

Development of Oxidation Resistant Valve Alloys for 900- 950°C Use

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2021 DOE Vehicle Technologies Office Annual Merit Review

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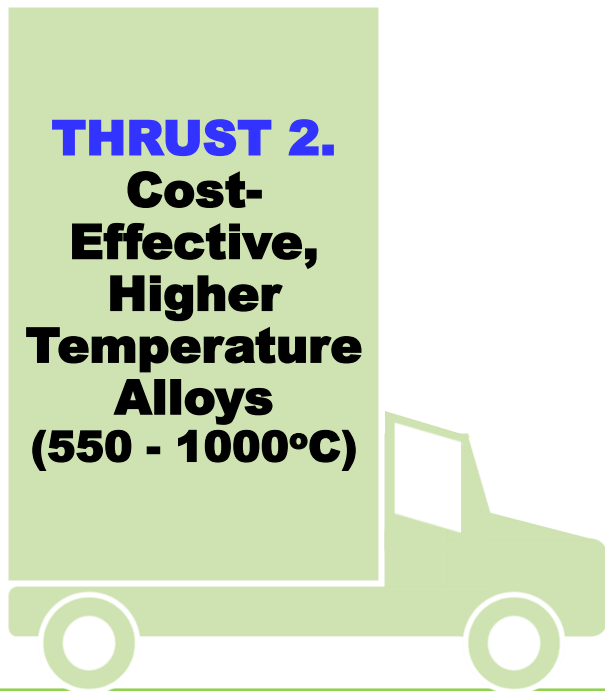
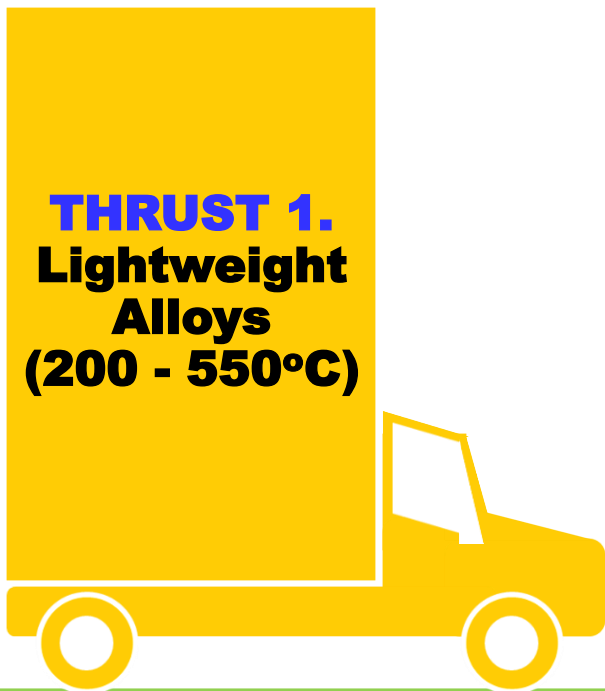
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Bridge to the future for medium and heavy-duty vehicle propulsion

VTO Powertrain Materials Core Program

3 National Labs, 30+ researchers, 4 Thrust Areas, 17 Tasks



TRL 1

TRL 4

Accelerating Development of Powertrain Alloys

Supported by Adv. Characterization & Computation

THRUST 4.

Atom Probe
Synchrotron
Microscopy
Neutrons

Thermodynamics
Modern Data Analytics
High Performance Computing

ICME

\$30M/5 years launched in FY19

Task 2A1 Overview: Oxidation Resistant Valve Alloys (900-950°C)

Timeline/Budget

- Task start: October 2018
- Task end: September 2022
- Percent complete: 70%
- **2A1 Budget**
 - FY20: \$400k
 - FY21: \$400K

Barriers

- Higher power density engines leading to higher peak exhaust valve temperatures requiring new materials
- Existing commercial alloys do not meet both the performance and cost targets for higher temperature use and lack of new industrial alloy development
- Long lead times for new materials commercialization
- Inadequate battery power density to electrify heavy duty, long haul freight

Thrust 2. Cost-Effective, Higher Temperature Alloys

- 2A. Advanced Affordable Wrought Powertrain Alloys*
- 2B. Affordable, High Performance Cast Powertrain Alloys*

