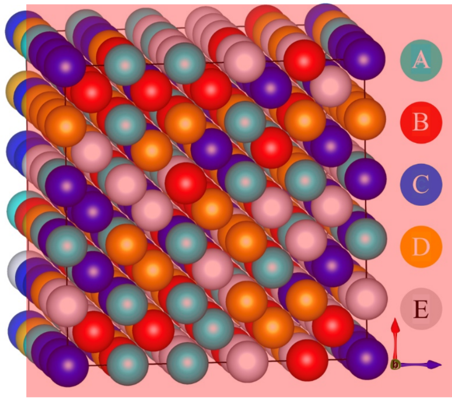
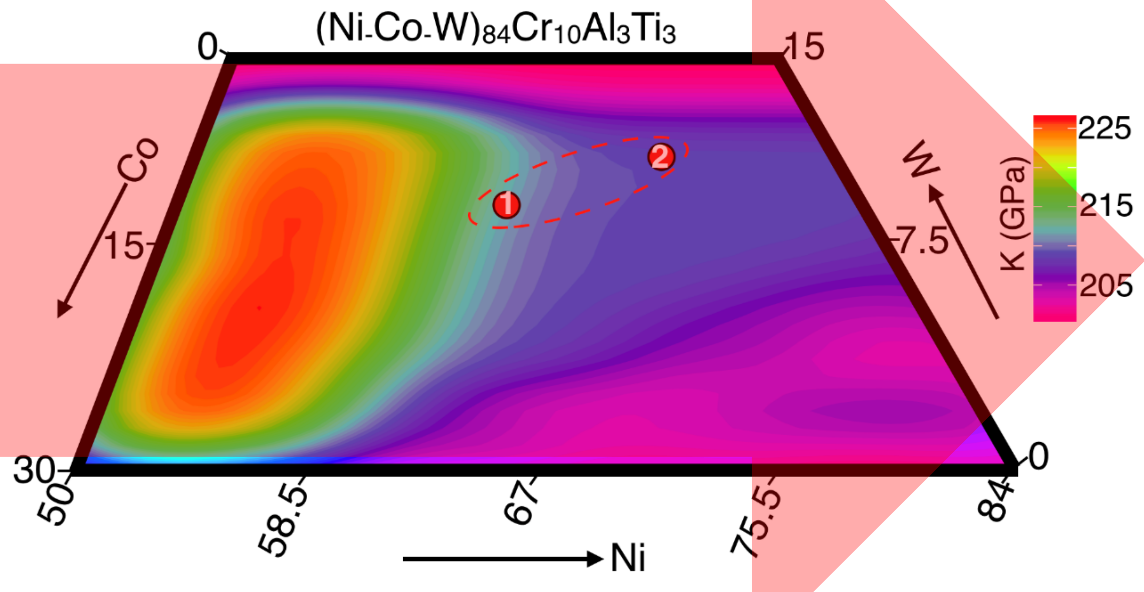
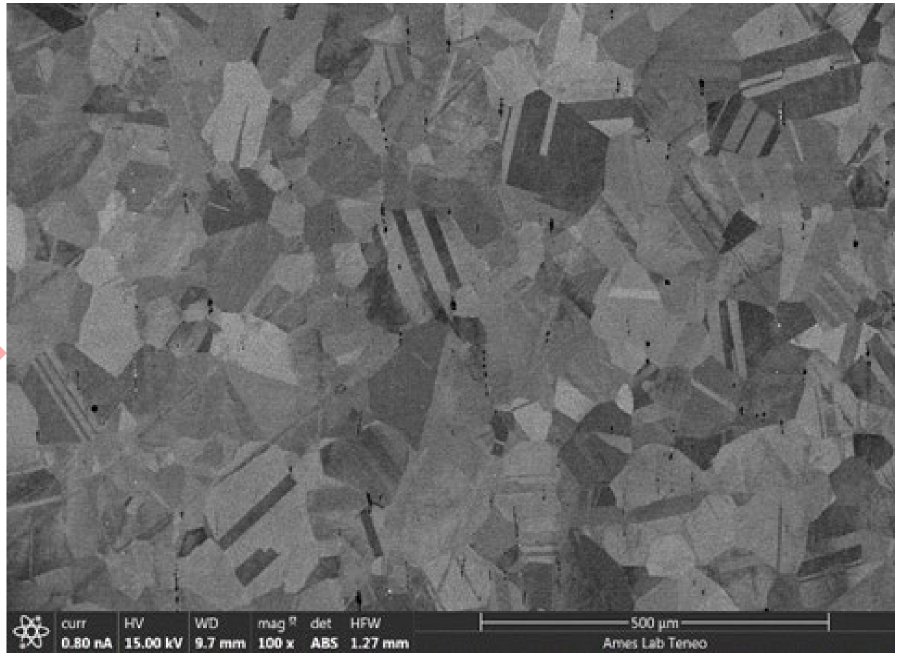






