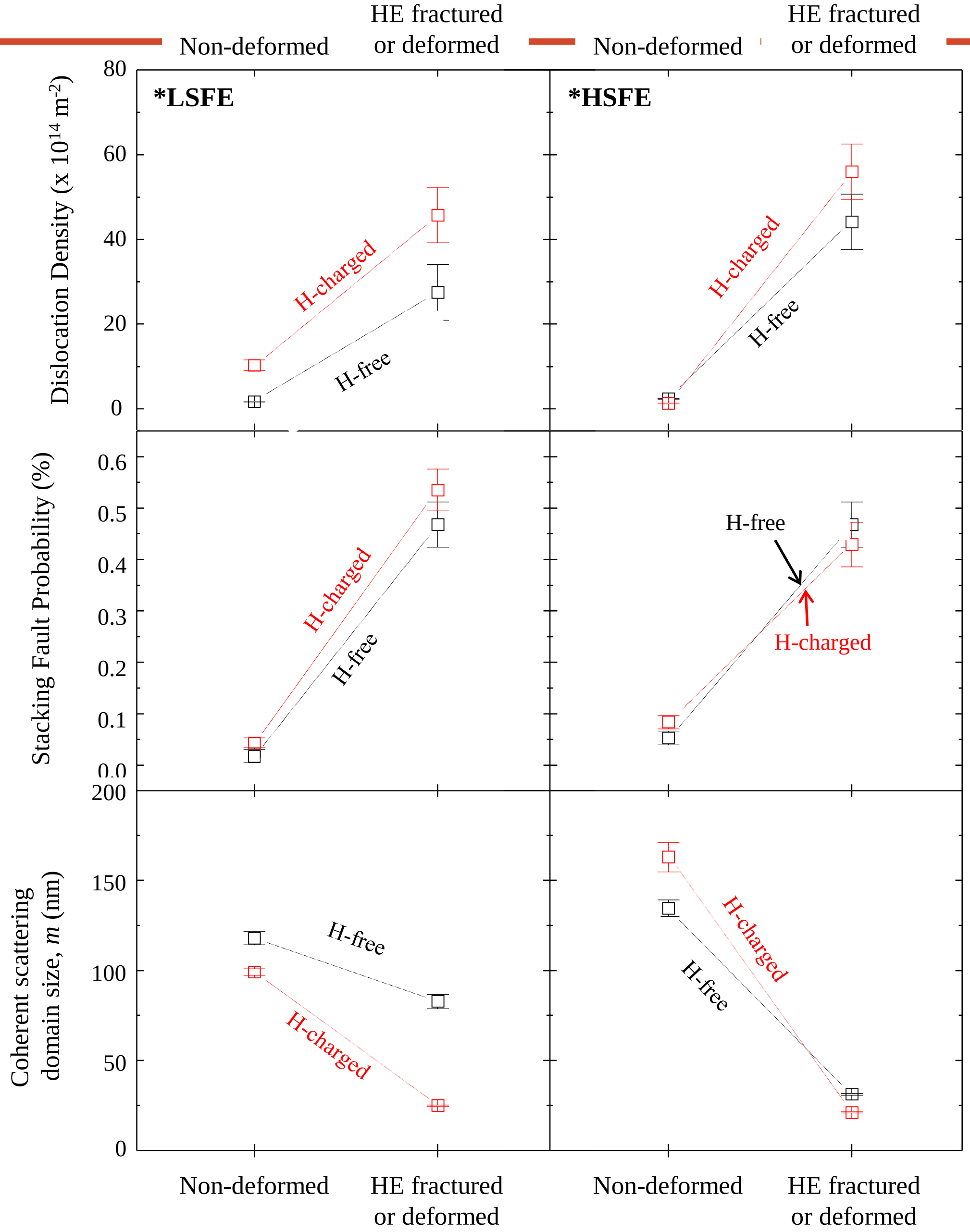
H-charged



Non-charged neutron data indicates stacking fault formation in lower stacking fault energy alloy