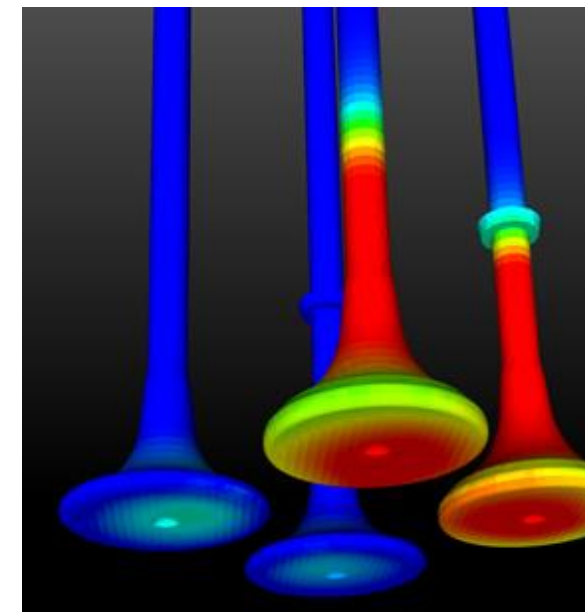
Task	Title	TRL	FY20	FY21
2A1	Oxidation Resistant Valve Alloys	Mid	\$400k	\$400k
2A2	Higher Temperature Heavy-Duty Piston Alloys	Low	\$200k	\$200k
2A3	High Temperature Coatings for Valve Alloys	Mid	\$175k	\$160k
2A4	High Temperature Oxidation	Low	\$175k	\$175k
2B1	Development of Cast, Higher Temperature Austenitic Alloys	Mid	\$275k	\$305k
2B2	Selective Material Processing to Improve Local Properties <i>PNNL</i>	Mid	\$300k	\$300k
Subtotals			\$1,225k	\$1,540k

Partners

- **Task 2A1 Lead**
 - Oak Ridge National Laboratory (ORNL)
- **Thrust 2 Partners**
 - Task 2A3
 - Task 2A4
- **Thrust 4A Partners**
 - Argonne National Laboratory (ANL)
 - Pacific Northwest National Laboratory (PNNL)
- **Thrust 4B Partners**
 - Oak Ridge National Laboratory (ORNL)
- **Industrial partners**
 - Special Metals
 - Tenneco/ Federal Mogul Powertrain (CRADA)

Relevance

- Exhaust gas temperatures are increasing in higher efficiency **heavy-duty engines, engines using alternate fuels, and in hybrid electric systems**
 - Estimated to increase from 870°C to 950°C (by 2025) and to 1000°C (by 2050)
- Commercially available Ni-based alloys (**IN[®]751, Udimet[®]520**)
 - Have insufficient strength at the higher temperatures, **OR**
 - Lack oxidation resistance, **OR**
 - Are prohibitively expensive
- **Objectives:** Develop cost-effective exhaust valve materials for 900 - 950°C use in advanced future engine concepts
 - Develop cost-effective alloys with balanced
 - High temperature tensile and fatigue strengths: $f(\text{cylinder pressure, valve diameter, temp})$, **and**
 - Oxidation resistance
 - Demonstrate use in exhaust valves with industrial partner



