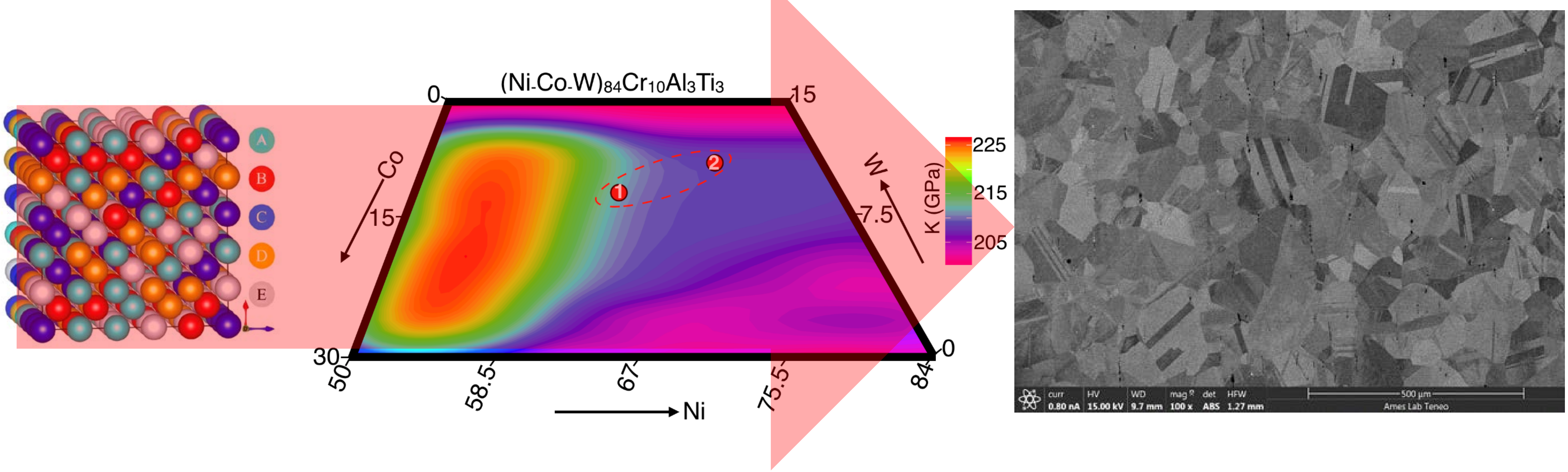

Predictive Design of Novel Ni-based Alloys

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U.S. DEPARTMENT OF ENERGY

IOWA STATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

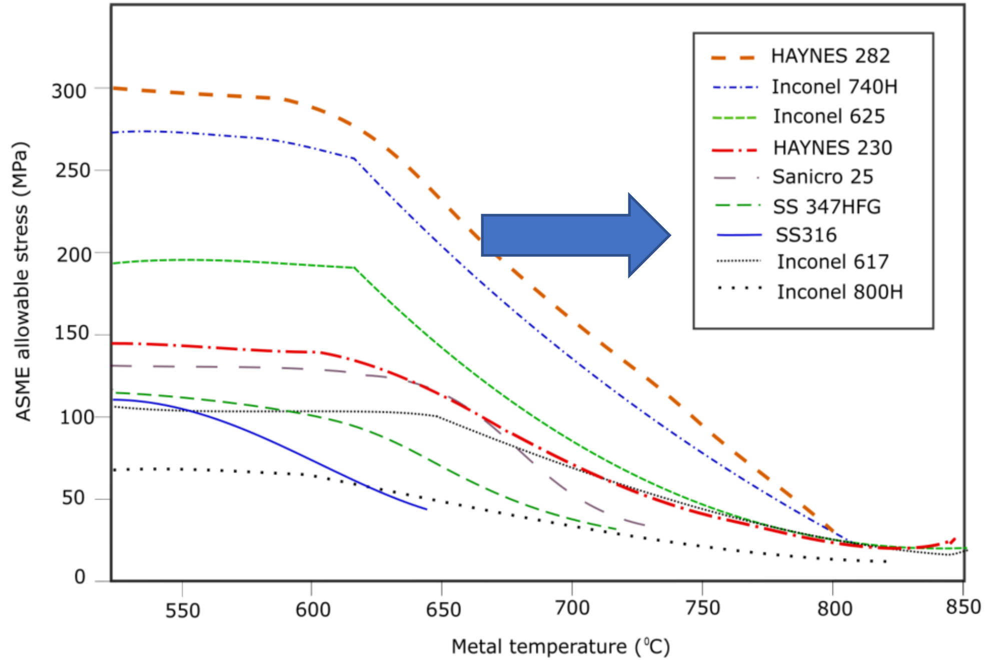
Project Description and Objectives

Develop new alloys that can perform at elevated temperatures in supercritical steam and CO_2 environment.

Use advanced computational tools, validated by targeted experiments, to increase operating temperature of Haynes-282 by 50°C

Enable AUSC to operate above 760°C and 5000 psi

Provide 'plug-in-play alloy' alloy compatible with current Ni-based alloy production.



Challenge is to develop an efficient, high fidelity multi-element alloy design tool

Also applicable to other applications

Timeline of the project milestones

Milestone Designation	Milestone Description	Revised Due date	Completion date
1	Baseline modeling of phase stability	09/30/2019	**12/31/2019**
2	Baseline characterization of H-282: dry air	09/30/2019	**09/30/2019**
3	Baseline modeling of Ames alloys	3/31/2020	**3/31/2020**
4	Fabricate and characterize Ames alloys	8/31/2020	**9/31/2020**
5	Finalize selection of Ames Alloys	12/31/2020	**12/31/2020**
6	Mechanical testing H- 282	9/30/2021	**9/30/2021**
7	Creep characteristics of Ames alloys	9/30/2021	**9/30/2021**
8	Oxidation resistance of Ames alloys	06/30/2022	**In progress (90%)**
9	Mechanical Properties of alloys with revised heat treatment	06/30/2022	**In progress (90%)**

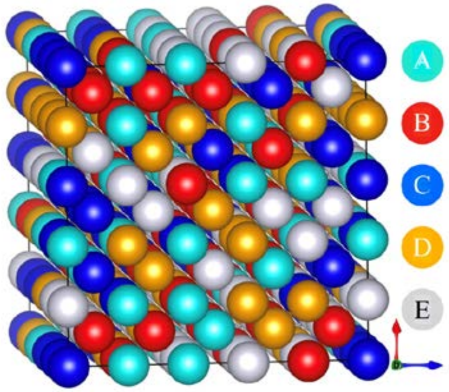
Current Status of Project

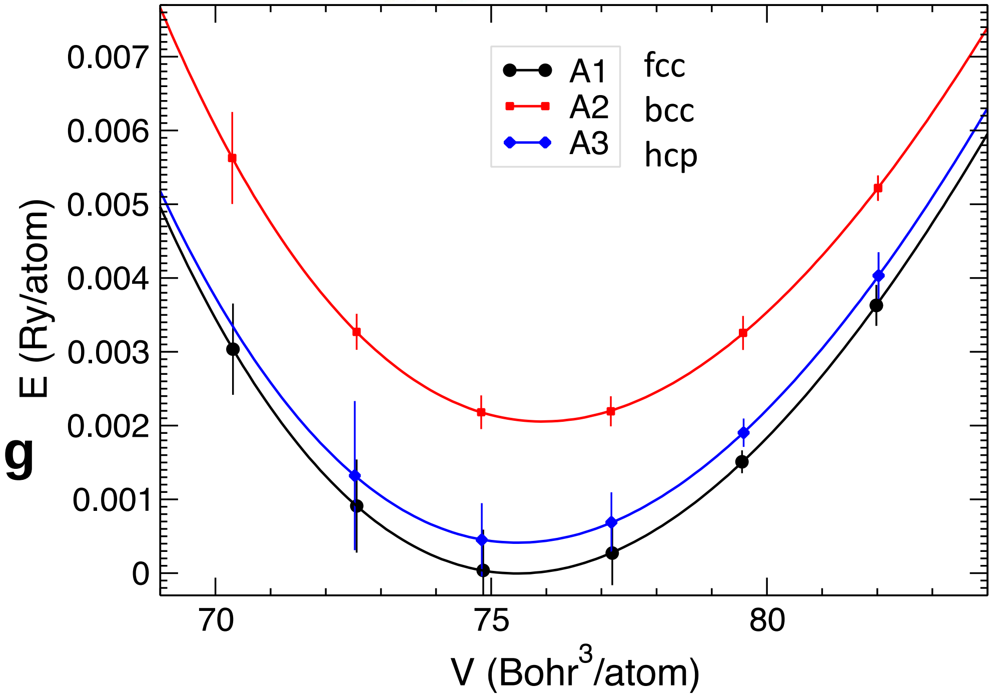
Modeling Approach

- **Korringa-Kohn-Rostoker method and coherent potential approximation (KKR-CPA)**
  - **Highly efficient electronic structure method that allow for complex chemistries using smaller model sizes compared to DFT.**
- **Mean-field approximation of the T_m**
  - **Includes short-range ordering and clustering**

Accurately models complex chemistries to predict phase stability

Singh, Prashant, Gupta, Shalabh, Thimmaiah, Srinivasa, Thoeny, Bryce, Ray, Pratik K, Smirnov, Andrei V, Johnson, Duane D & Kramer, Matthew J. Vacancy-mediated complex phase selection in high entropy alloys. *Acta Mater* **194**, 540-546 (2020).





The equation of state E(V) calculation for the fcc, bcc, and hcp phases for Haynes-282: $Ni_{0.567}Cr_{0.224}Co_{0.099}Mo_{0.052}Ti_{0.026}Al_{0.032}$