Predictive Design of Novel Ni-based Alloys

D.D. Johnson and M.J. Kramer

Ames Laboratory, US-DOE, Ames, IA 50011

U.S. DEPARTMENT OF ENERGY

IOWA STATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

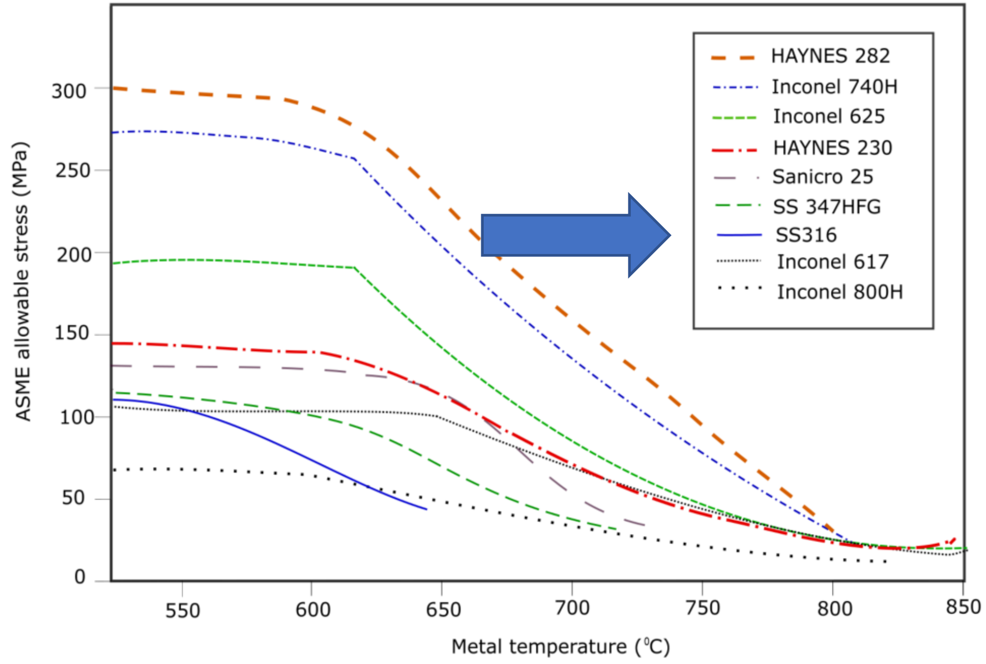
Project Description and Objectives

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

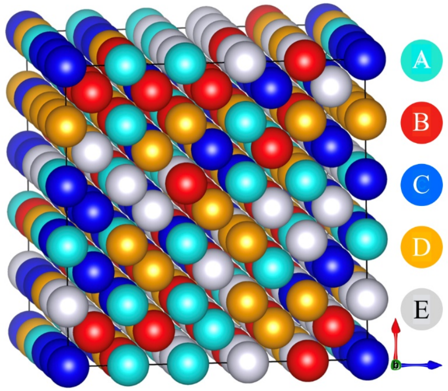
Current Status of Project

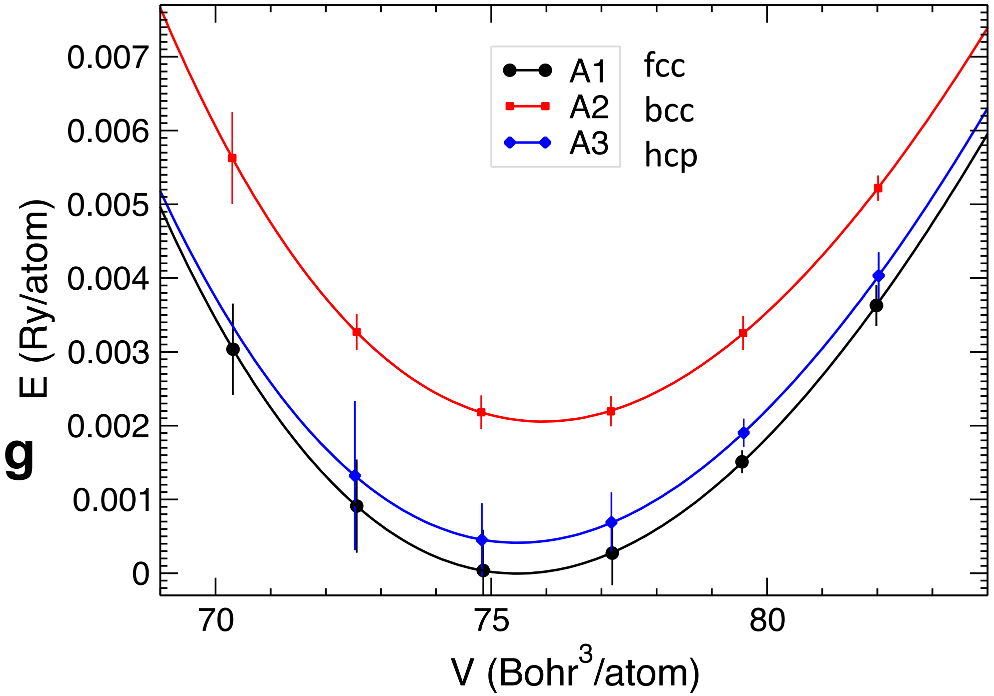
Modeling Approach

- **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: $Ni_{0.567}Cr_{0.224}Co_{0.099}Mo_{0.052}Ti_{0.026}Al_{0.032}$

AMES LABORATORY
U.S. DEPARTMENT OF ENERGY
IOWA STATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

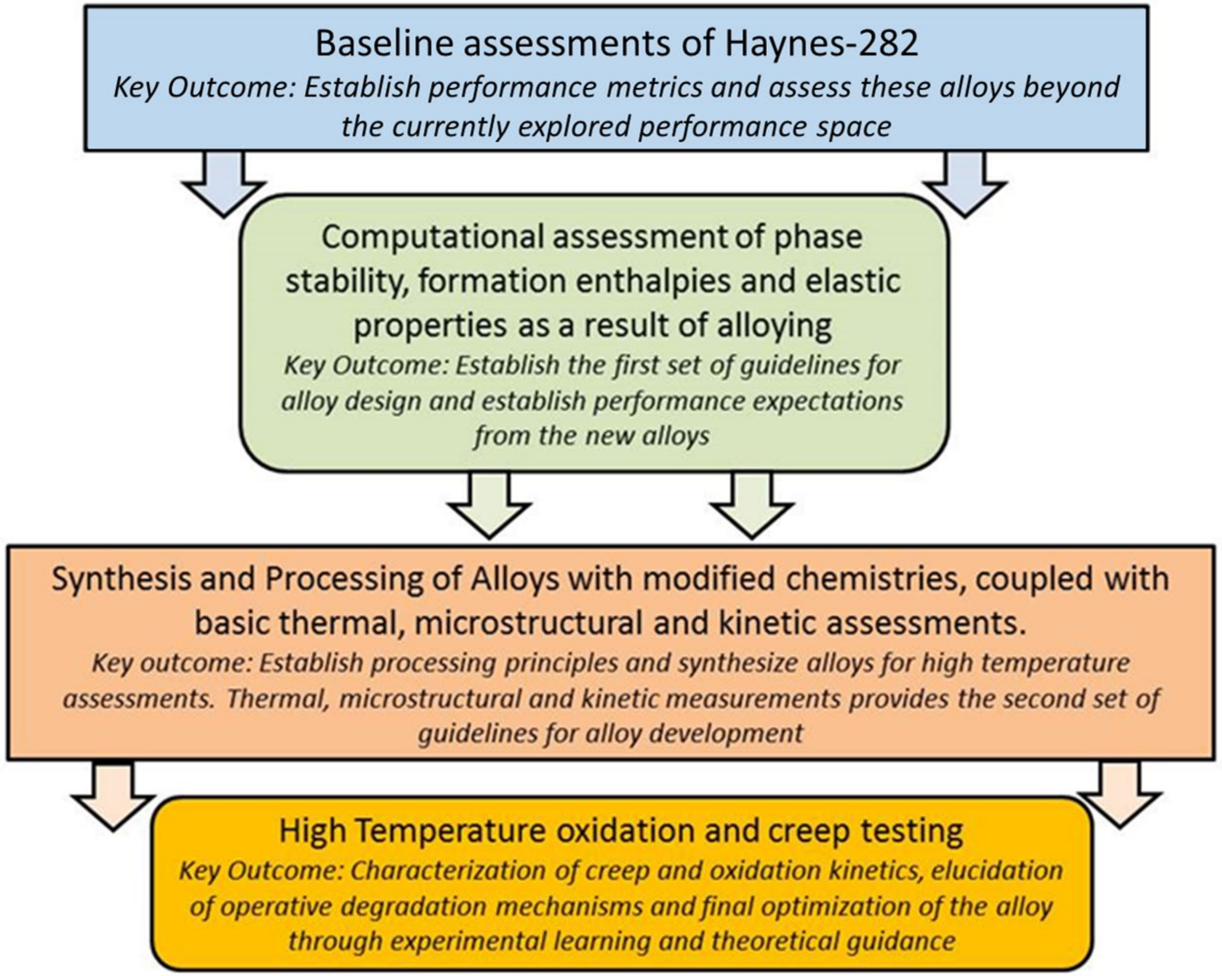
Current Status of Project

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 , (Si) for oxidation stability
  - Reduce Co (lower cost)

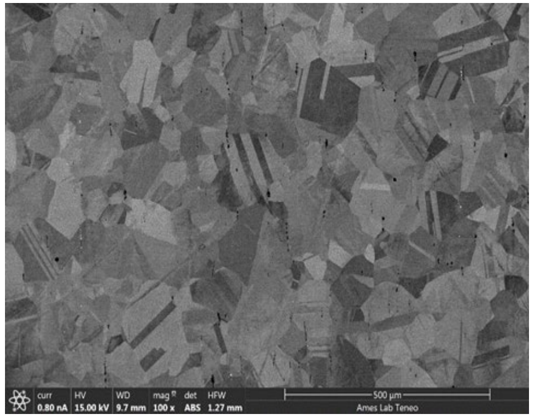


Also see: Acta Materialia **189**, 248-254 (2020)

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**



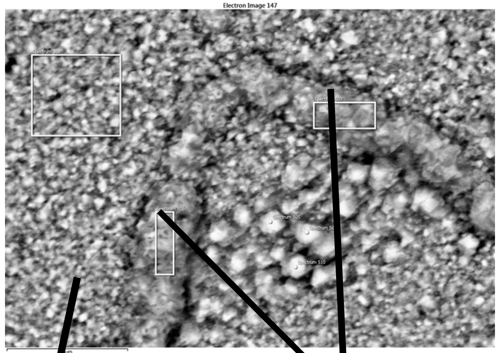
As-received microstructure of Haynes-282

Alloy Selection and Testing

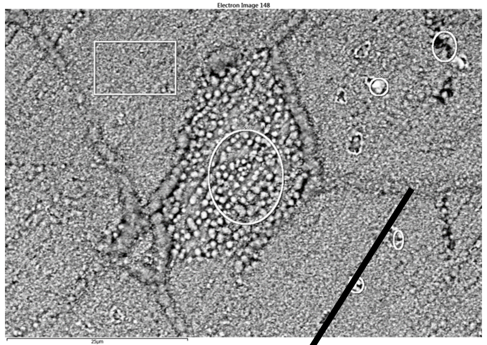
- **Characterize alloys across prospective phase space**
  - **DSC, XRD, SEM, Ultrasound**
- **Further evaluate 'best samples' for**
  - **Oxidation resistance**
  - **Mechanical properties**