Commercial Alloys of Interest are Ni-Based

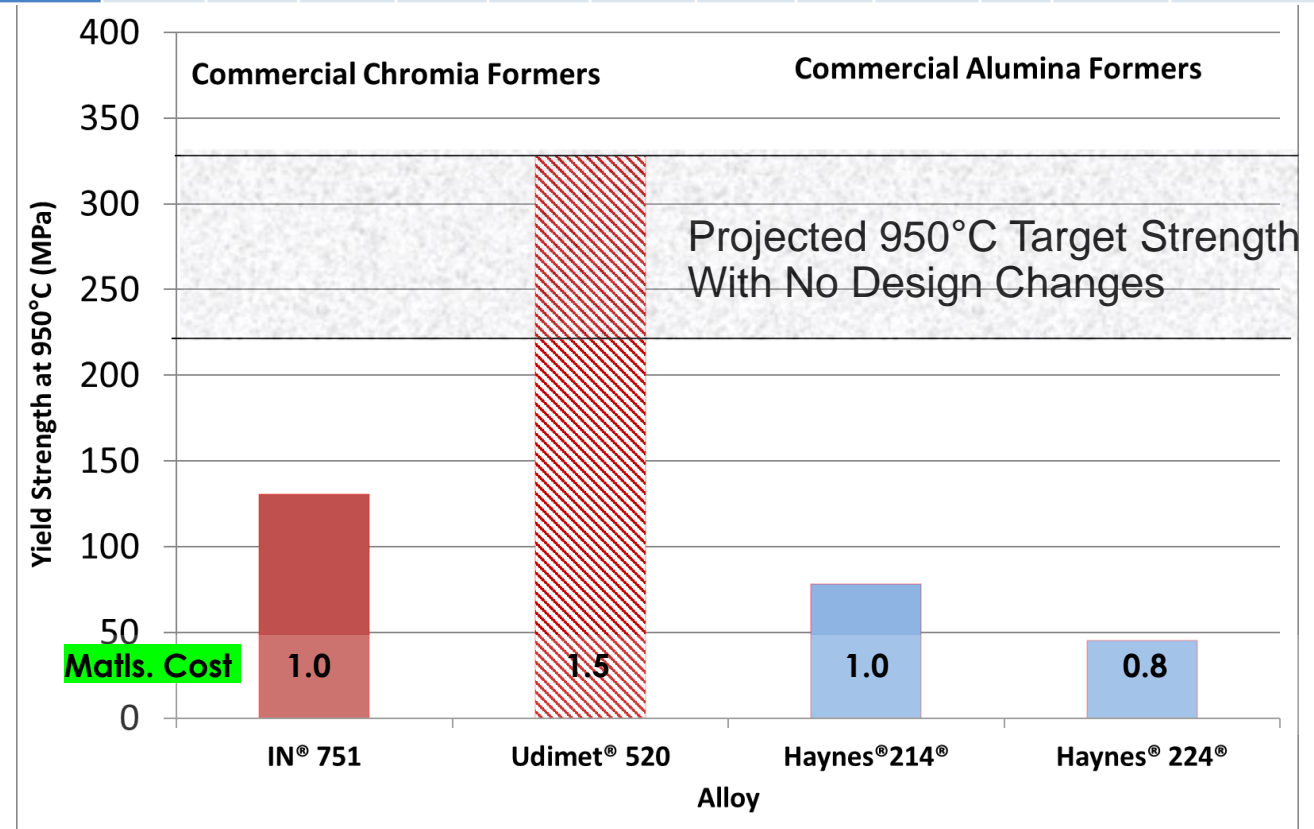
• Chromia-scale formers (limited to $\leq \sim 850-900^{\circ}\text{C}$)

- Current valve alloy IN[®]751 cannot be used above $\sim 850^{\circ}\text{C}$
 - Loss of strength due to dissolution of γ' [(Ni₃(Al, Ti))]
- Other alloys (e.g. Udimet[®]520) are expensive due to high levels of Ni + Co and manufacturing challenges
- **Poor oxidation resistance above $\sim 850-900^{\circ}\text{C}$**

• Alumina-scale formers (desirable for $\geq \sim 900^{\circ}\text{C}$)

- Good oxidation resistance in water vapor containing environments
- **Commercial alumina-formers have inadequate strength at $900-950^{\circ}\text{C}$**

Alloy	Ni	Co	Fe	Cr	Mo	Si	Mn	Al	Ti	W	C	Comments
IN [®] 751	71.32	0.04	8.03	15.7	-	0.09	0.08	1.2	2.56	-	0.03	Chromia-former
Udimet [®] 520	57.65	11.7	0.59	18.6	6.35	0.05	0.01	2.0	3.0	-	0.04	Chromia-former
Haynes [®] 214 [®]	72.3	<0.15	3	16	<0.2	0.07	<0.5	4.5	<0.5	<0.5	0.04	Alumina-former
Haynes [®] 224 [®]	44.75	<2	27.5	20	<0.5	0.3	<0.5	3.6	0.3	<0.5	0.05	Alumina-former