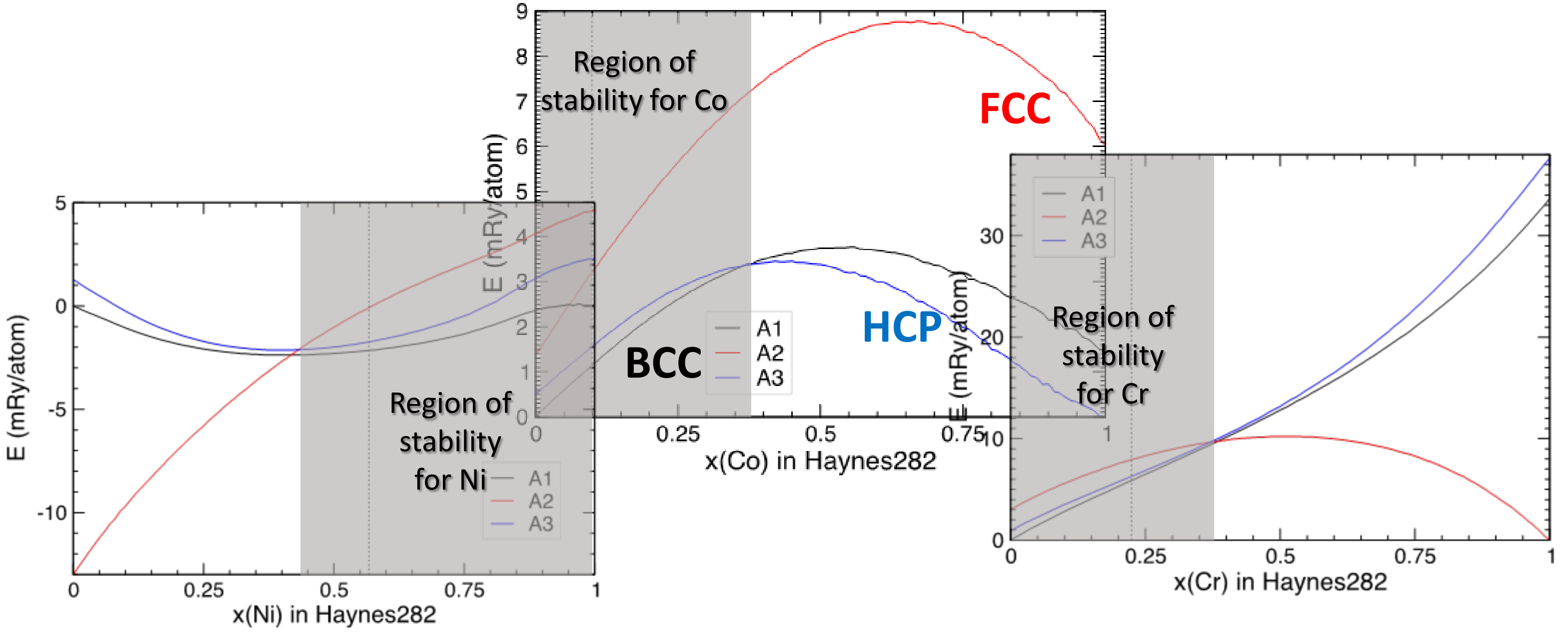
Model Prediction

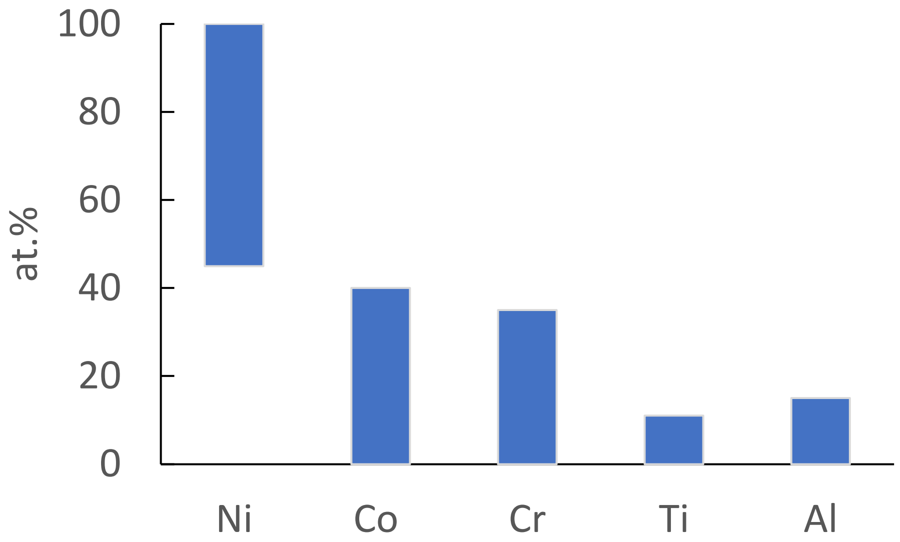
Significant compositional range for alloy optimization

Investigate role of major element substitutions.

- Shaded regions show the extend to solid solution for each element (Ni, Co and Cr) in a fcc matrix compared to bcc and hcp)

Ni > 45 at. %; Co < 40 at. %; Cr < 35 at. %; Mo < 17 at. %; Ti < 11 at. %; Al < 15 at. %



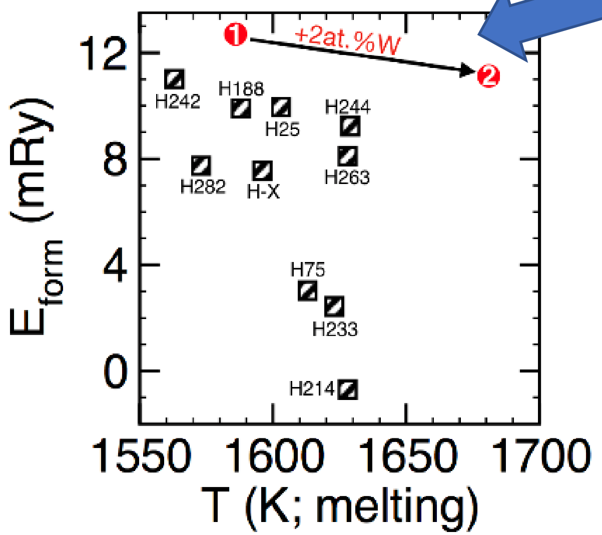


Energies are shown relative to that of an elemental solid X in Haynes-282

Role of refractories

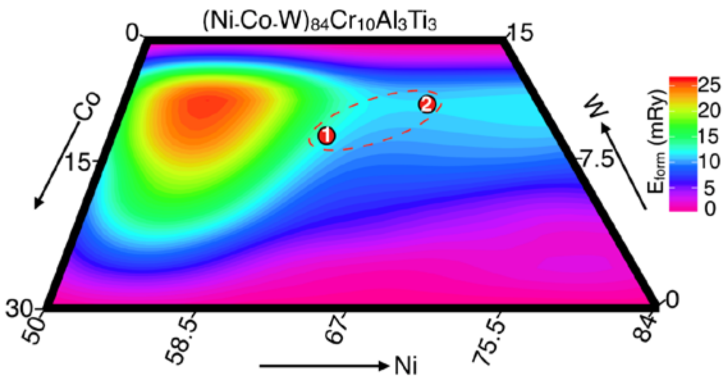
Mo, Ta, W and Re

Suggests small amounts of refractories can have dramatic effect on stability



The calculated formation enthalpy (E_{form}) with experimentally-determined melting temperature (T_m) for common Haynes alloys.

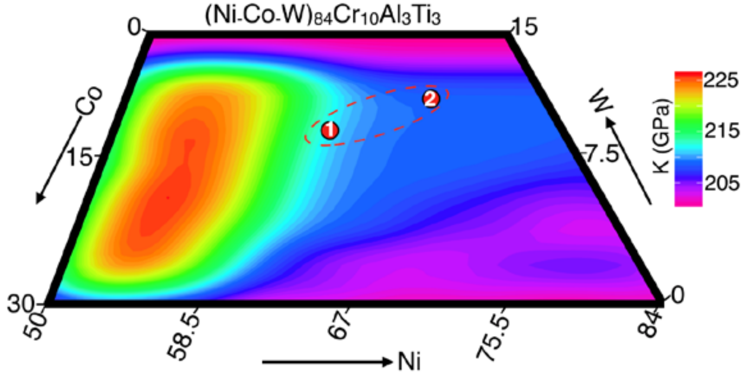
Formation Enthalpy



Refractory elements increases E_{form} over a broad compositional range in Co but a narrower range in Ni.

Bulk Moduli

Refractory elements increases bulk moduli over an even broad compositional range in Co but narrower in Ni.



Similar trends were seen with Mo (less dramatic) and Re (more dramatic).

Role of Fe, Hf, Nb, Si, V incorporated into the 2nd generation

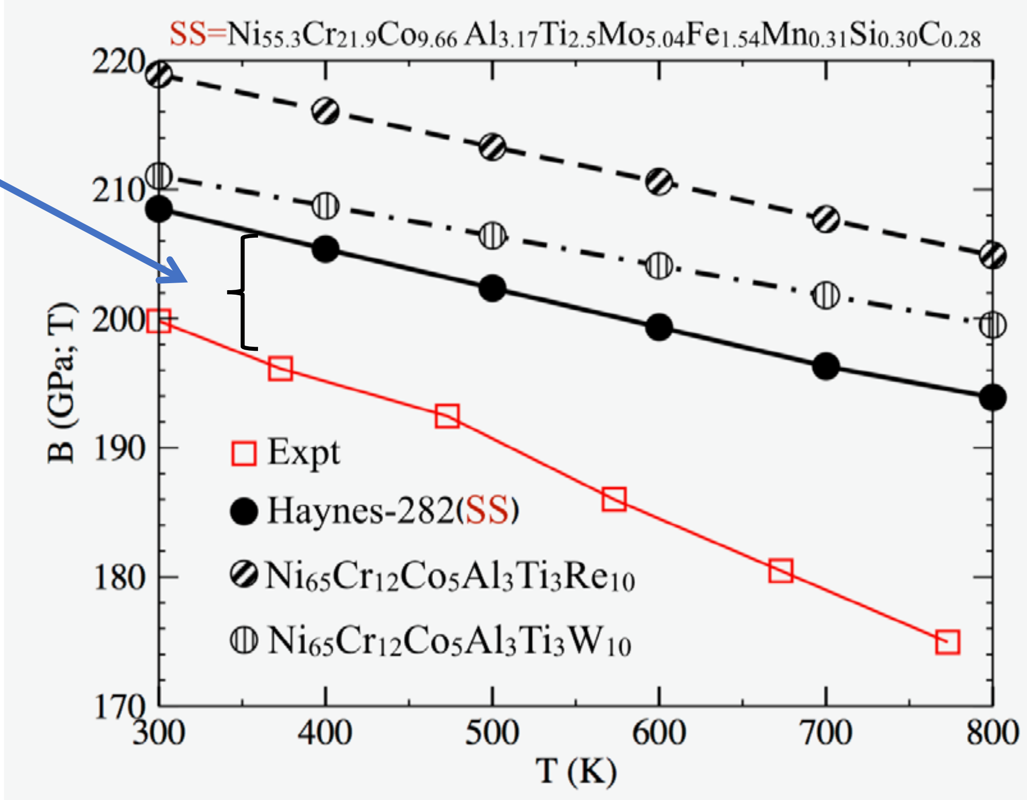
Role of refractories on bulk moduli

Haynes-282 bulk moduli was calculated (•) and compared to experimental data (□).

- **Calculation overestimated by ~ 8-20 GPa (within 10%)**

Model alloy $Ni_{65}Cr_{12}Co_5Al_3Ti_3X_{10}$ X = Mo, Re, W

- **Understand role of refractory elements**
  - **Moduli and T_m increased with increasing valance electrons**
  - **Are there chemical substitutions that can mimic this effect?**
    - **Necessary to reduce cost and density**



Similar trends were seen with Mo (less dramatic).