Surface Oxidation of Haynes-282

760 °C/60 h



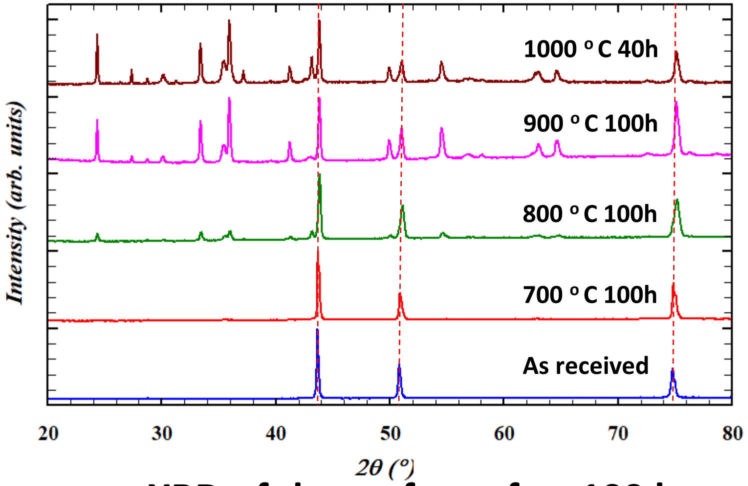
800 °C/20 h



Cr_2O_3 + high TiO_2 on ridges (negligible Mo)

MoO_3+ Cr_2O_3 + NiO

Element	Wt % H-282/oxide
Ni	55/47
Cr	19/26
Co	10/6
Mo	9/6
Ti	2/2.3
Al	1.5/1.8



XRD of the surface after 100 hrs oxidation in dry air

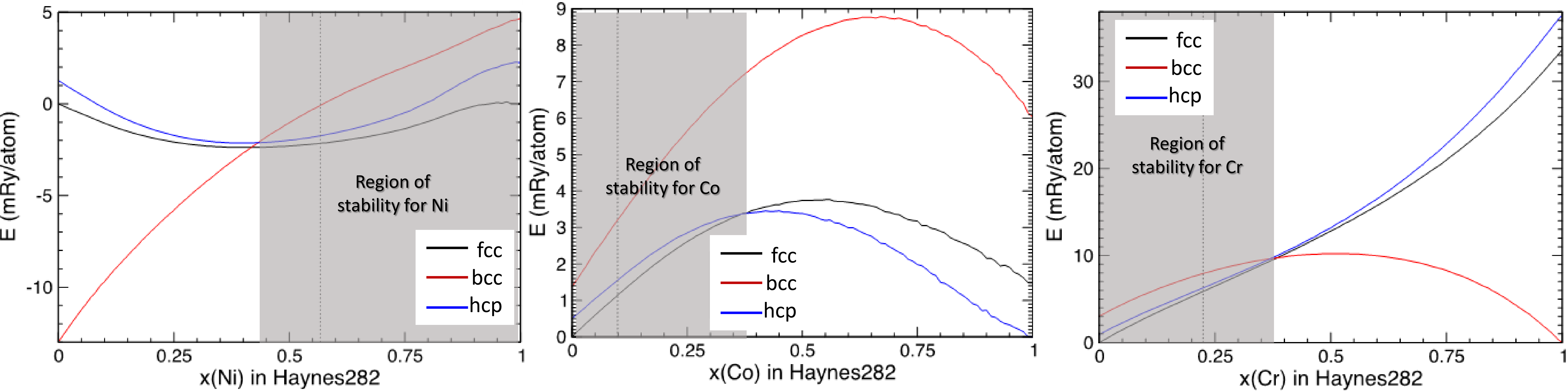
Model Prediction

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. %



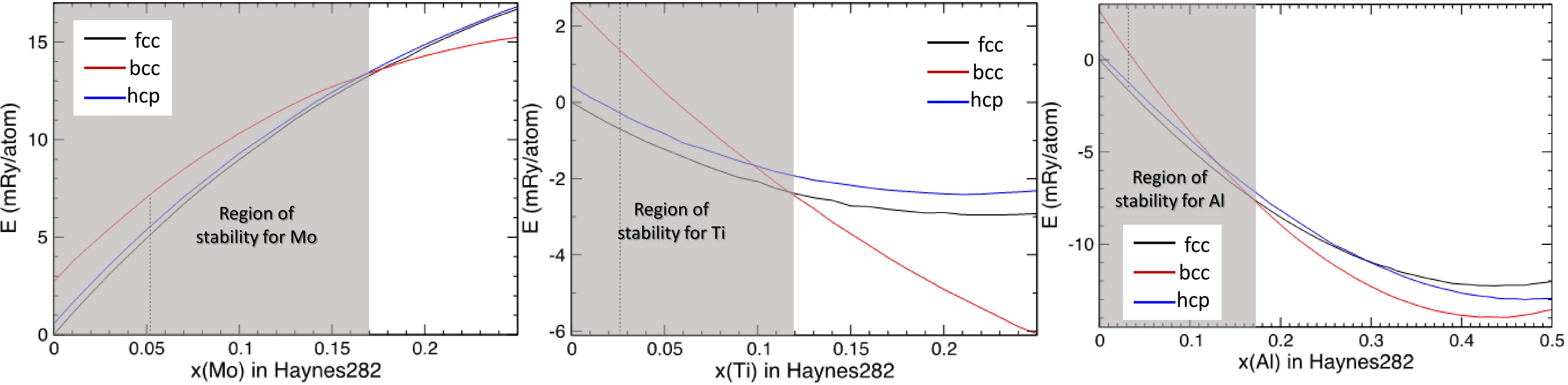
Energies are shown relative to that of an elemental solid X in Haynes-282

Model Prediction

Investigate role of minor element substitutions.

- **Shaded regions show the extend to solid solution for each element (Mo, Ti and Al) in a fcc matrix compared to bcc and hcp)**

Mo < 17 at. %: Ti < 11 at. %: Al < 15 at. %

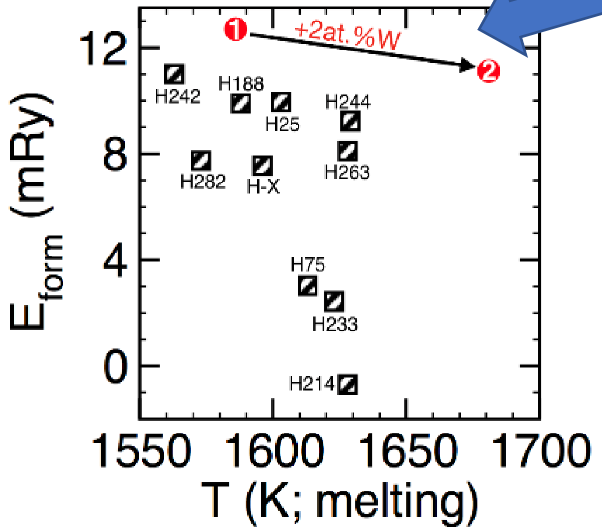


Energies are shown relative to that of an elemental solid X in Haynes-282

AMES LABORATORY
U.S. DEPARTMENT OF ENERGY
IOWA STATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

Role of refractories

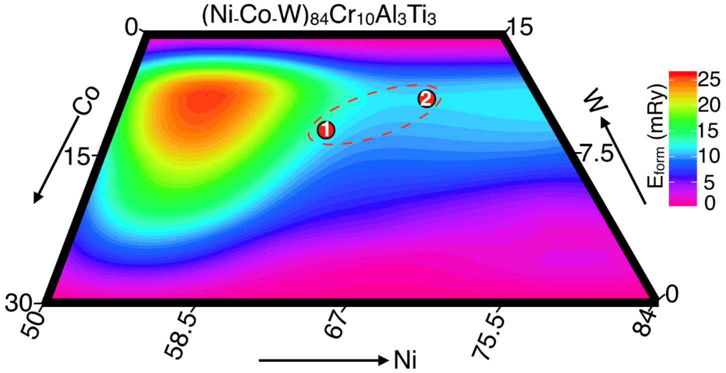
Mo, Ta, W and Re



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.