Hydrogen promotes stacking fault formation at lower strains

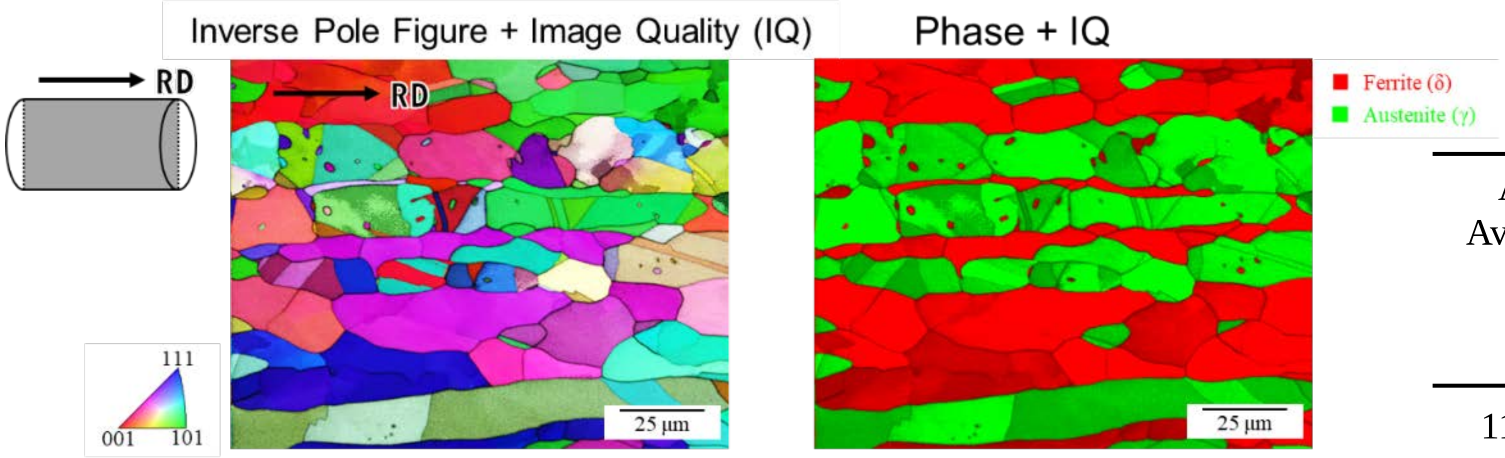
Accomplishments: Neutron Diffraction of Austenitic Alloys



Dislocation density and coherent scattering domain size also affected by hydrogen

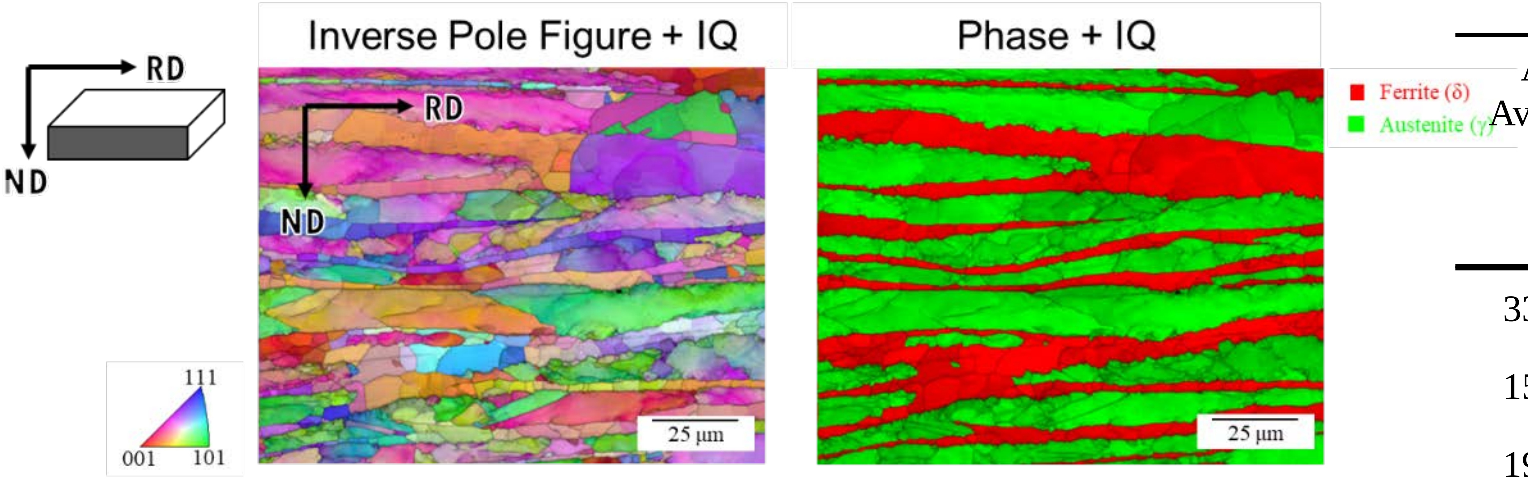
Accomplishments: Duplex Alloy H-Embrittlement Resistance

255 Duplex



Area-Weighted Average Grain Size (µm)		Phase Fraction (pct)	
γ	δ	γ	δ
11.61	28.48	39	61