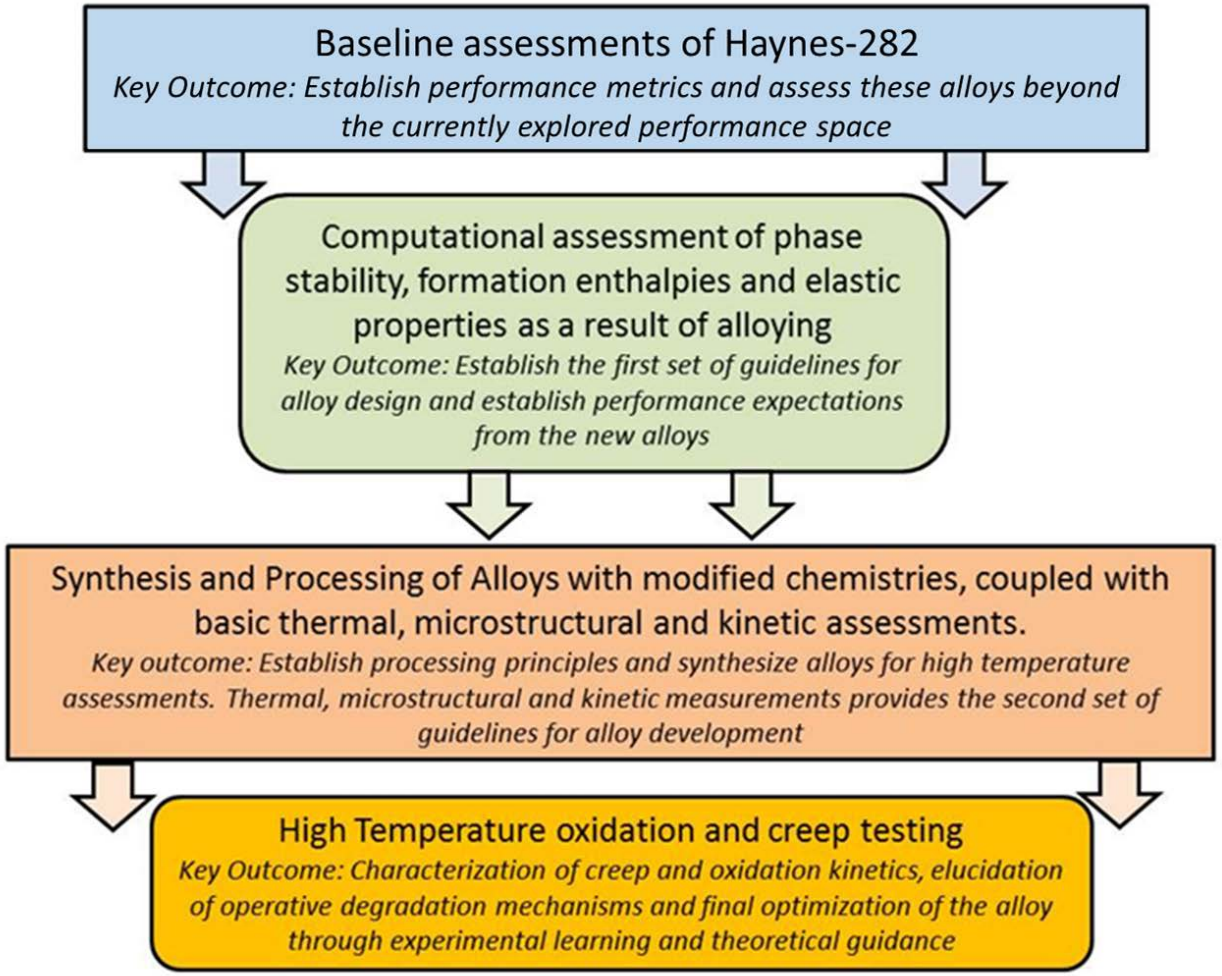
Current Status of Project

Modeling Validation

- **Compare predicted values for**
  - **Phase stability**
  - **Melting Temperatures (T_m)**
  - **Elastic Moduli**

Alloy Design Criteria

- **Identify promising regions of phase space for:**
  - **T_m ~ > 50°C of Haynes 282**
  - **Elastic Moduli > 10% higher**
  - **Sufficient Cr, Al for oxidation stability**
  - **Reduce Co (cost)**



Also see: Acta Materialia **189**, 248-254 (2020)

Role of refractories on phase stability

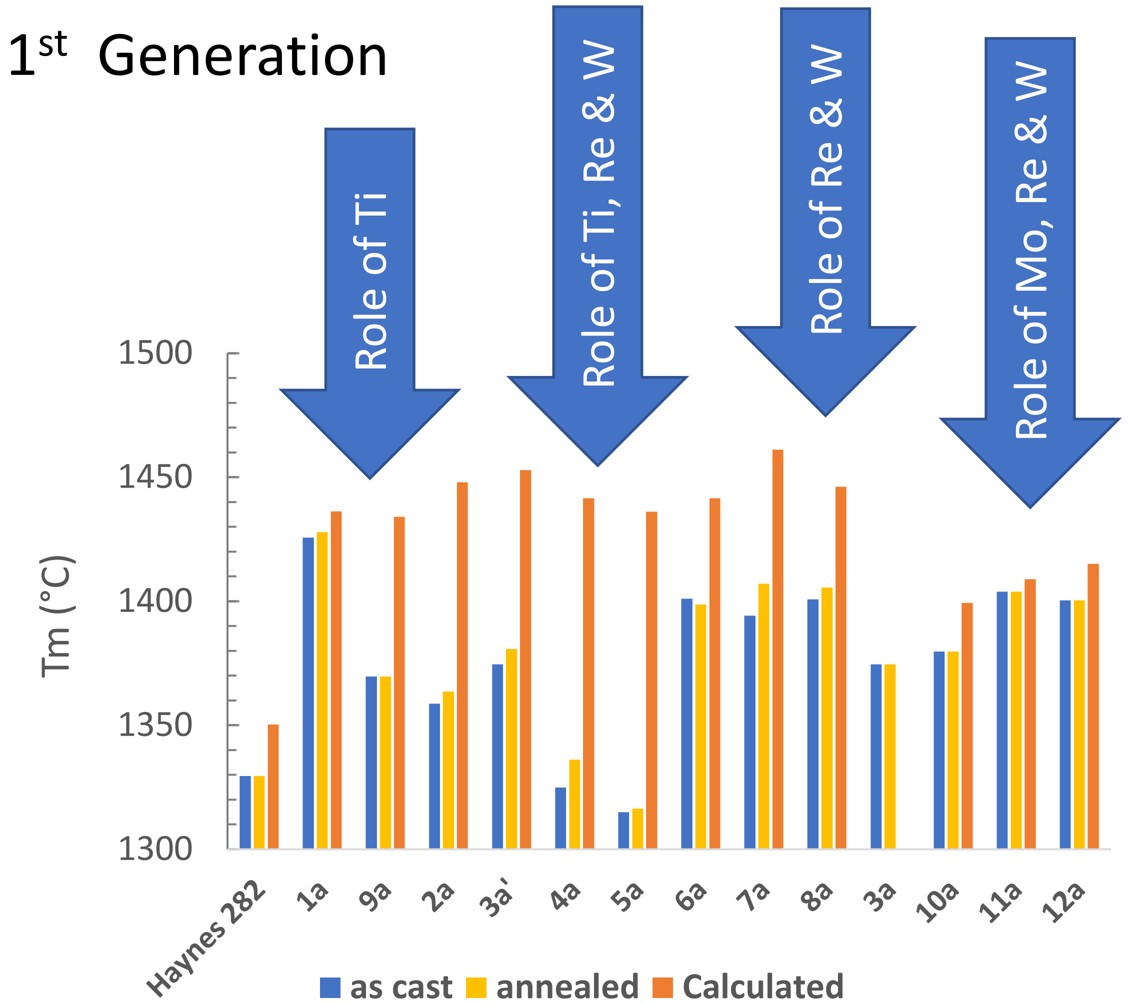
Experimental and calculated T_m onsets of 1st generation samples compared to Haynes 282.

Alloys fabricated and characterized to validate model predictions.

- **Model didn't correctly predict T_m for phase separate samples**
  - **Identified limits for the high T solid solution**
- **Model captured the trends in T_m for Mo, Re and W.**