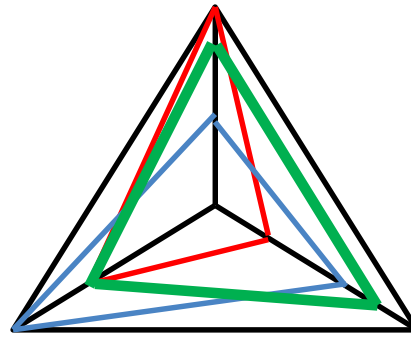
FY20-FY21 Milestones

Month/ Year	Milestone Description	Status
Sep. 2020	Complete initial fatigue testing at 900°C on industrial scale chromia-forming alloys and in collaboration with industrial partner, identify path for either down-select or additional scale-up of alloys	Completed
Dec. 2020	Complete assessment of effect of heat-treatment on microstructure, tensile, and fatigue properties of the two additional scaled-up chromia-forming alloys in collaboration with CRADA partner and propose compositional modifications	Completed
Mar. 2021	Complete design and fabrication of laboratory scale heats of alumina-forming alloys with targeted yield strengths of ≥ 40 Ksi at 950°C	Completed
Jun. 2021	<p>Complete evaluation of high temperature tensile properties of new laboratory-scale alumina-forming alloys and initial microstructural characterization</p> <p>Go: Identify atleast one alloy with yield strength ≥ 40 Ksi (276 MPa) at 950°C-</p> <p>Continue with current alloy development scheme</p> <p>No-Go: Identify alternate alloy development or heat-treatment schemes to improve high temperature strength</p>	Completed (Go)
Sep. 2021	Summarize fatigue properties at 900°C for a total of three industrial scale chromia-forming alloys and in collaboration with CRADA partner compare with targets and develop plan for scale-up	On-track

Overall Approach: Two Parallel Paths Are Being Followed

OVERALL APPROACH

High Temperature Strength



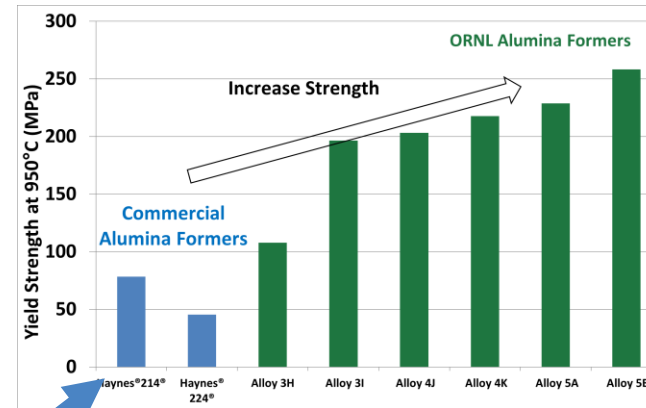
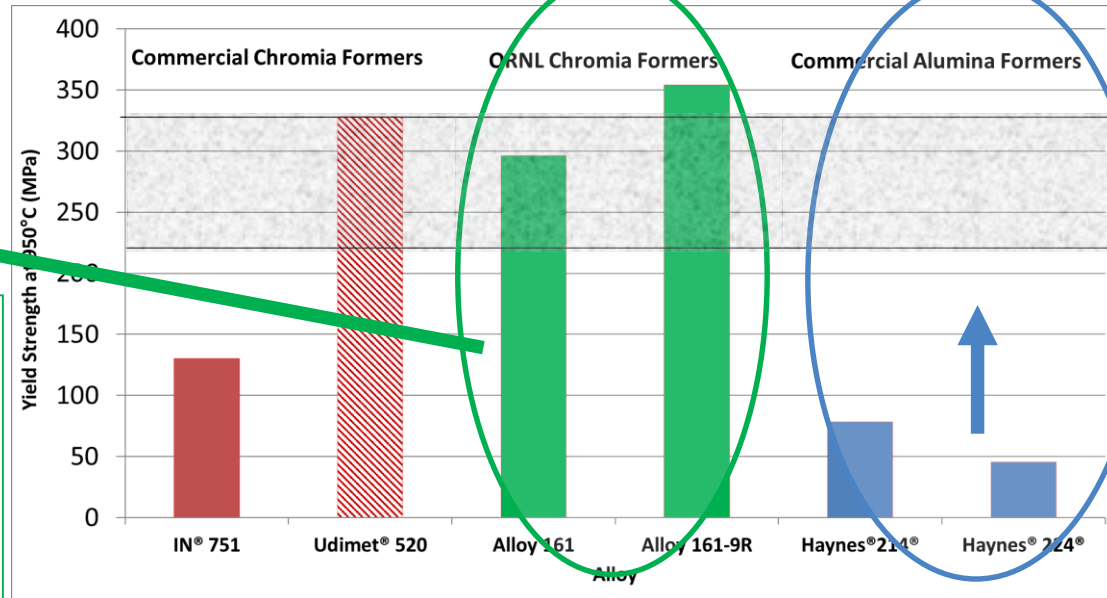
Achieve good strength and oxidation/corrosion resistance at low cost