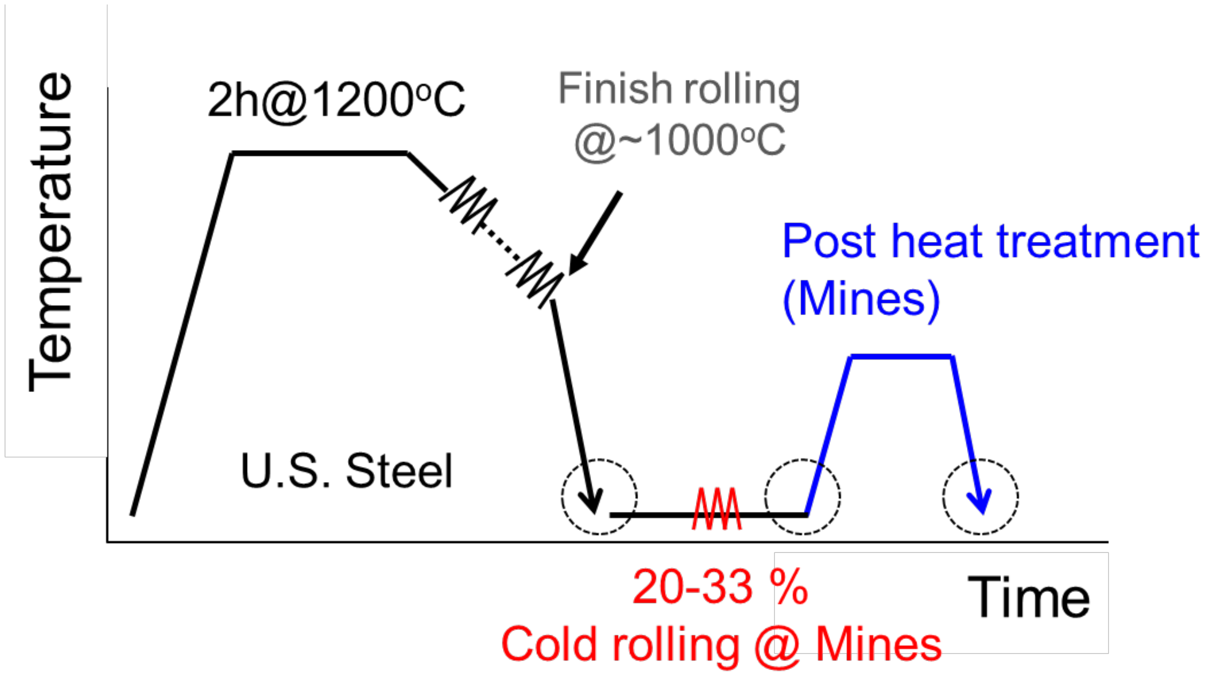
High Mn Designed Alloy



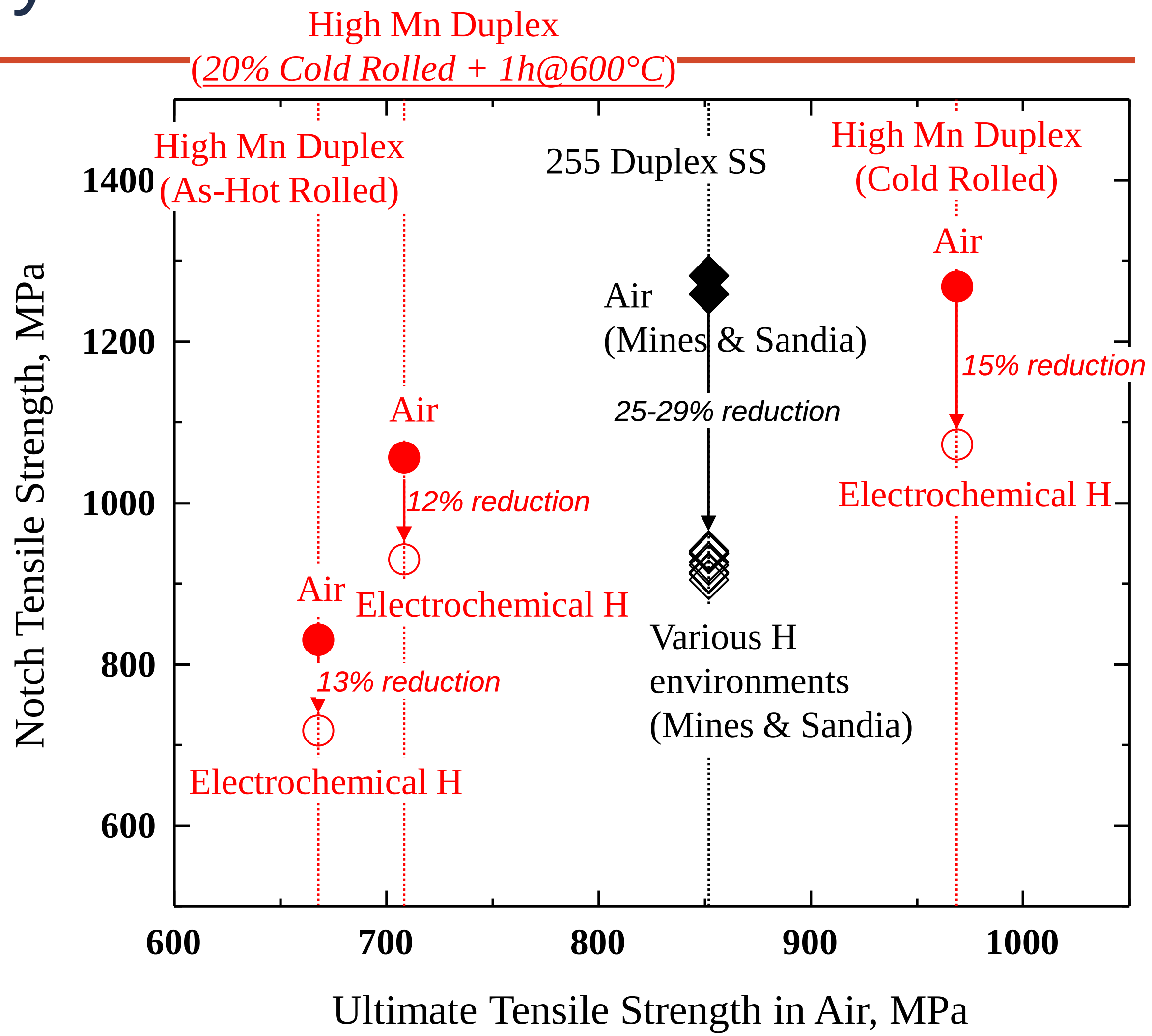
Area-Weighted Average Grain Size (µm)		Phase Fraction (pct)	
γ	δ	γ	δ
33.80	25.08	58	42
15.64	27.54		
19.72	28.34		