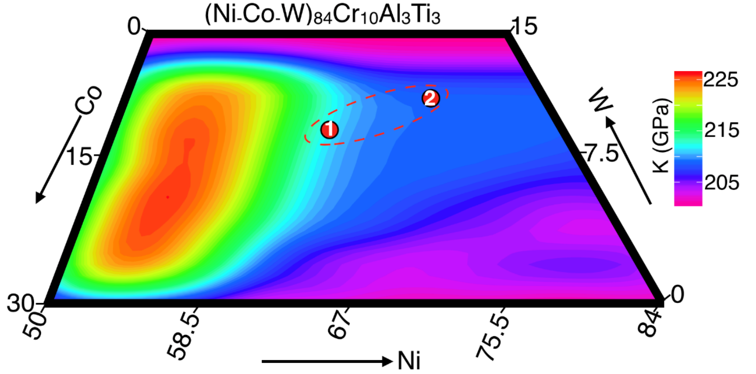
Formation Enthalpy



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

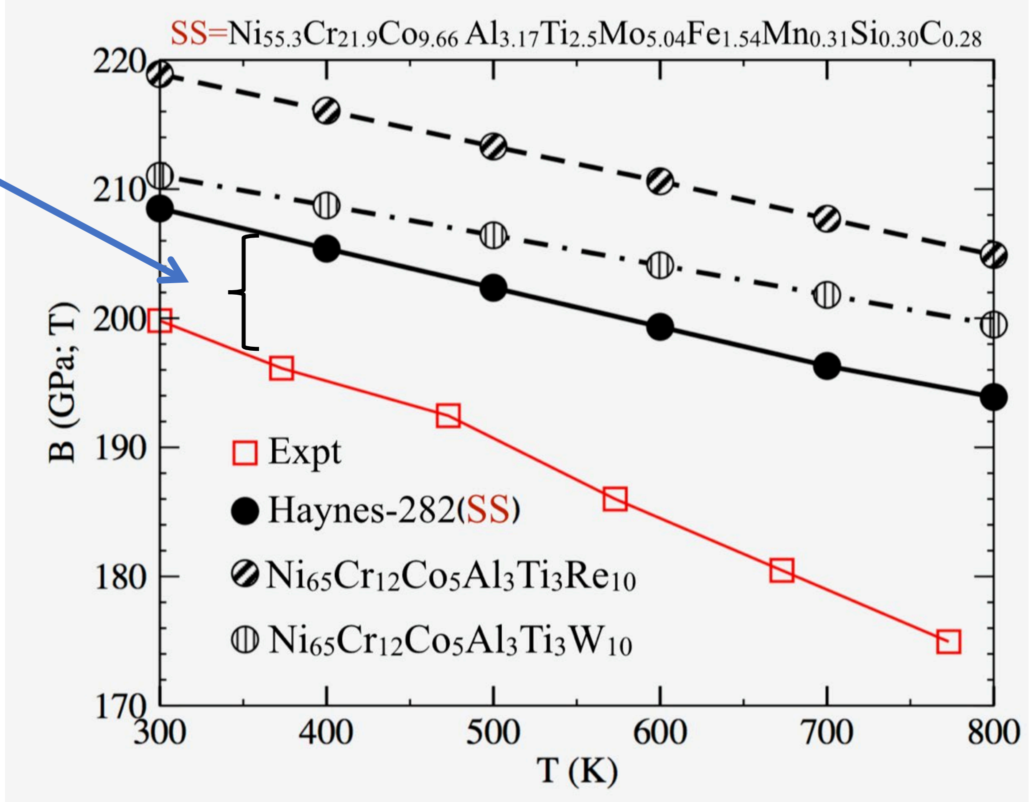
Role of refractories on bulk moduli

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).

Role of refractories on phase stability

1st Generation

Experimental (DSC)melting data compared to Haynes-282.

Model alloys selected to validate specific predictions

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

- **Deviation from prediction**

ID	Composition	Melting T Onset	Melting T Peak	Melting T End
H282	$Ni_{55.3}Cr_{21.9}Co_{9.7}Al_{3.2}Ti_{2.2}Mo_{5.0}Fe_{1.5}Mn_{0.3}Si_{0.3}C_{0.3}$	1329.5	1362.7	1369.9
1A	$Ni_{76.5}Cr_{14.1}Co_{5.9}Al_{3.5}$	1427.8	1442.1	1445.2
9A	$Ni_{75.6}Cr_{11.63}Co_{5.81}Al_{3.5}Ti_{3.5}$	1369.7	1396.1	1404.8
2A	$Ni_{65}Cr_{12}Co_{5}Re_{3}W_{8}Al_{3}Ti_{4}$	1358.7	1411.1	1424.2
3A’	$Ni_{67}Cr_{12.4}Co_{5.2}Re_{8.2}Al_{3.1}Ti_{4.1}$	1374.5	1413	1470
4A	$Ni_{65}Cr_{12}Co_{5}Re_{8}Al_{3}Ti_{7}$	1324.9	1369.2	1402.7
5A	$Ni_{65}Cr_{12}Co_{5}W_{8}Al_{3}Ti_{7}$	1315	1369.3	1384.3
6A	$Ni_{69}Cr_{10}Co_{5}W_{10}Al_{3}Ti_{3}$	1401	1431.5	1439.9
7A	$Ni_{69}Cr_{10}Co_{5}Re_{10}Al_{3}Ti_{3}$	1394.2	1436.3	1494.3
8A	$Ni_{69}Cr_{10}Co_{5}W_{5}Re_{5}Al_{3}Ti_{3}$	1400.8	1442.7	1449.2
10A	$Ni_{71.4}Cr_{13.2}Co_{5.1}Mo_{5.1}Al_{3.06}Ti_{2.04}$	1379.7	1405.7	1410.8
11A	$Ni_{71.4}Cr_{13.2}Co_{5.1}W_{5.1}Al_{3.06}Ti_{2.04}$	1403.8	1434.4	1440.7
12A	$Ni_{71.4}Cr_{13.2}Co_{5.1}Re_{5.1}Al_{3.06}Ti_{2.04}$	1400.4	1442.7	1452.3