M2045
(Scale-up of ORNL Alloy 161)



Oxidation/Corrosion Resistance

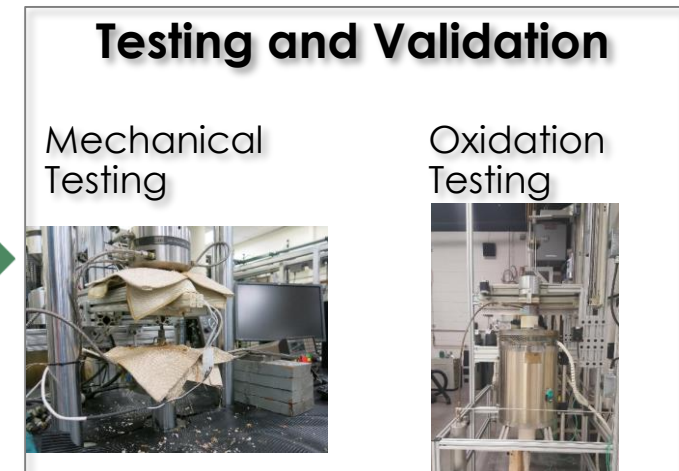
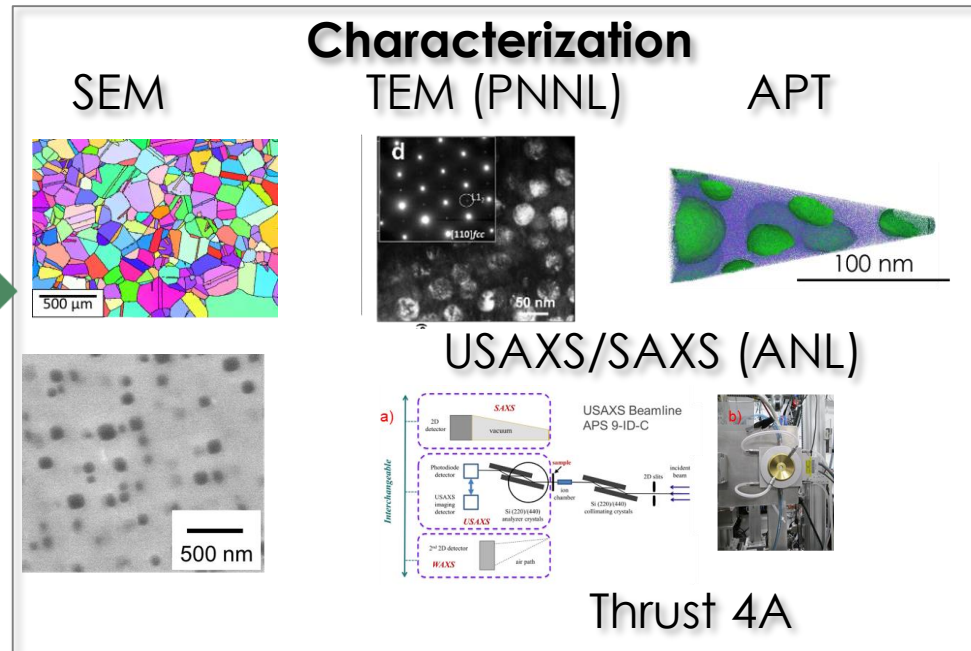
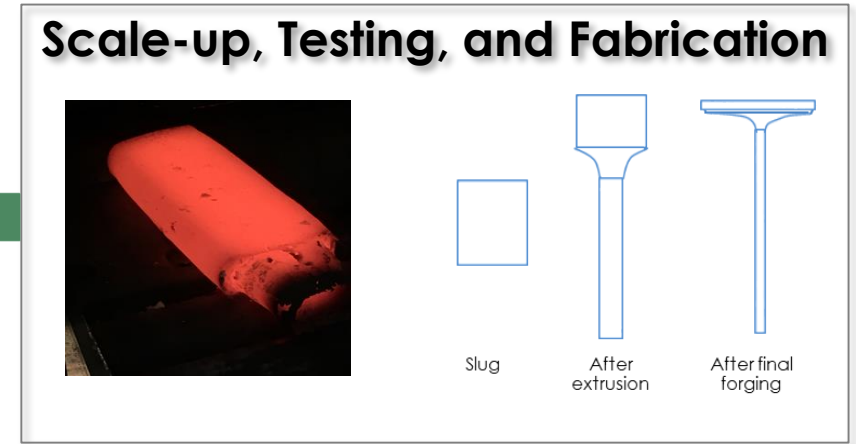
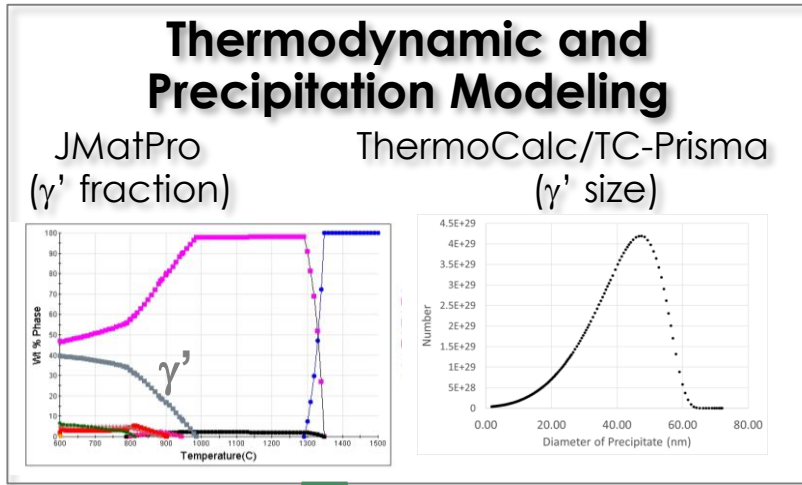
Cost Effectiveness