Alloy design and thermomechanical processing
affects phase fraction and morphology

Accomplishments: Duplex Alloy H-Embrittlement Resistance

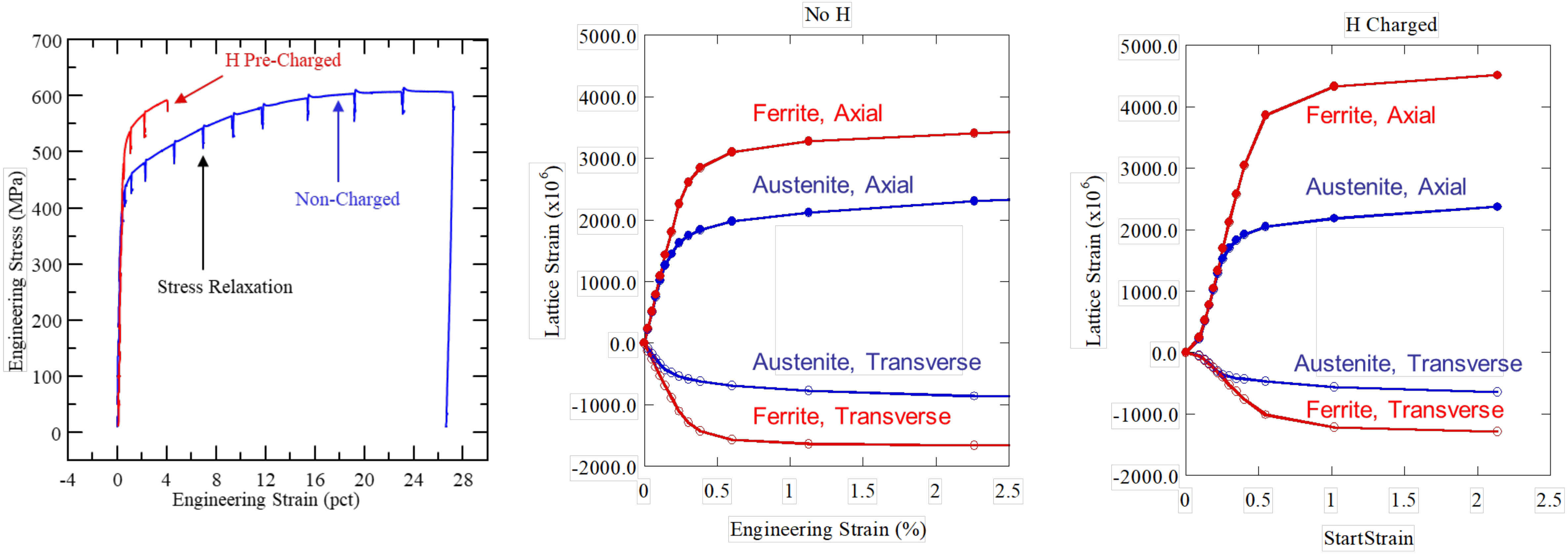


Cold working and aging can be tailored for strengthening



Alloy Design + Thermomechanical Processing resulted in comparable strength and *better HE performance* than baseline 255 Duplex stainless