Ti > 3% and refractories > 5% resulted in bcc phases

Deviation from prediction

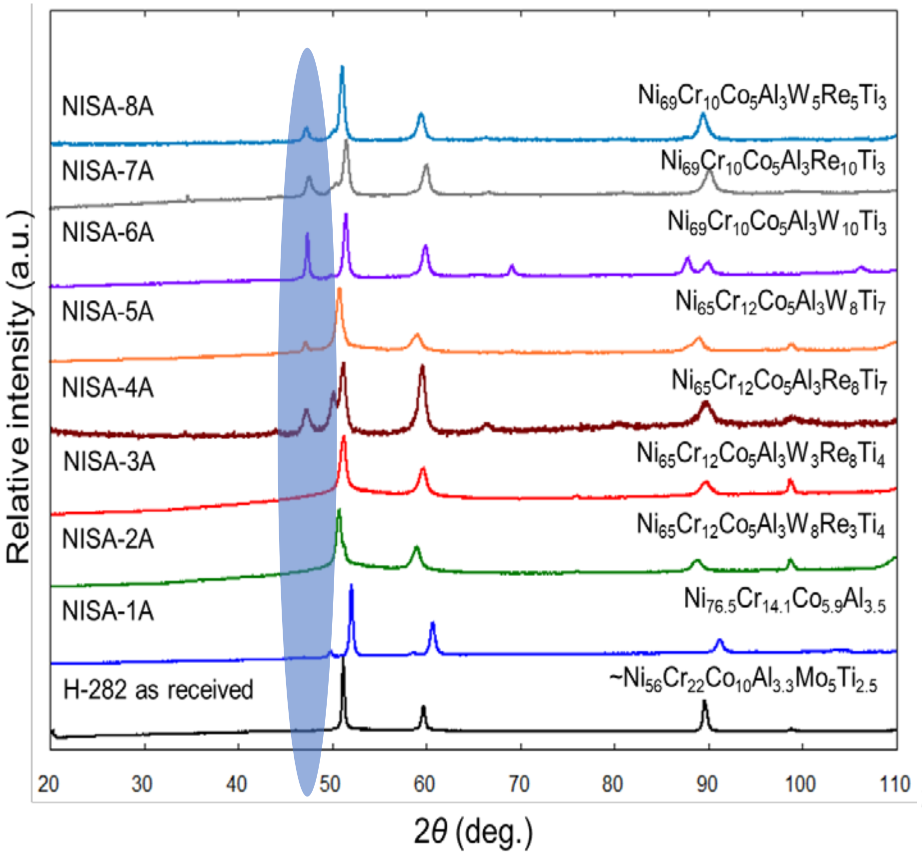


Refined suite of compositions

2nd generation results

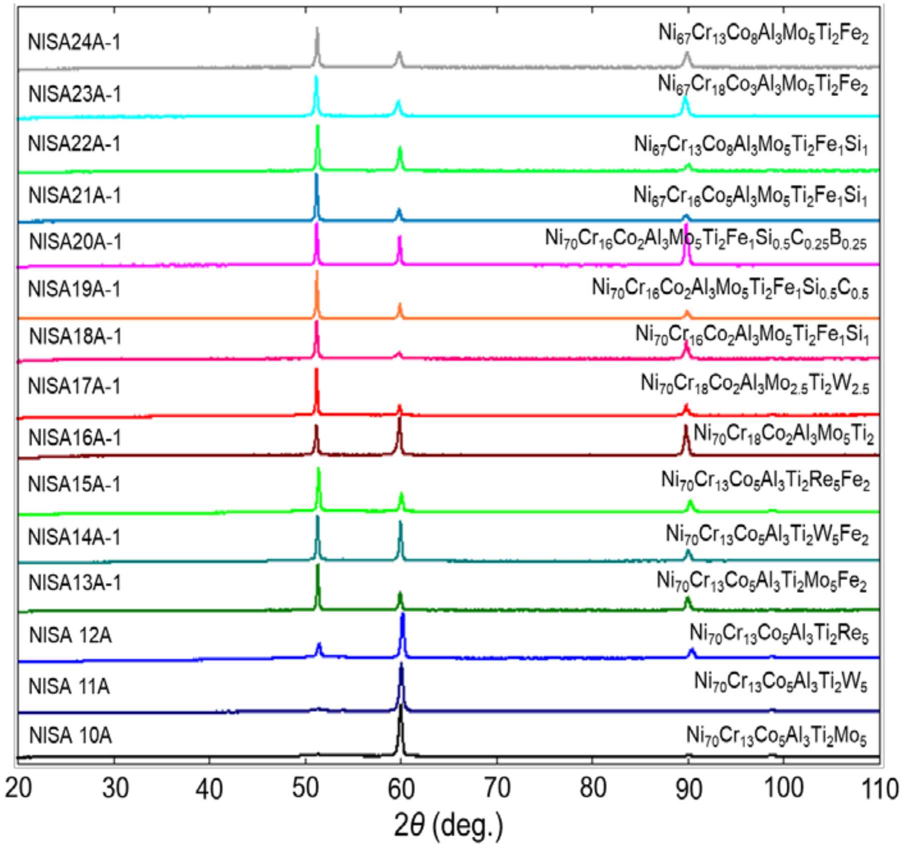
- **Target compositions w/ fcc matrix**
- **Investigate larger range of Ni, Co and Cr**
- **Include B, C, Fe and Si**

1st Generation alloy



fcc, bcc and $L1_2$ phases present

2nd Generation alloy



Nearly single phase fcc, 10-12A are not heat treated and show texturing along [200]

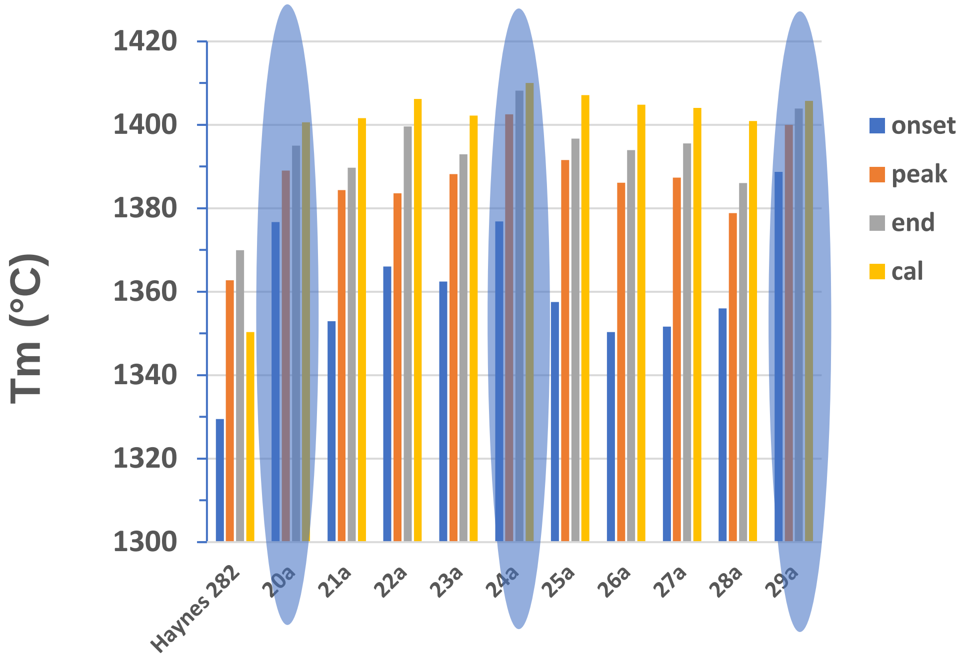
Refined suite of compositions

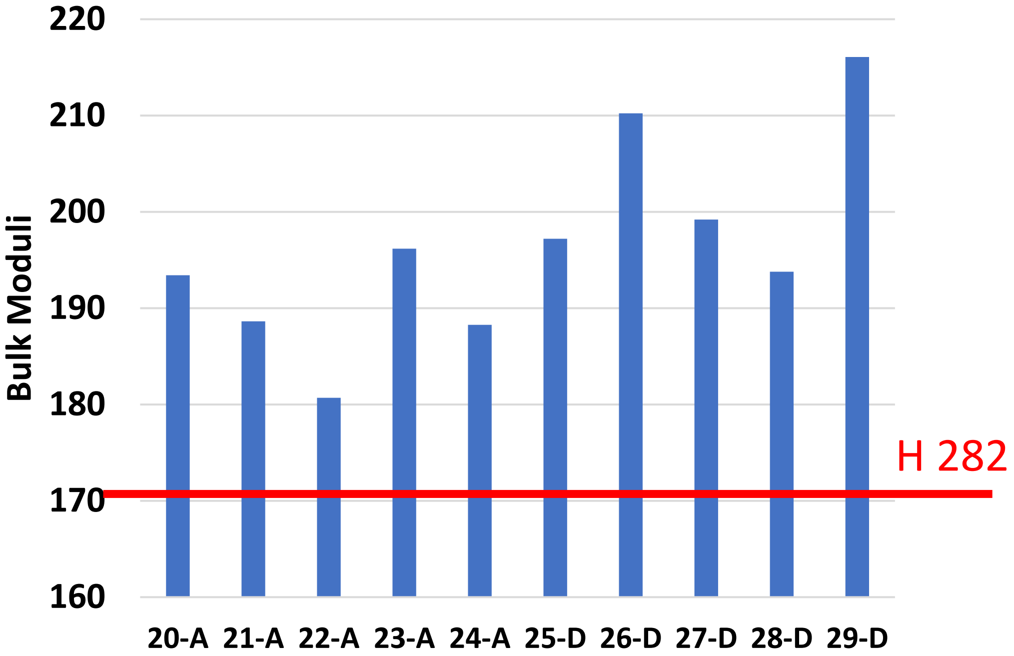
2nd generation results

Identified a broad range of compositions with T_m > 50°C of Haynes 282

RT Moduli is effective criteria for further down selection.

- **Ideal for implementing advanced search algorithm and machine learning for optimization**





Current Status of Project

Baseline Characterization of Haynes-282

- Alloy sheet from Haynes (also provided additional data on oxidation and microstructure)
  - Initial oxidation characteristics;
  - Phase assemblages and $T_{m;}$
  - Elastic Moduli

Alloy Selection and Testing

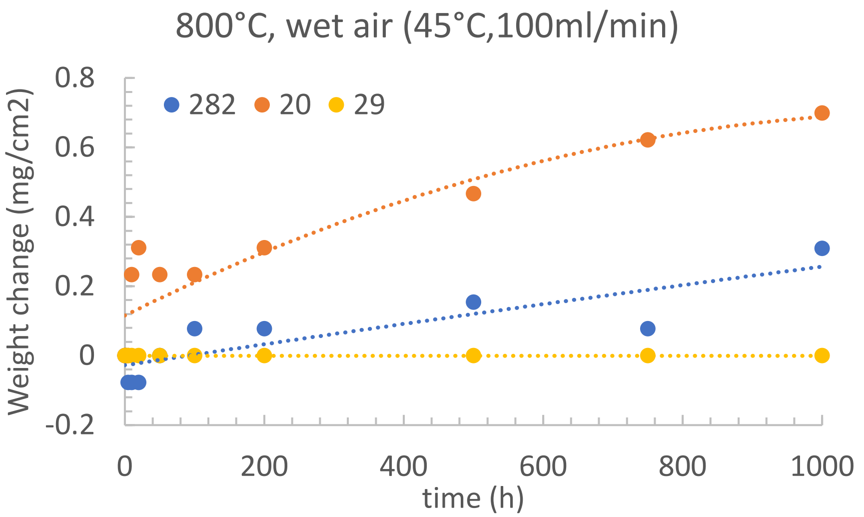
Characterize alloys across prospective phase space