Path 1
Chromia-forming ($\leq 900^{\circ}\text{C}$)
Scale-up and commercialize best lower-cost ORNL Alloys

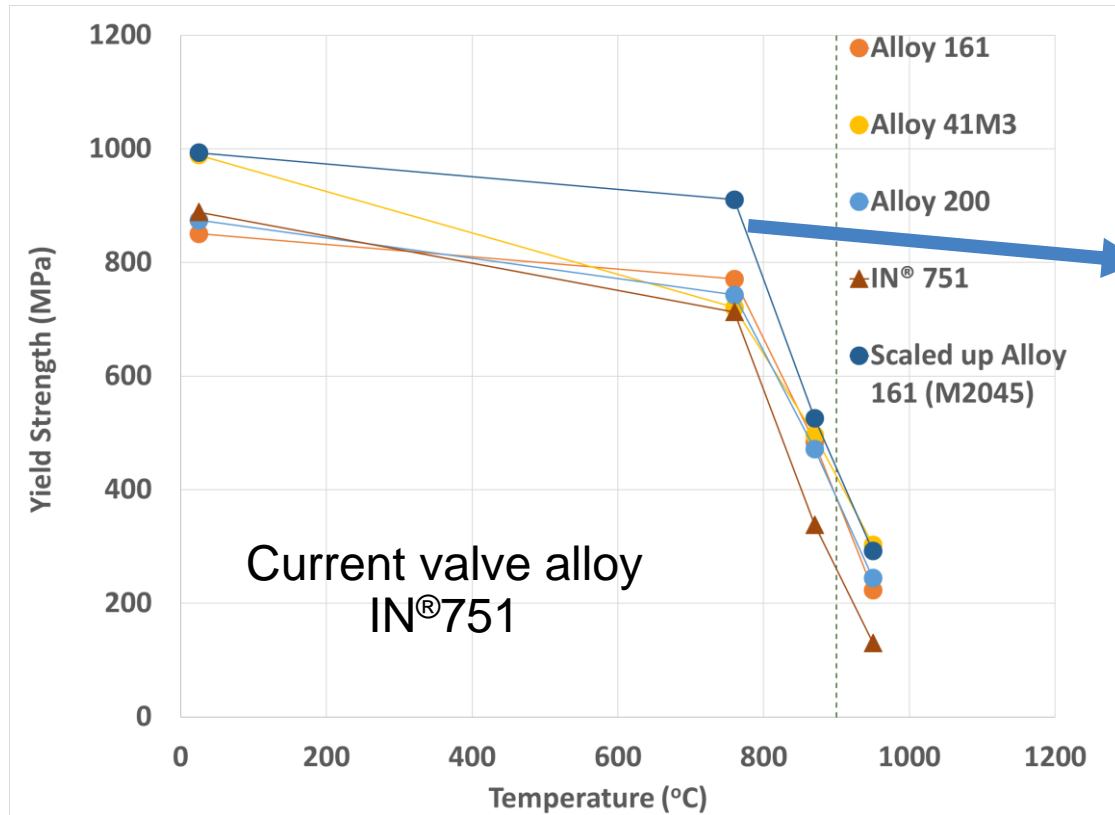
Path 2
Alumina-forming ($\geq 900^{\circ}\text{C}$)
Develop higher strength alloys using computational modeling