Accomplishments: Neutron diffraction of Duplex Alloys

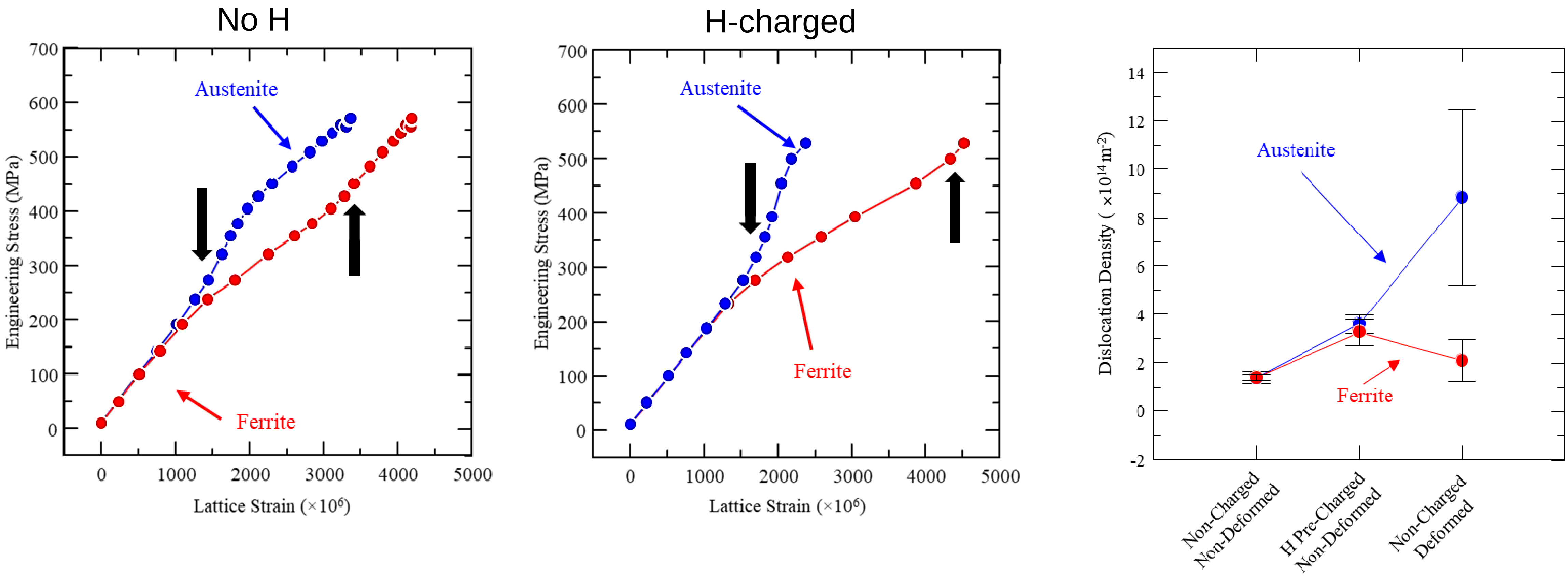


High Mn Duplex

LANSCE measurements indicate H effects on stress partitioning between ferrite and austenite phases

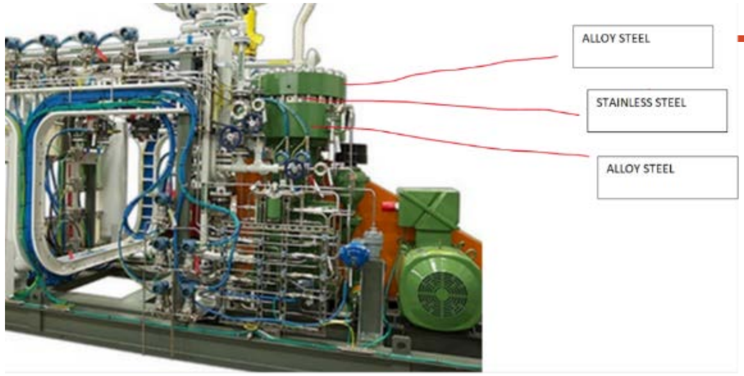
Accomplishments: Neutron diffraction of Duplex Alloys