Role of Ti

Role of Ti, Re & W

Role of Re & W

Role of Mo, Re & W

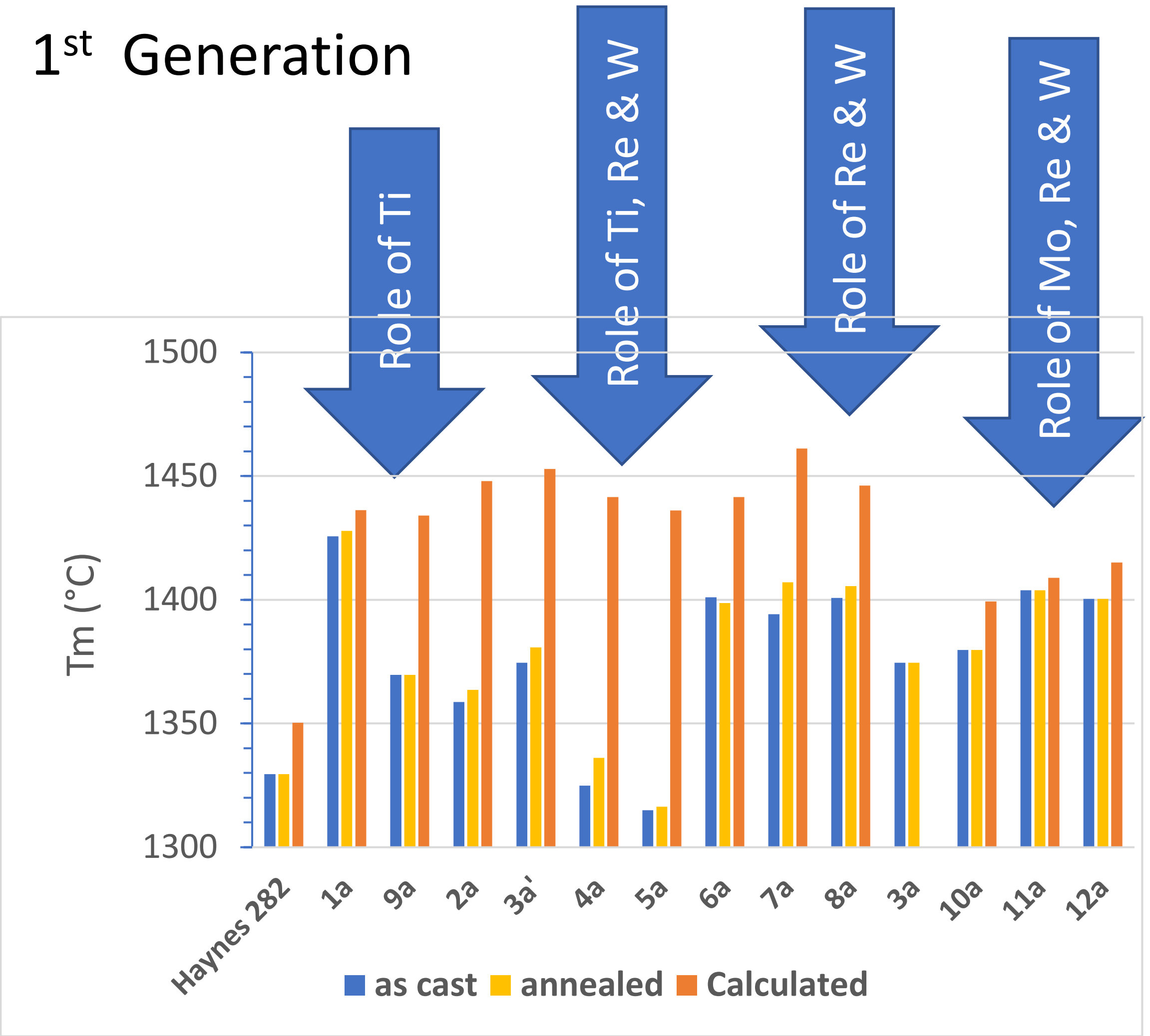
Role of refractories on phase stability

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.**

1st Generation

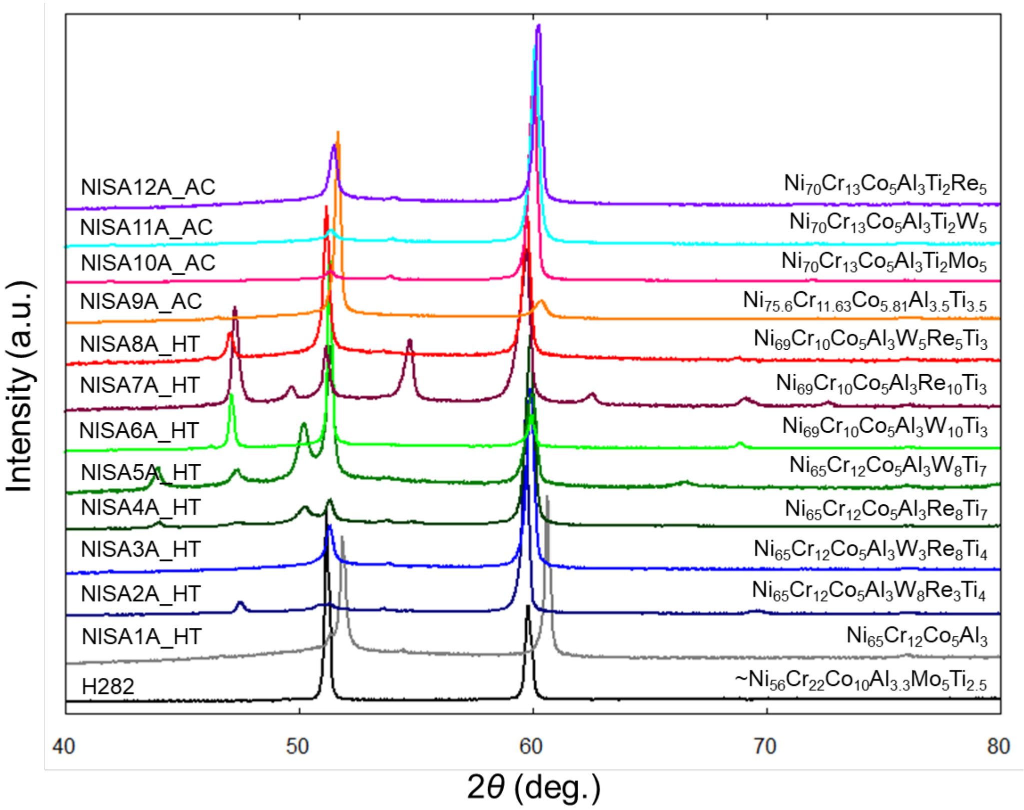


Refined suite of compositions

2nd generation results

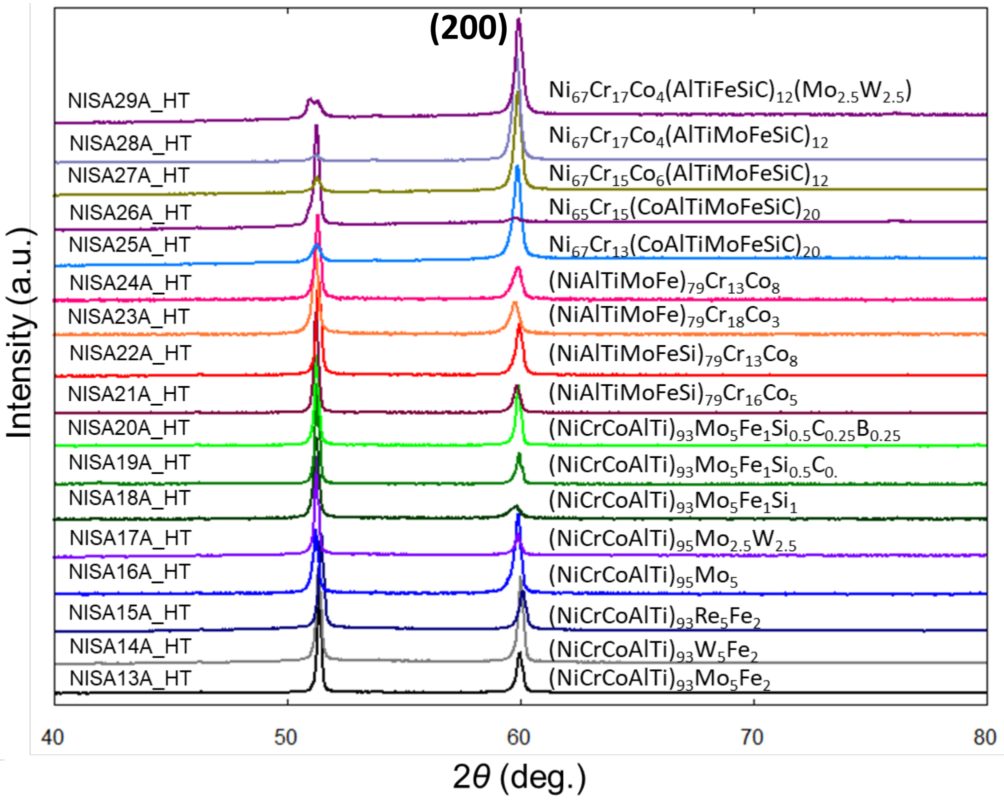
- Target compositions w/ fcc matrix
- Investigate larger range of Ni, Co and Cr
- Include B, C, Fe and Si

1st Generation alloy



fcc, bcc and $L1_2$ phases present

2nd Generation alloy

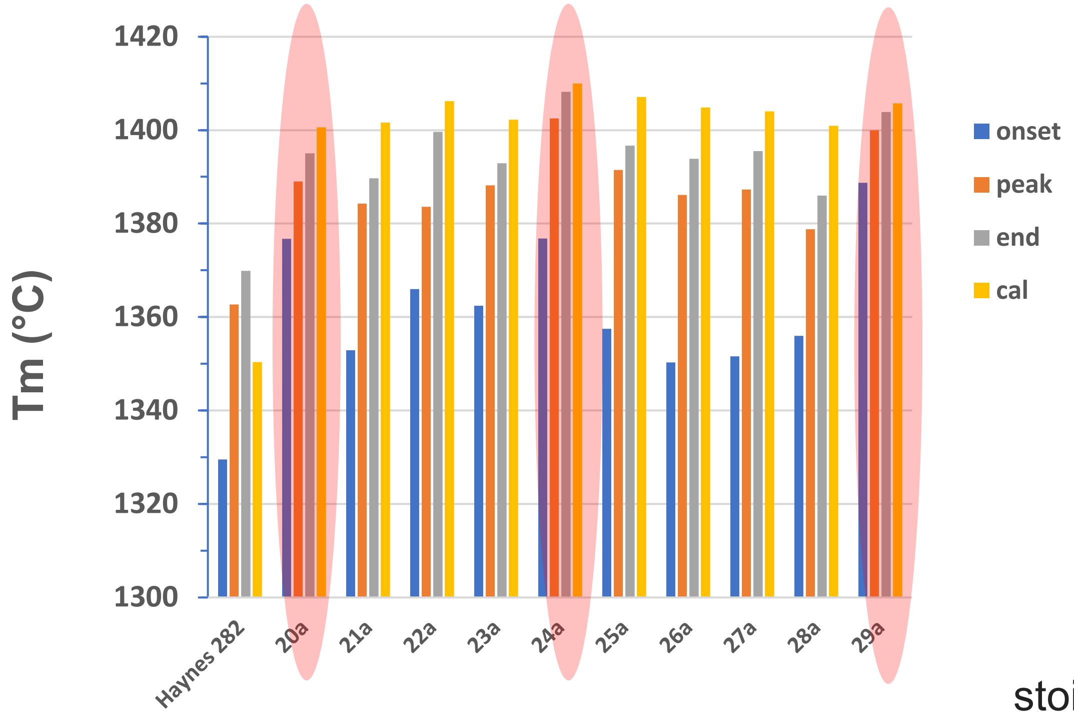


Nearly single phase fcc,
as cast show texturing along [200]