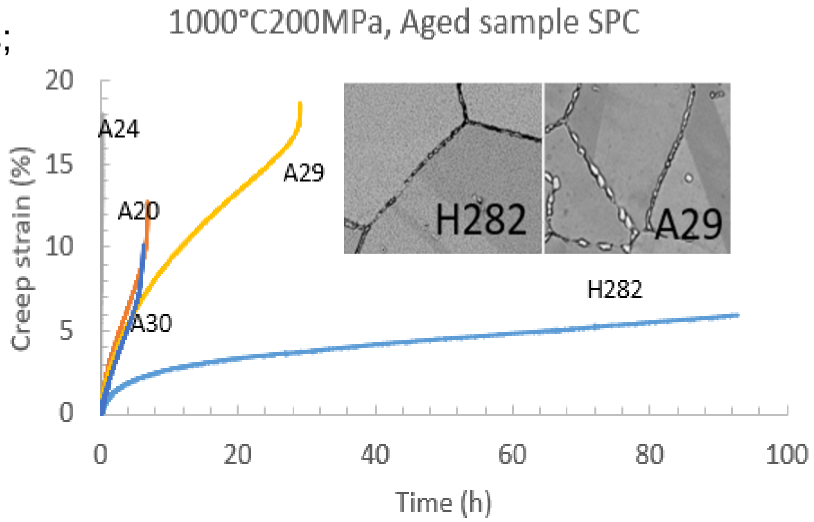
DSC, XRD, SEM, Ultrasound

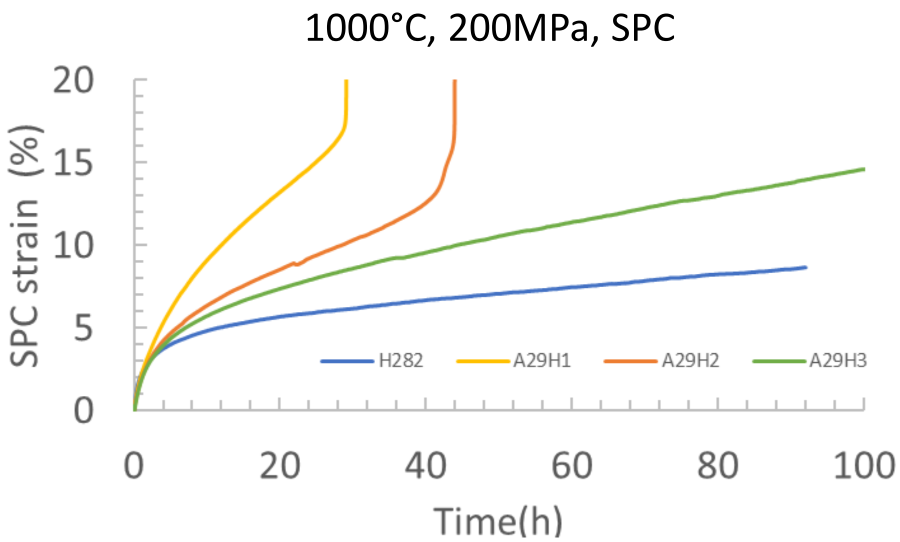
Further evaluate 'best samples' for

Oxidation resistance

Mechanical properties/creep properties







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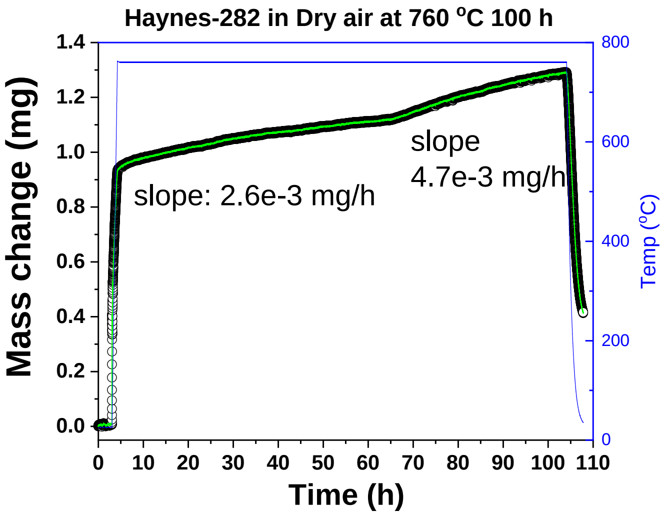
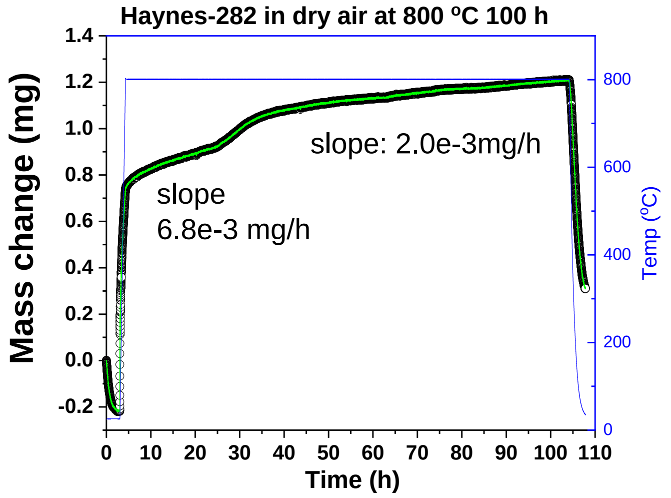
Baseline Characterization-Haynes 282

Oxidation (TGA)

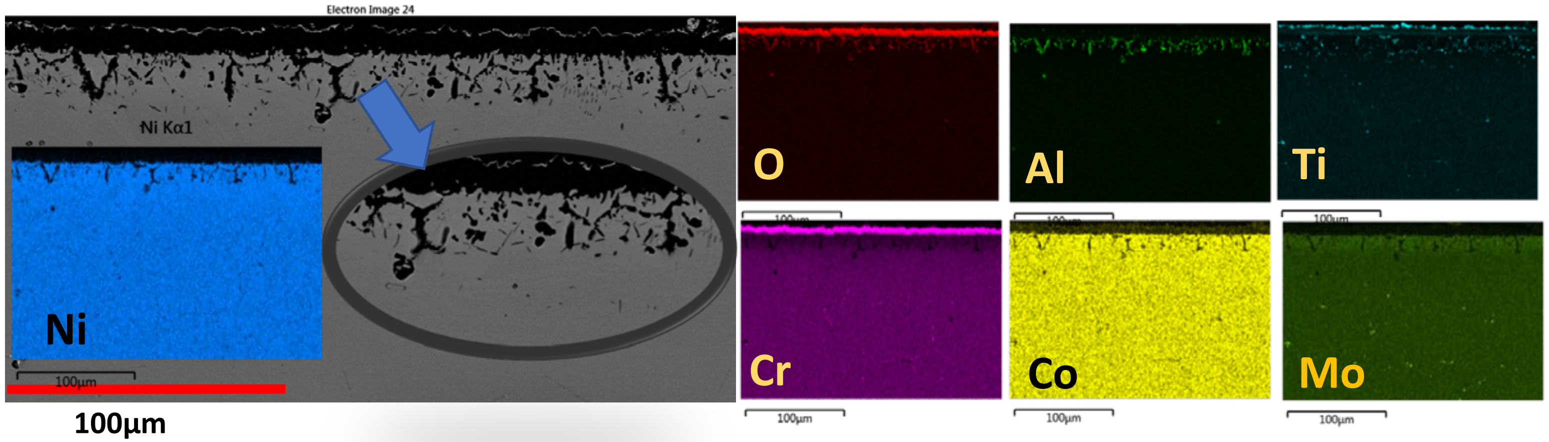
- Synthetic air, 760, 800, 900 & 1000 °C isothermal holds 20-100 hrs
- Two-step steady state oxidation
  - How does changes in alloy composition alter the transient and steady-state oxidation?





Cross-sectional SEM

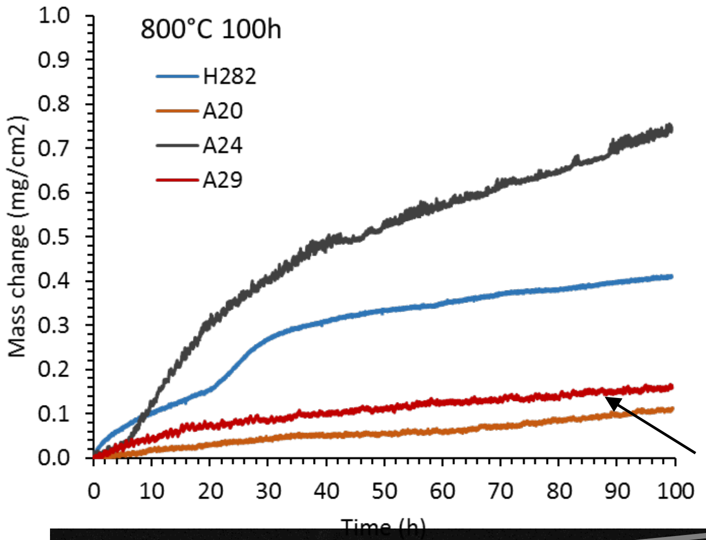
- ~10 µm continuous oxide layer
  - Primarily Cr_2O_3, TiO_2 and NiO (XRD)
  - Oxide penetration (~20 µm), mostly Al_2O_3 , No MoO_3

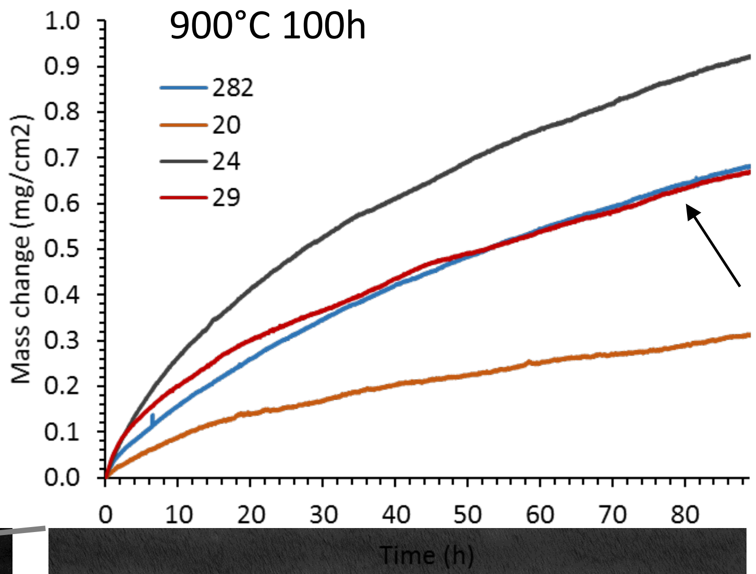


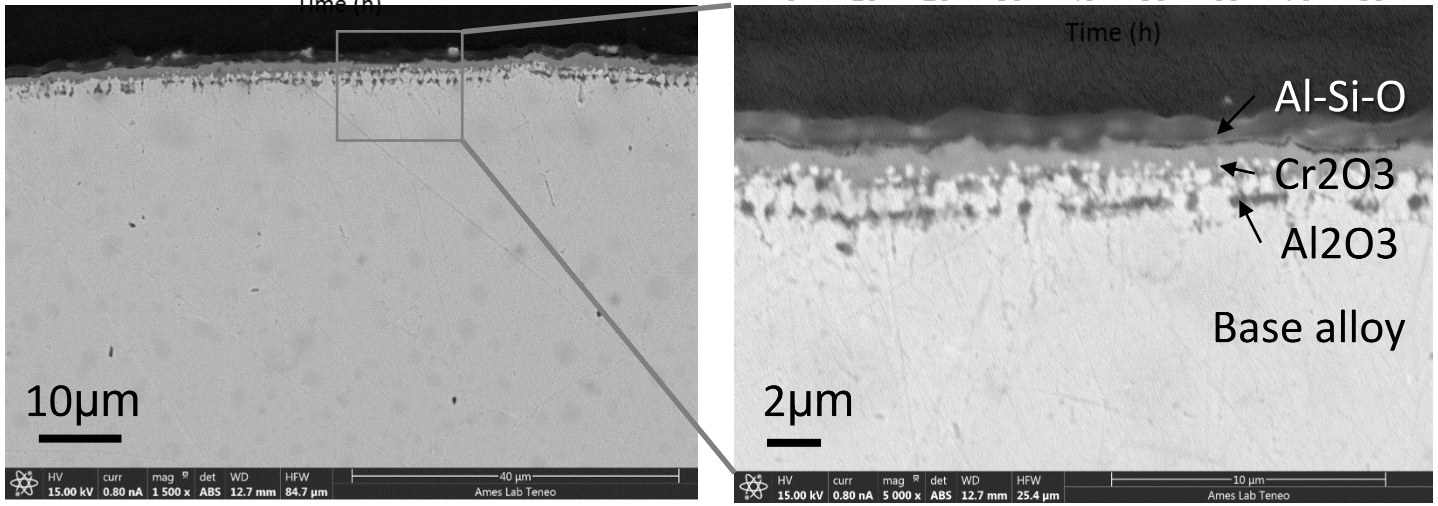
Electron back-scatter image (top) and elemental EDS maps for Haynes-282 after oxidation at 760 °C/100h