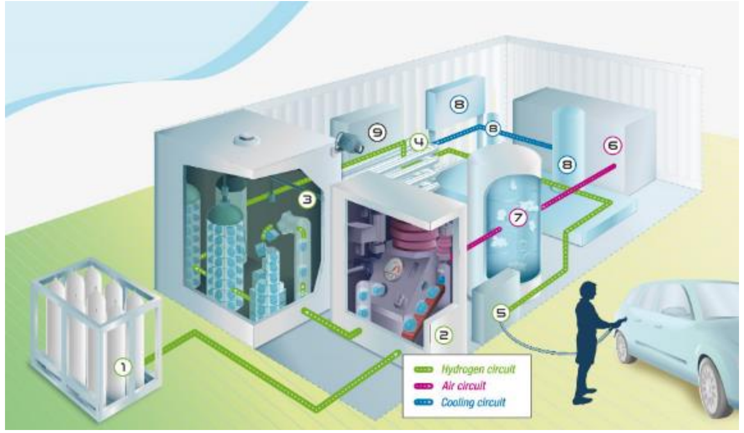
High Mn Duplex

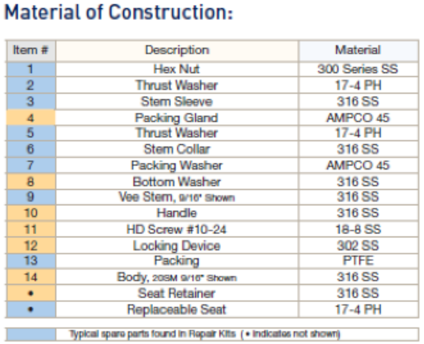


LANSCE measurements indicate H effects on stress partitioning between ferrite and austenite phases

Accomplishments: Technoeconomic Analysis



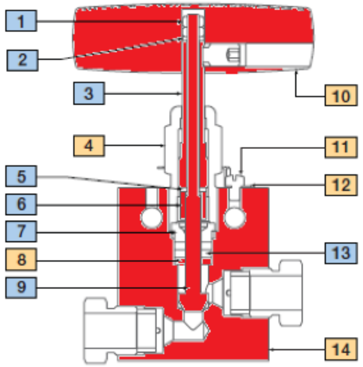




Material of Construction:

Item #	Description	Material
1	Hex Nut	300 Series SS
2	Thrust Washer	17-4 PH
3	Stem Sleeve	316 SS
4	Packing Gland	AMPCO 45
5	Thrust Washer	17-4 PH
6	Stem Collar	316 SS
7	Packing Washer	AMPCO 45
8	Bottom Washer	316 SS
9	Vee Stem, 9/16" Shown	316 SS
10	Handle	316 SS
11	HD Screw #10-24	18-8 SS
12	Locking Device	302 SS
13	Packing	PTFE
14	Body, 20SM 9/16" Shown	316 SS
•	Seat Retainer	316 SS
•	Replaceable Seat	17-4 PH

🟦	Typical spare parts found in Repair Kits (• indicates not shown)