Refined suite of compositions

2nd generation results

- Increased T_m
- Narrow the range of melting



ID	Composition	Melting T		
		Onset	Peak	End
H282	$Ni_{55.3}Cr_{21.9}Co_{9.7}Al_{3.2}Ti_{2.2}Mo_{5.0}Fe_{1.5}Mn_{0.3}Si_{0.3}C_{0.3}$	1329.5	1362.7	1369.9
13A	$(NiCrCoAlTi)_{93}Mo_5Fe_2$	1380.3	1404.4	1410.6
14A	$(NiCrCoAlTi)_{93}W_5Fe_2$	1407.0	1435.7	1441.4
15A	$(NiCrCoAlTi)_{93}Re_5Fe_2$	1411.3	1441.7	1460.5
16A	$(NiCrCoAlTi)_{95}Mo_5$	1362.6	1388.8	1393.7
17A	$(NiCrCoAlTi)_{95}Mo_{2.5}W_{2.5}$	1380.4	1407.7	1413.1
18A	$(NiCrCoAlTi)_{93}Mo_5Fe_1Si_1$	1351.4	1386.0	1392.9
19A	$(NiCrCoAlTi)_{93}Mo_5Fe_1Si_{0.5}C_{0.5}$	1356.8	1382.5	1389.5
20A	$(NiCrCoAlTi)_{93}Mo_5Fe_1Si_{0.5}C_{0.25}B_{0.25}$	1376.7	1389.0	1395.0
21A	$(NiAlTiMoFeSi)_{79}Cr_{16}Co_5$	1352.9	1384.3	1389.7
22A	$(NiAlTiMoFeSi)_{79}Cr_{13}Co_8$	1366	1383.6	1399.6
23A	$(NiAlTiMoFe)_{79}Cr_{18}Co_3$	1362.4	1388.2	1392.9
24A	$(NiAlTiMoFe)_{79}Cr_{13}Co_8$	1376.8	1402.5	1408.2
25A	$Ni_{67}Cr_{13}(CoAlTiMoFeSiC)_{20}$	1357.5	1391.5	1396.7
26A	$Ni_{65}Cr_{15}(CoAlTiMoFeSiC)_{20}$	1350.3	1386.1	1393.9
27A	$Ni_{67}Cr_{15}Co_6(AlTiMoFeSiC)_{12}$	1351.6	1387.3	1395.5
28A	$Ni_{67}Cr_{17}Co_4(AlTiMoFeSiC)_{12}$	1356.0	1378.8	1386.0
29A	$Ni_{67}Cr_{17}Co_4(AlTiFeSiC)_{12}(Mo_{2.5}W_{2.5})$	1388.7	1400.0	1403.9

Mo-W-Re

Fe, Cr:Co

Mo:W

Adding Si-C-B

Fe, Si w/ Cr:Co

Ni:Cr

Ni:Cr:Co

Cr:Co

Mo:W

stoichiometries are fixed for elements in the parentheses for each grouping

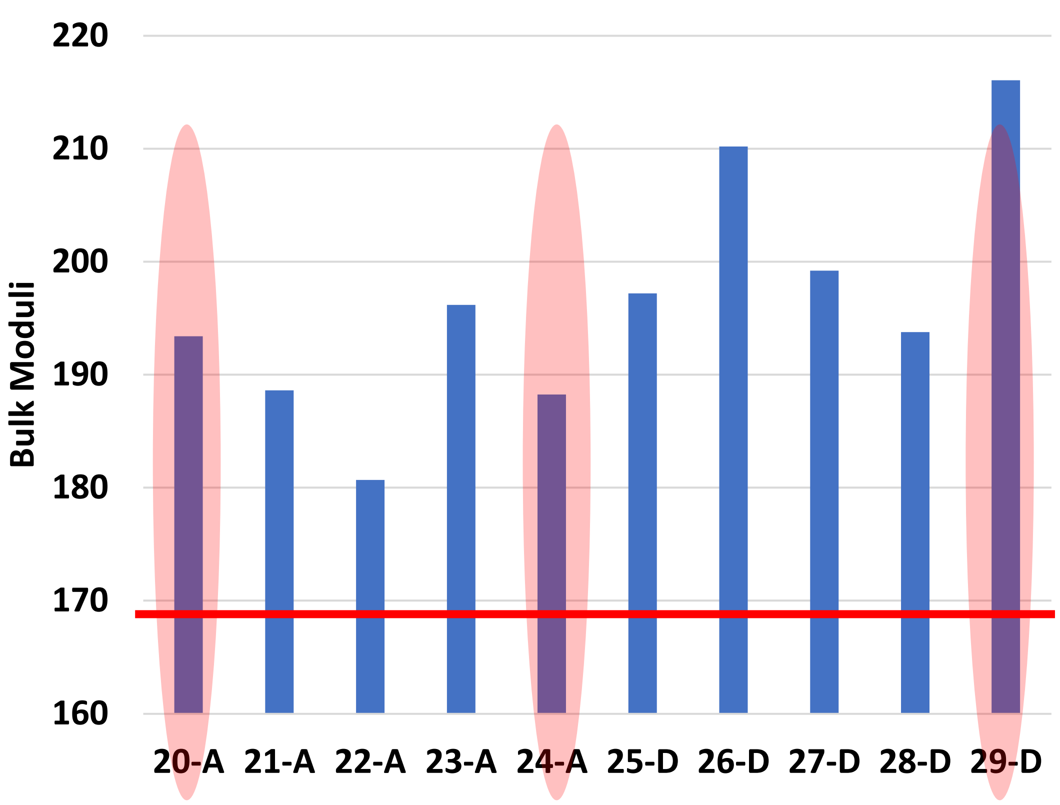
Refined suite of compositions for down selection process

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

Samples 20, 24 and 29 were selected for further study

2nd Generation



Highlighted samples have the highest T_m

Down Selection

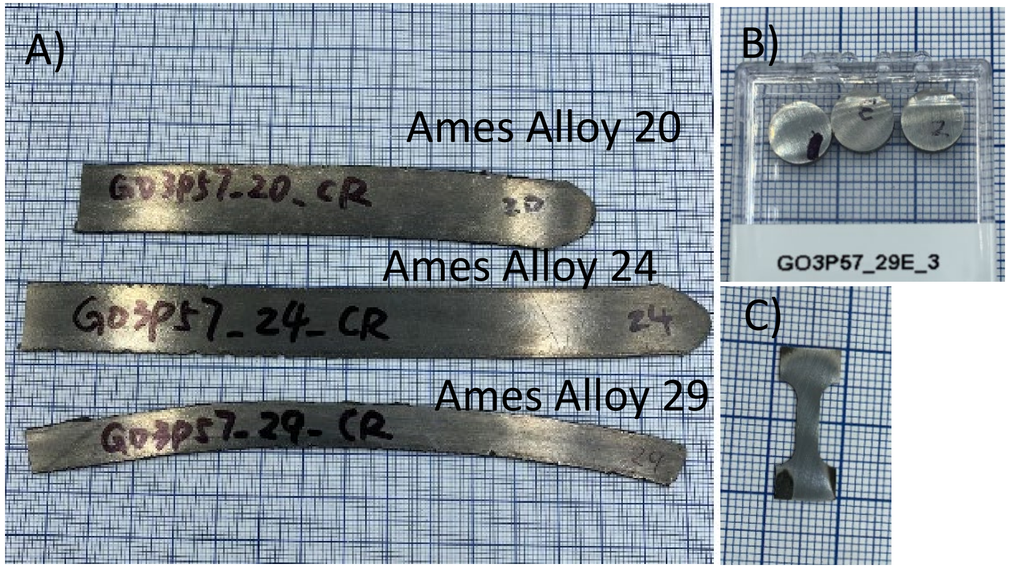
Made Larger Castings for more detailed testing