Paper in preparation

Oxidation: Haynes 282 vs Ames alloys





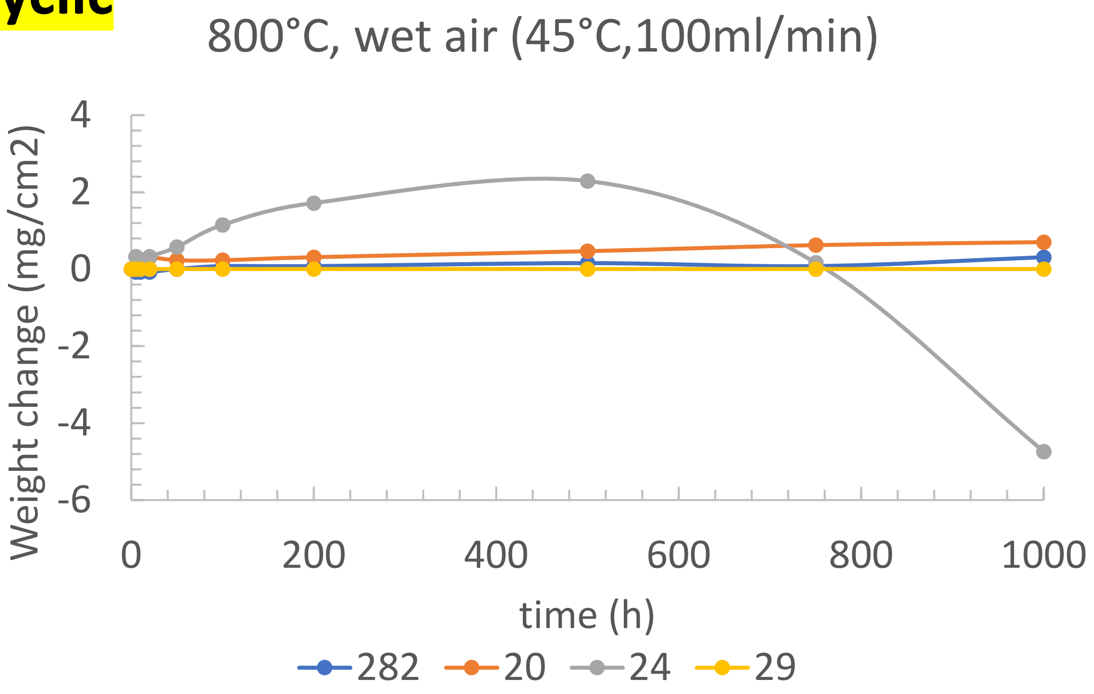


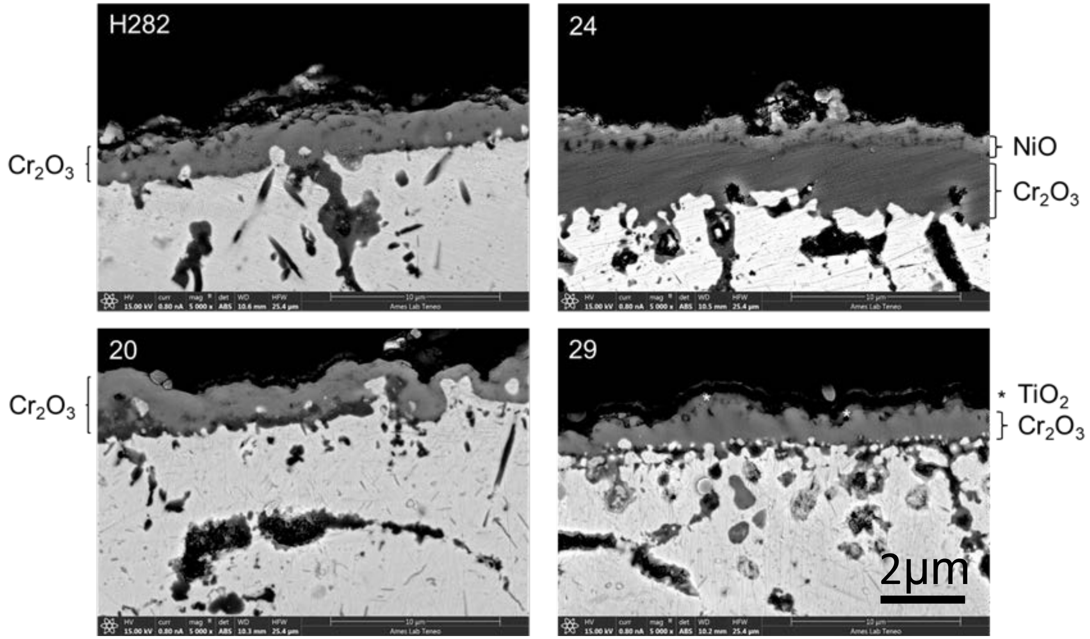
Ames A29 800°C 100h dry air oxidation

- Better oxidation resistance for Ames #20, 29 samples.
- Even with less Cr, Co, the scale on #20, 29 seems to be more protective at 800°C and 900°C.
- Ames 24 shows how small changes in Cr, Si can have profound changes in oxidation resistance.

Oxidation: Haynes 282 vs Ames alloys, wet air

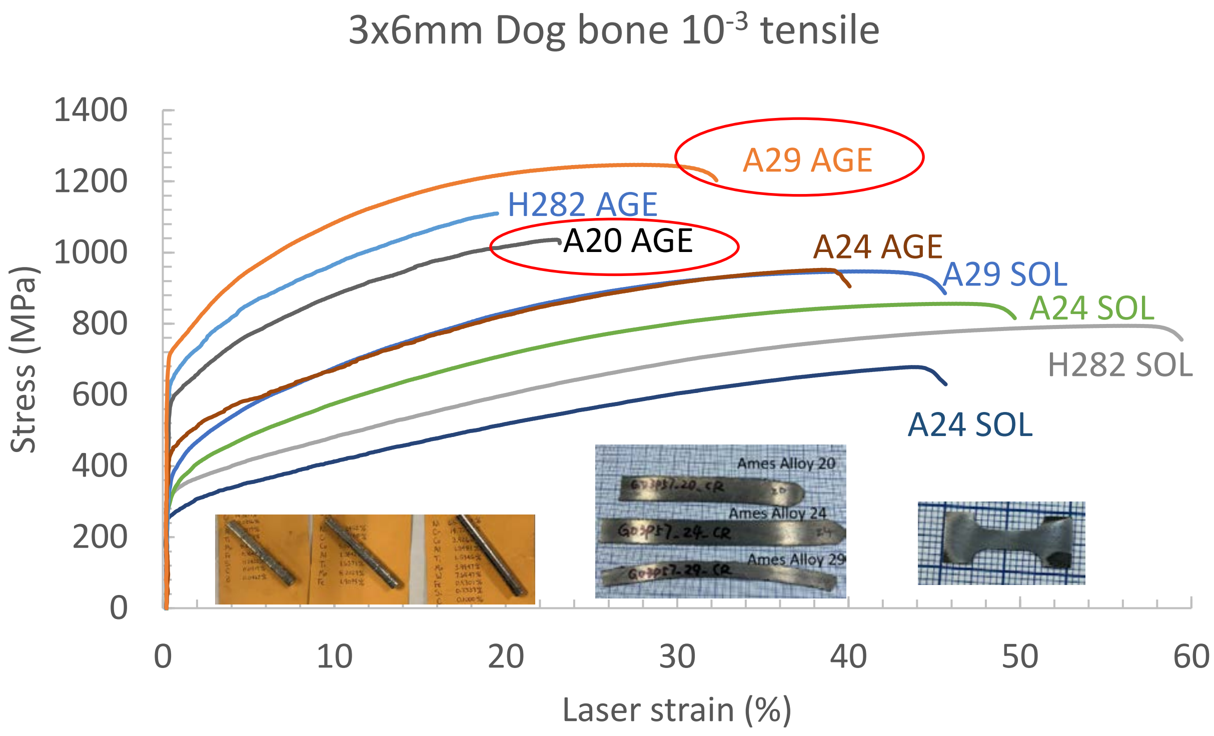
Cyclic

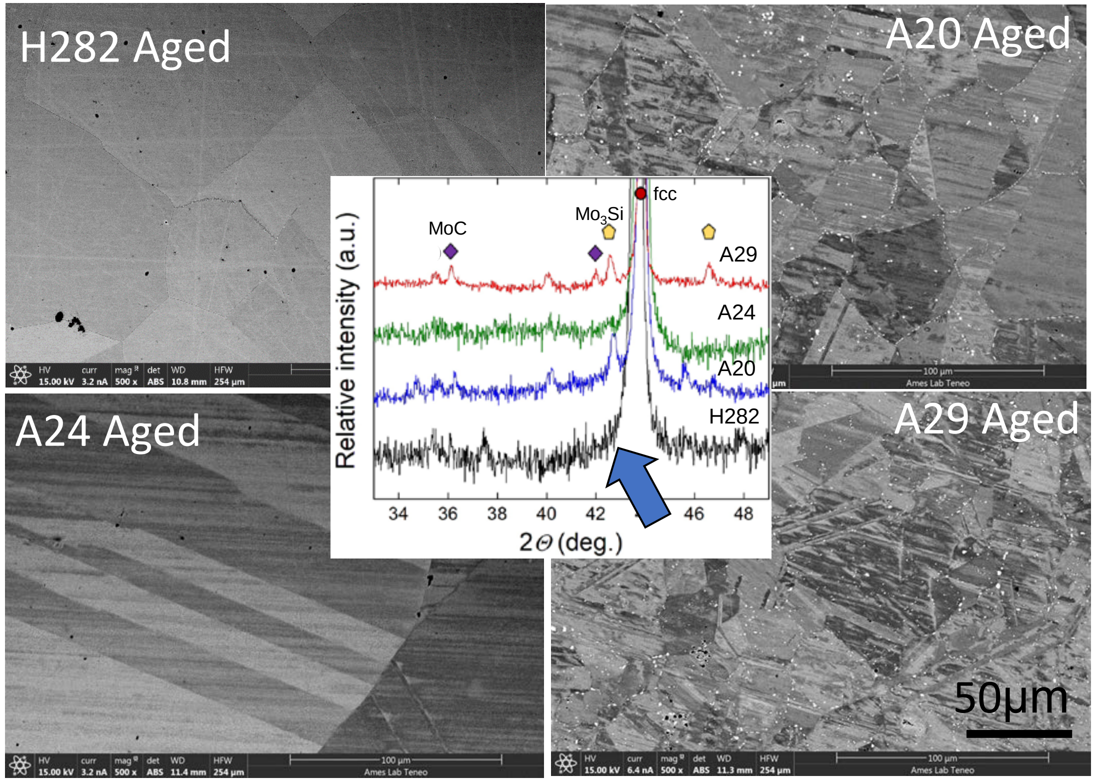


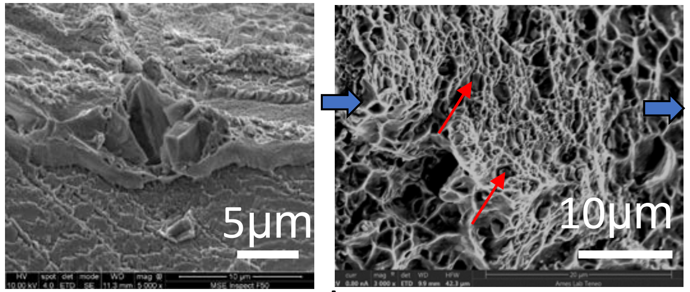


- Improved oxidation resistance for A29 at wet air condition. Its scale is thinner and has Mo(W)-O embedded in the top scale.