<u>Estimated liquid steel prices</u>

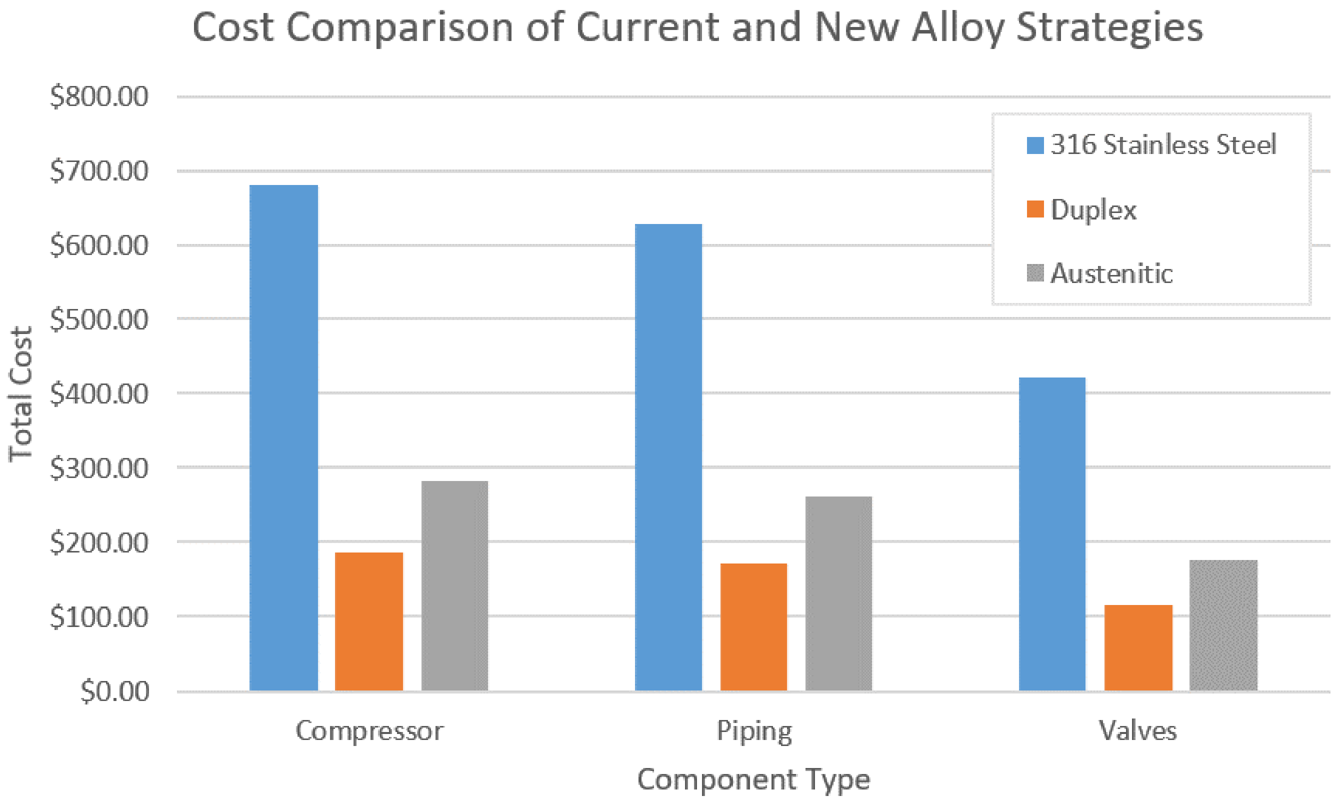
316 SS: $6,658/ton

<u>New alloys</u>

Med. Mn Duplex: $1,824/ton

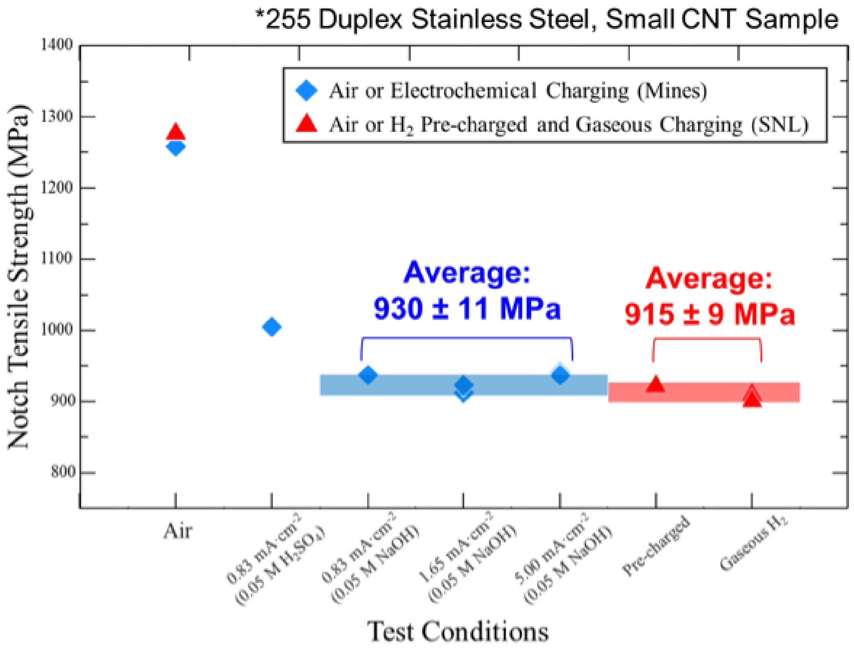
High Mn Austenitic: $2,769/ton

Important to consider additional cost assumptions

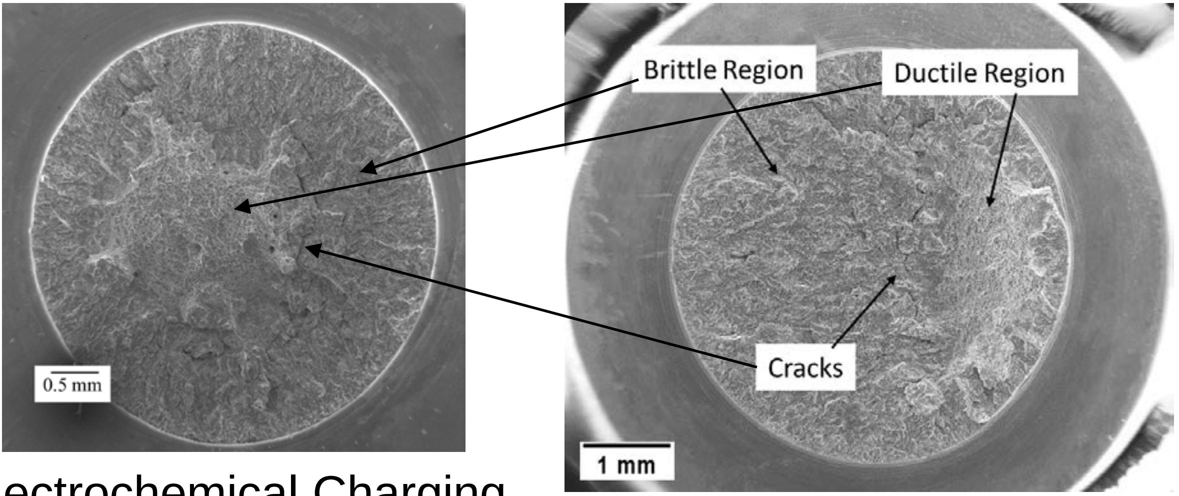


Responses to 2023 Review Comments

- “The project provides a clear description of the metallurgical factors needing to be addressed, a logical plan for composition modification, and elegant and unique neutron-scattering work.” **Overall Score: 3.5**
- Hydrogen testing methodology, e.g. electrochemical versus gaseous charging
  - ➢ We are employing notched tensile testing in both electrochemical and gaseous hydrogen charging environments as well as select fracture toughness experiments in gaseous hydrogen