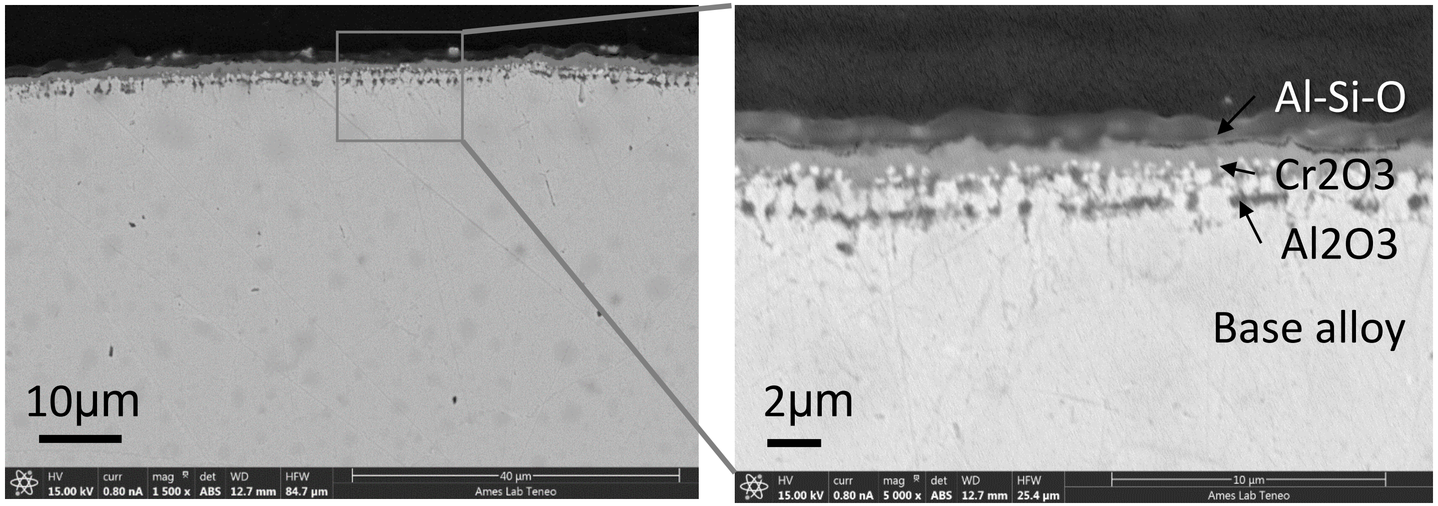
Hot and then Cold rolled

Tensile Testing at RT

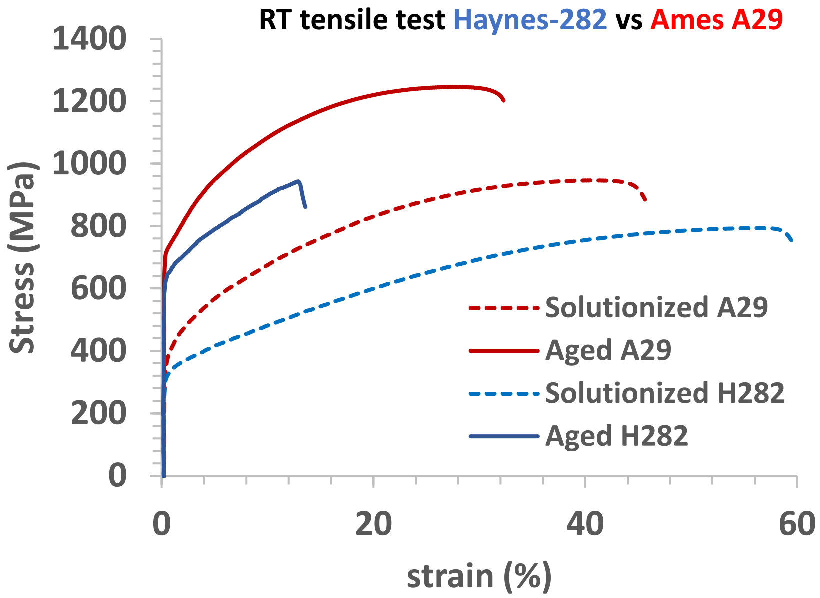
Solutionized and aged

Oxidation dry air





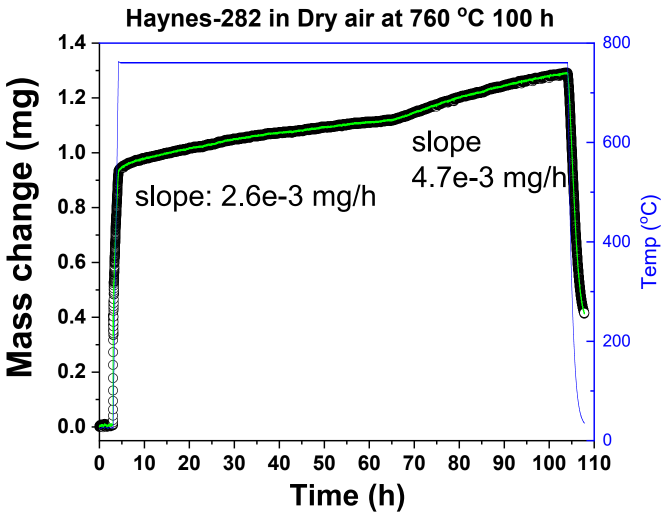
Ames A29 800°C 100h dry air oxidation

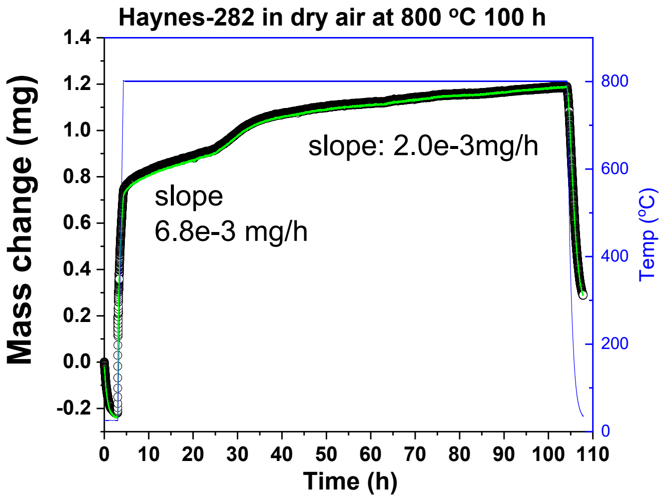


Baseline Characterization-Haynes 282

Oxidation (TGA)

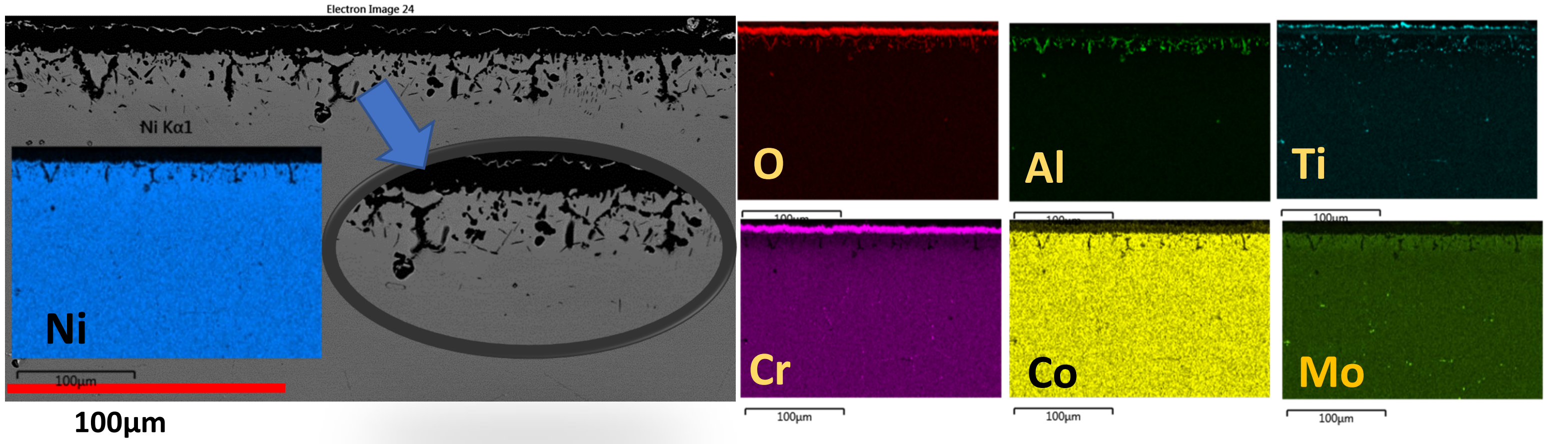
- Synthetic air, 760, 800, 900 & 1000 °C isothermal holds 20-100 hrs
- Two-step steady state oxidation
    - How does changes in alloy composition alter the transient and steady-state oxidation?