RT mechanical properties and fabricability







H282 Aged A29 Aged

- Balanced strength and ductility for Ames #20, 29 samples.
- Precipitates of Mo_3Si present in #20 and #29 samples.
- Precipitates found inside the ductile dimples likely contributed to crack defections

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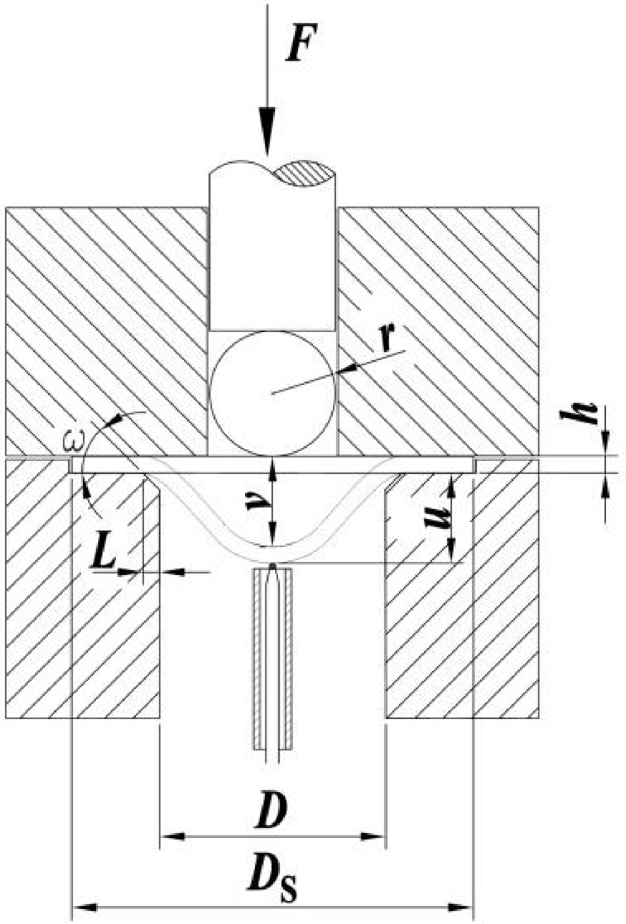
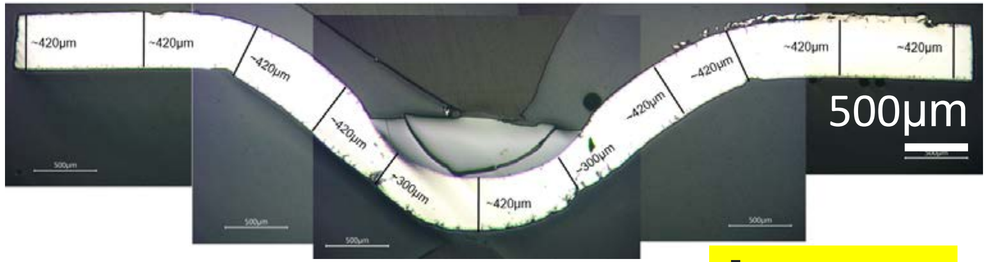
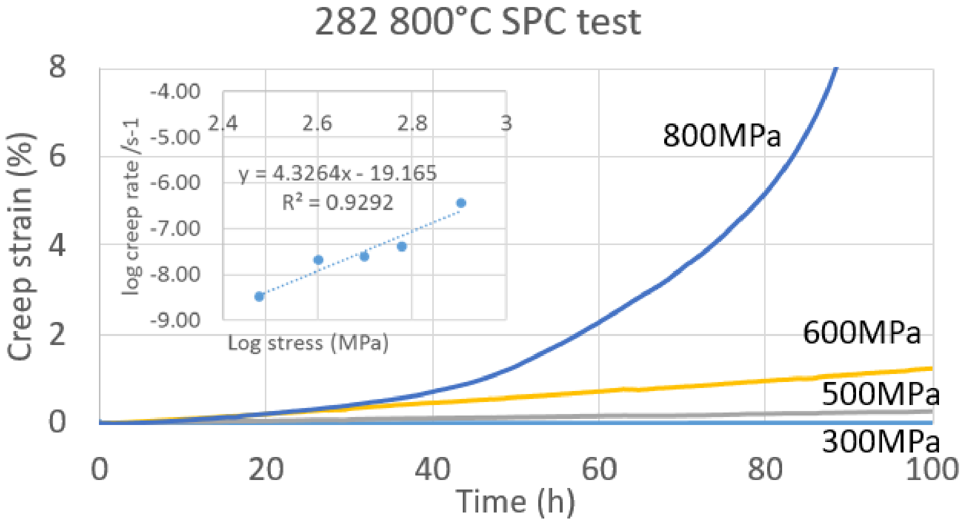
High temperature creep properties: Haynes 282





Φ = 8mm

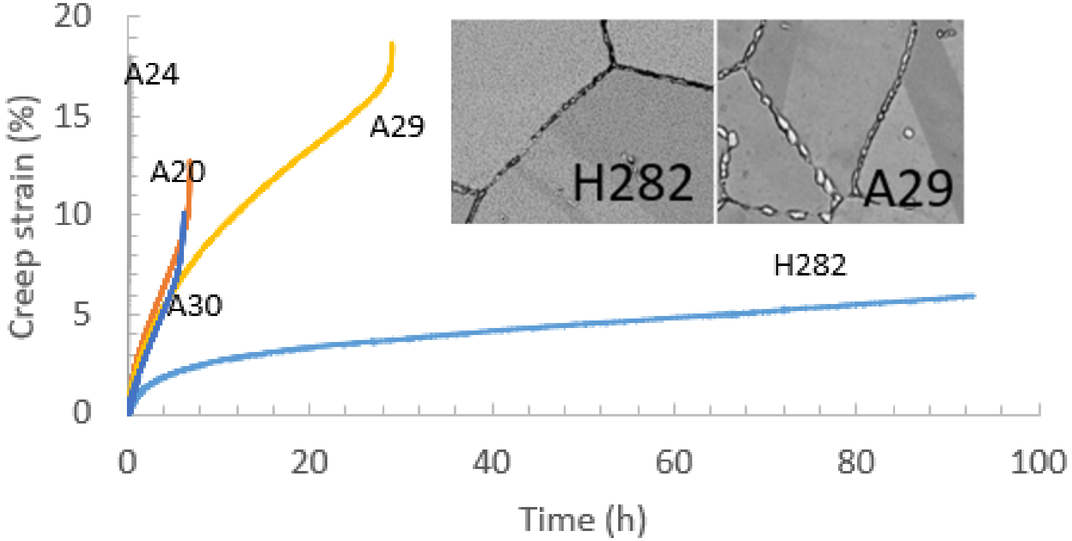


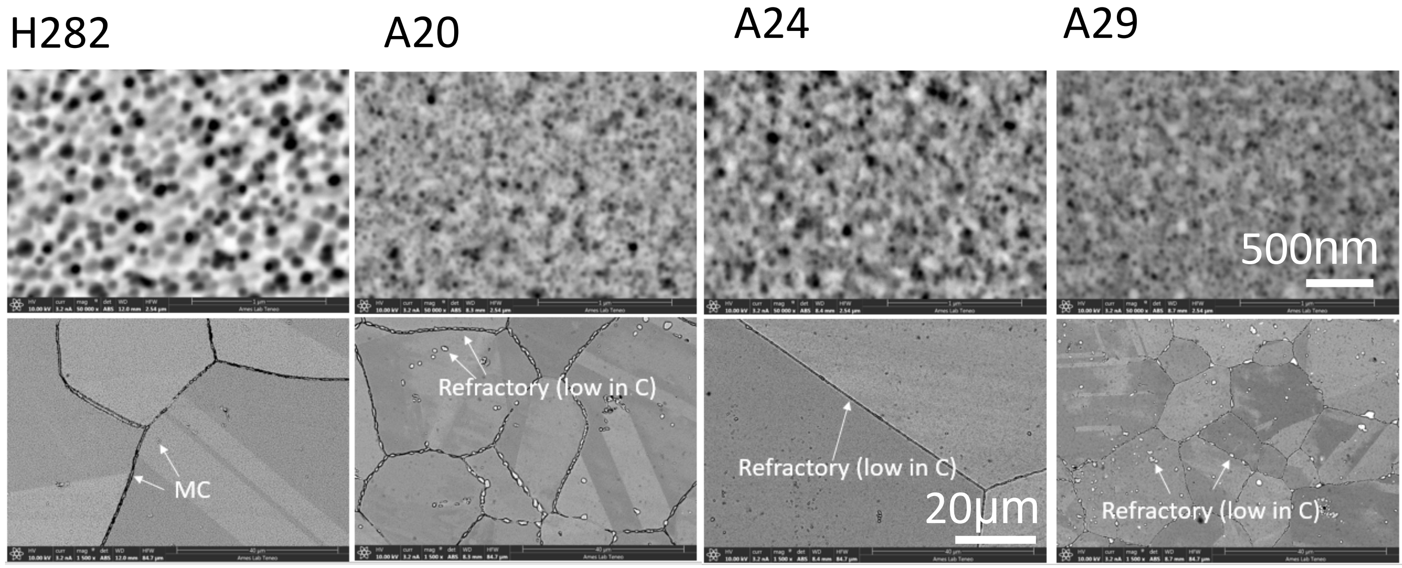
- Creep properties measured on benchmark Haynes 282 alloys using our newly set up HT small punch creep testers.
- Small punch creep testers allow rapid determination of creep properties of small sized sample.

Paper in preparation

High temperature creep properties

1000°C, 200MPa, Aged sample SPC



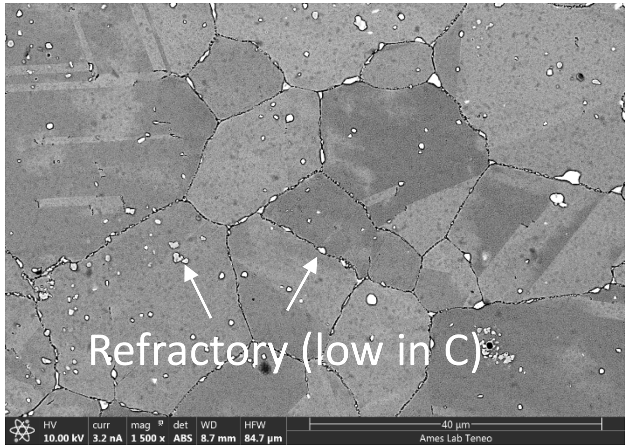


- Creep properties shows strong relation with composition and microstructure effect presumably the primary refractory precipitates in the grain boundaries.
- Revised heat treatments are need for A20, A29 alloys for HT creep resistance.