255 Duplex Stainless Steel



Electrochemical Charging

In-situ Gaseous Charging

Responses to 2023 Review Comments

- "It is unclear how the neutron scattering information will help reveal the deformation mechanisms for the alloys under investigation."
  - The focus of the neutron diffraction work is on the onset of stacking fault formation, which is indicative of planar slip, and is affected by both stacking fault energy and hydrogen.
  - We are also observing hydrogen effects on stress partitioning in the duplex alloy and dislocation density.
  - We will target linking hydrogen embrittlement susceptibility and future alloy design to these clearly observed deformation mechanisms.

Collaboration and Coordination

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

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
- Assessment of next steps for industrial implementation

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

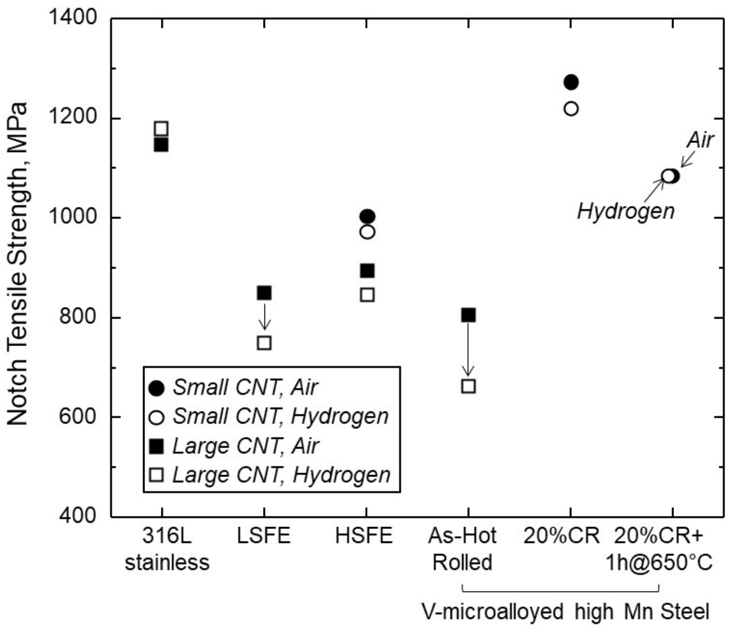
- Remainder of FY 2023

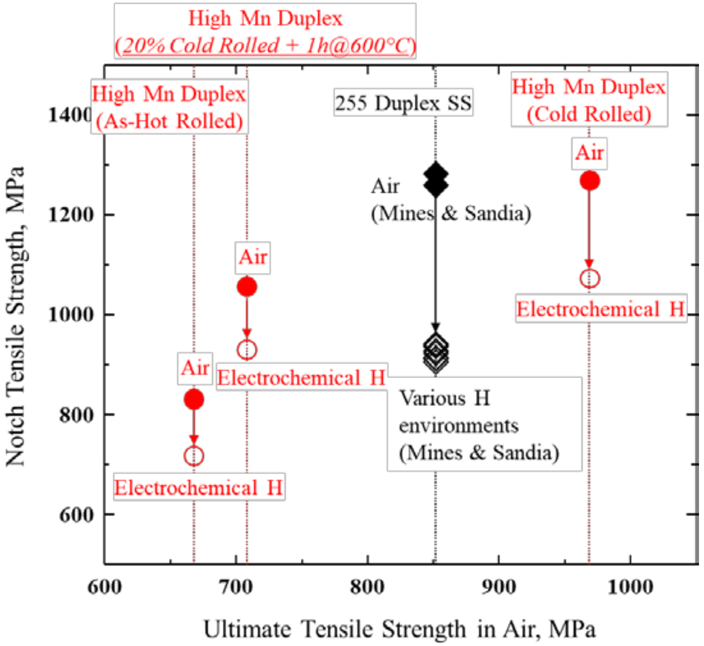
Material	Processing Condition	Expected Microstructure
Duplex Steel Ingot 2 (25.4 mm thick)	As-received (Hot Rolled)	Alternating Austenite and Ferrite Bands
	Heat Treatment (1000 – 1100 °C)	Equiaxed Austenite and Ferrite Grains
	Warm Rolling (~30 pct)	Alternating Austenite and Ferrite Bands

  - *Identify most promising alloy and process conditions based on strength, hydrogen embrittlement resistance, and cost*
- Completion Date: May 31, 2024
  - We will continue exploring processing paths and associated HE resistance (Y. Kong Ph.D thesis)
  - We will continue to engage with industry partners to maintain industrial relevance and explore tech transfer opportunities

Summary

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





- 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