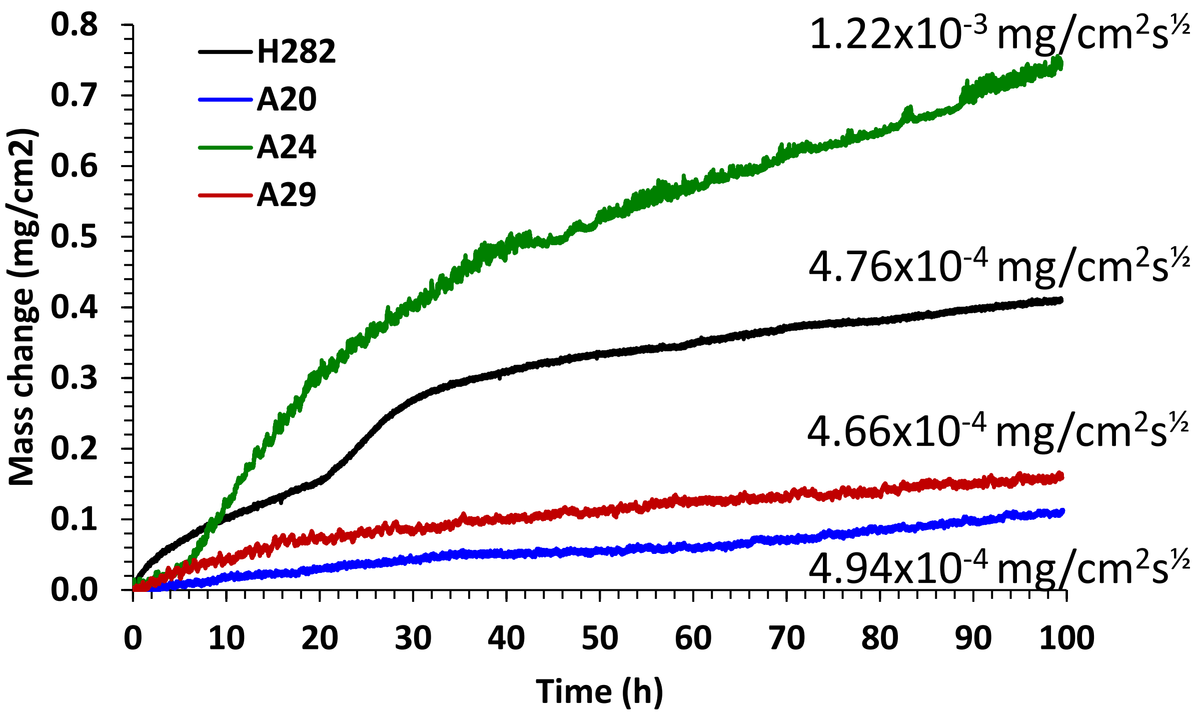
Cross-sectional SEM

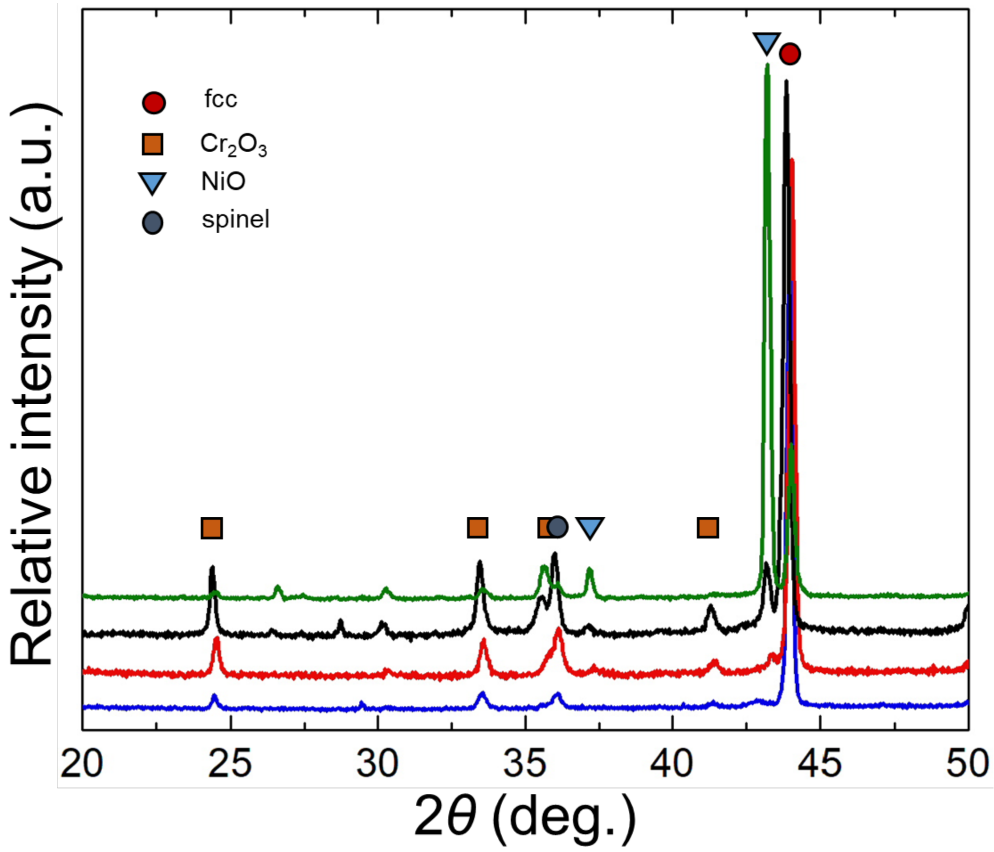
- ~10 µm continuous oxide layer
    - Primarily Cr_2O_3, TiO_2 and NiO (XRD)
    - Oxide penetration (~20 µm), mostly Al_2O_3 , No MoO_3



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

Oxidation: Haynes 282 vs Ames 20, 24 & 29 at 800°C





XRD of coupon surface

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

Next Steps

In depth analysis of the down-selected alloys

- Role of Mo:W on:
  - T_m and moduli
  - Relationship between calculated moduli and yield strength
- Role of Ni:Cr:Co
  - Small changes also have large effects on T_m and moduli
- Roles of B,C, Si
  - Dramatically effect short term oxidation

High Temperature tensile and creep strength

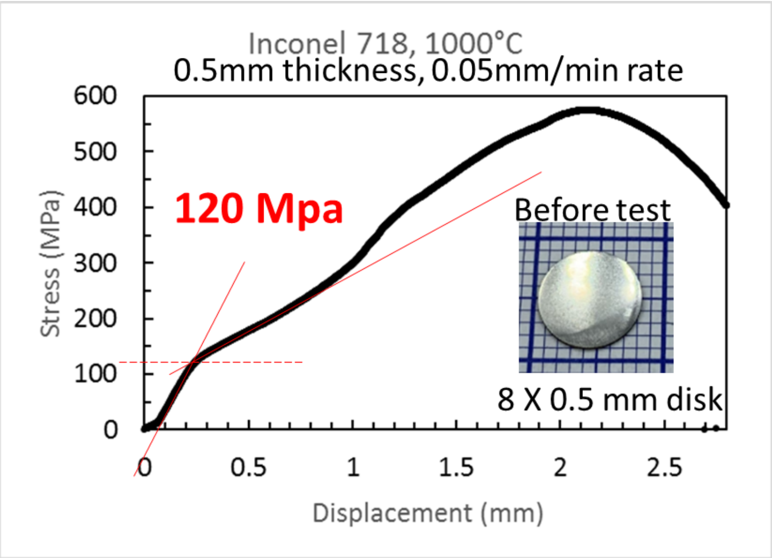
- Optimize aging protocols
  - Role of t, T and minor alloy content on carbide formation and γ”

Evaluate oxidation resistance compared to Haynes 282

- Perform 100 hrs oxidation test in dry air at 760, 800 and 900°C
- Extended oxidation test in dry and wet at 800°C

Challenges

- **Predicting lifetime performance**
  - **KKR-CPA is accurately predicting overall alloy performance for complex chemistries**
    - **Range of Stability**
    - **Moduli (as a function of T)**
  - **Can we extend these methods to predict stability at elevated T?**
  - **Need rapid screening methods to predict alloy performance under realistic conditions including:**
    - **Corrosion/oxidation**
    - **Creep**
    - **Aging**



Ames has developed a small punch test to rapidly evaluate small sample creep properties up to 1350°C.

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 FE 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 refractory alloys to withstand even higher temperatures and aggressive environments.
- 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.

Acknowledgment

"This material is based upon work supported by the Department of Energy Award Number AL-19-510-097."