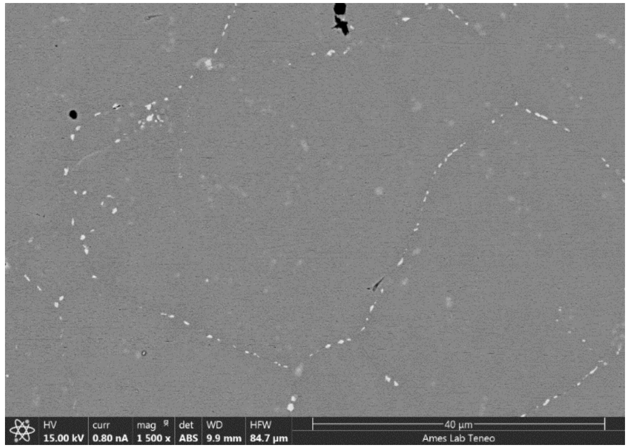
Paper in preparation

Refined heat treatment on A29

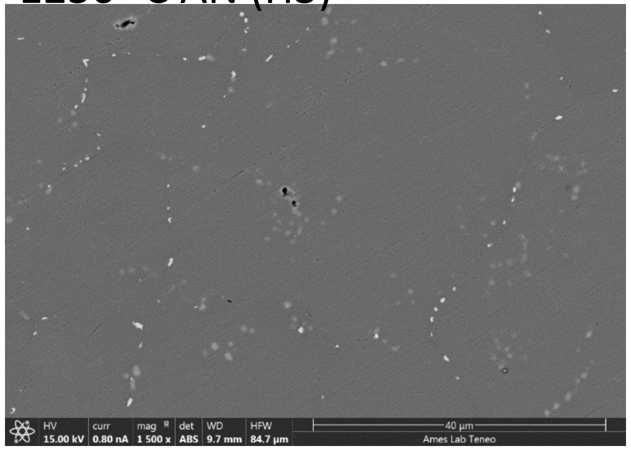
1150 °C AN (H1)



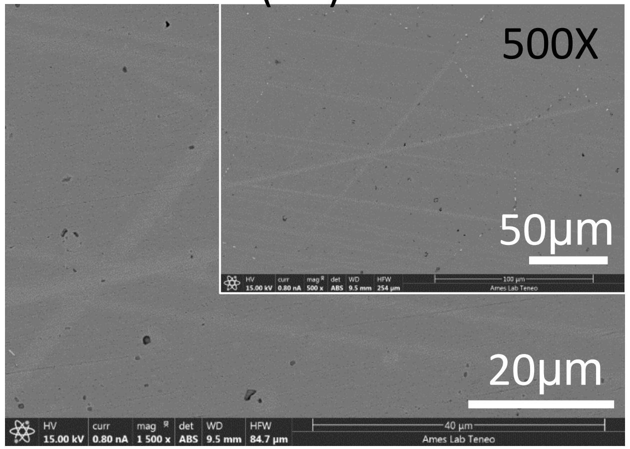
1200 °C AN (H2)

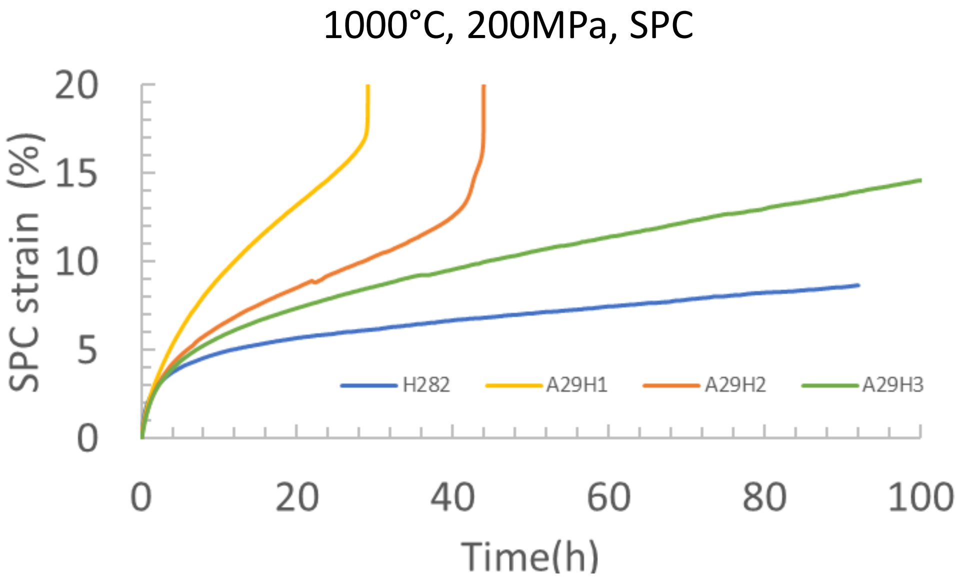


1250 °C AN (H3)



1300 °C AN (H4)





- Higher annealing temperature helps refine the grain boundary precipitates.
- With improved heat treatment, the creep properties of A29 is comparable to H282.

Paper in preparation

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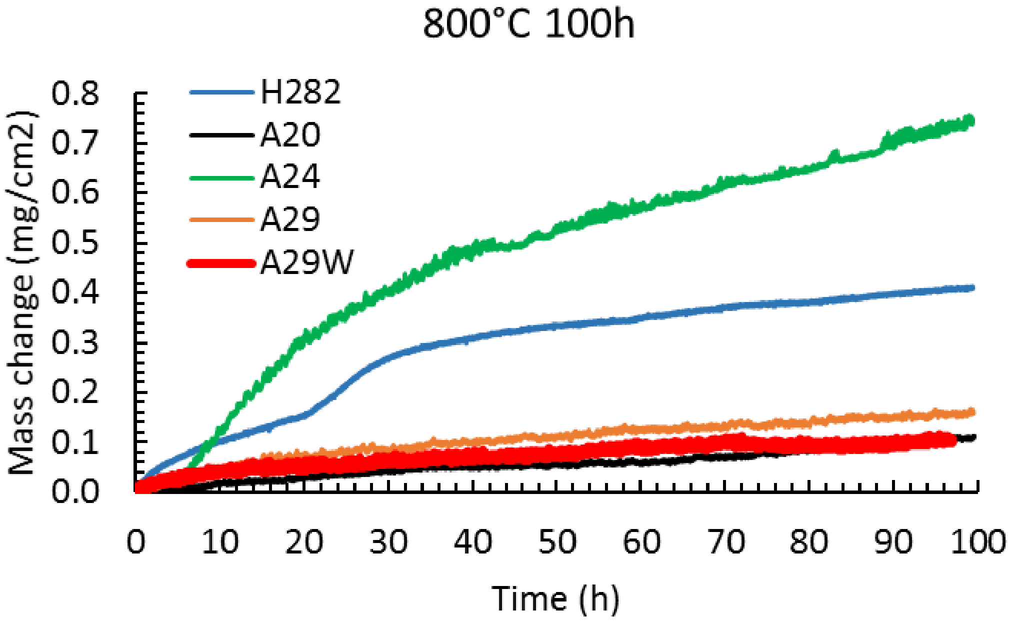
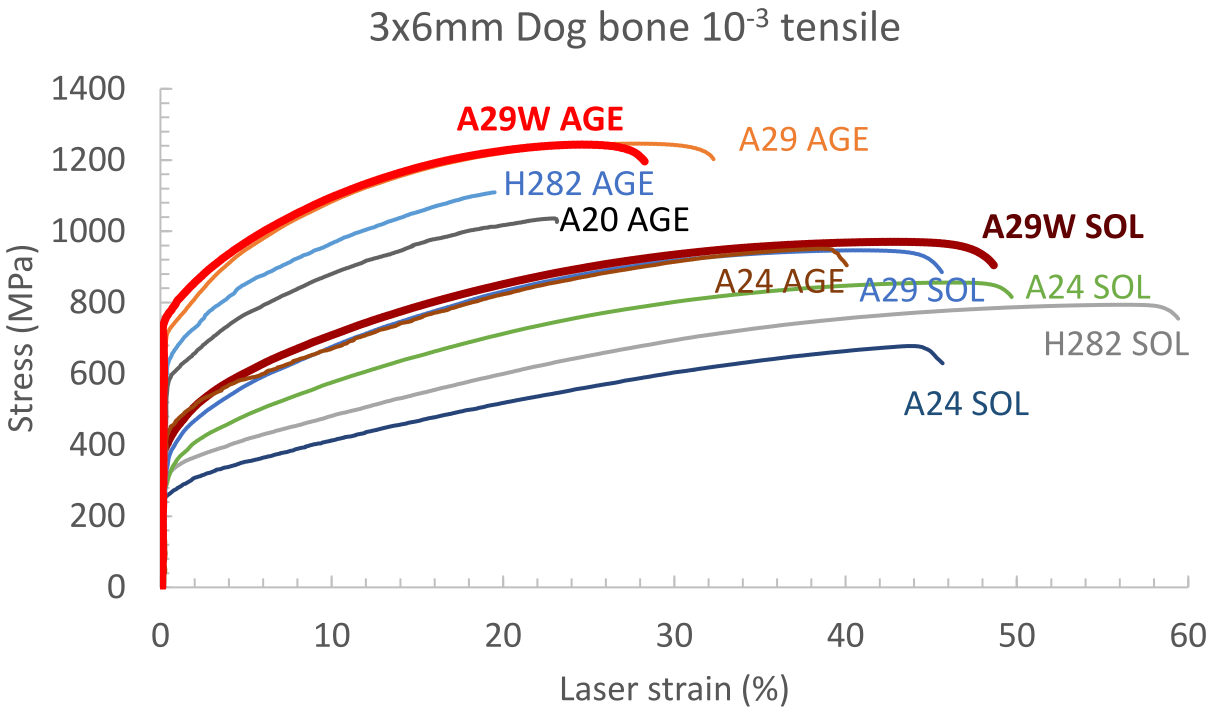
Effect of W on A29





- Replacing the Mo by W results in:
  - Increased oxidation resistance at 800°C
  - increased strength with minimum reduction of ductility.
- Creep tests and heat treated on the new alloy is in progress.

Preparing Project for Next Steps

Market Benefits/Assessment

- Increase operating T of Haynes-282 by 50°C
  - Higher operating efficiencies
  - Longer lifetime
- Materials failures represent a significant fraction of power plant operating costs.
- Accurate and efficient modeling can reduce time to market.

Technology-to-Market Path

- Adoption: The optimized alloy’s fabrication will fit into existing plants.
- Remaining technology challenges: Life-time assessment.
- New research: Develop methods to predict phase evolution/formations under operating conditions
- Haynes is providing materials and data.

Concluding Remarks

- Computationally efficient multi-elemental approach validated for Ni-based alloys will enable FECM to address these challenges:
  - Development of new alloy materials that have the potential to improve the performance and/or reduce the cost of existing fossil fuel technologies.
  - **Development of materials for new energy systems and capabilities**.
  - Development of alloys based on refractory metal elements to withstand the high temperatures and aggressive environments.
    - **Better stability in wet combustion environment for H-based fuels.**
- Current approach optimizes alloy composition based on phase stability and elastic moduli.
  - Model identified a broad range of promising compositions.
  - Developing suite of characterization tools to rapidly assess promising candidate compositions.

Special thanks to Haynes for supplying the samples and data, Olena Palasyuk, Prashant Singh, Arne Swanson, and Chaochao Pan for their work on the project and funding by FECM Crosscuts Program.