New Generation of Alloys Designed Using Computational Modeling, Laboratory Scale Alloy Fabrication, and Testing

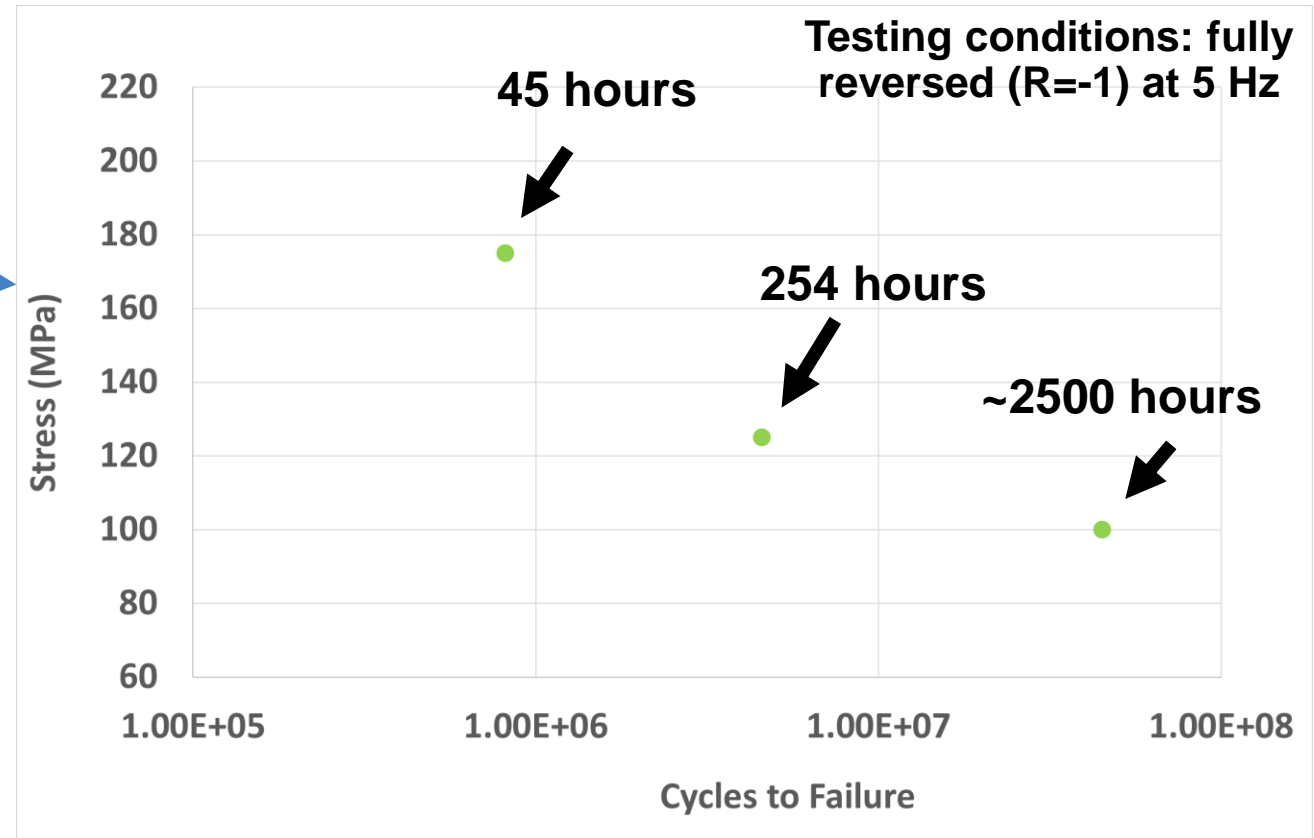


Industrial Heat M2045 of Alloy 161 Shows Good Tensile and Fatigue Properties at 900°C (up to ~ 2500 hours)

Multiple ORNL alloys show better tensile properties compared to IN[®]751 at 900°C

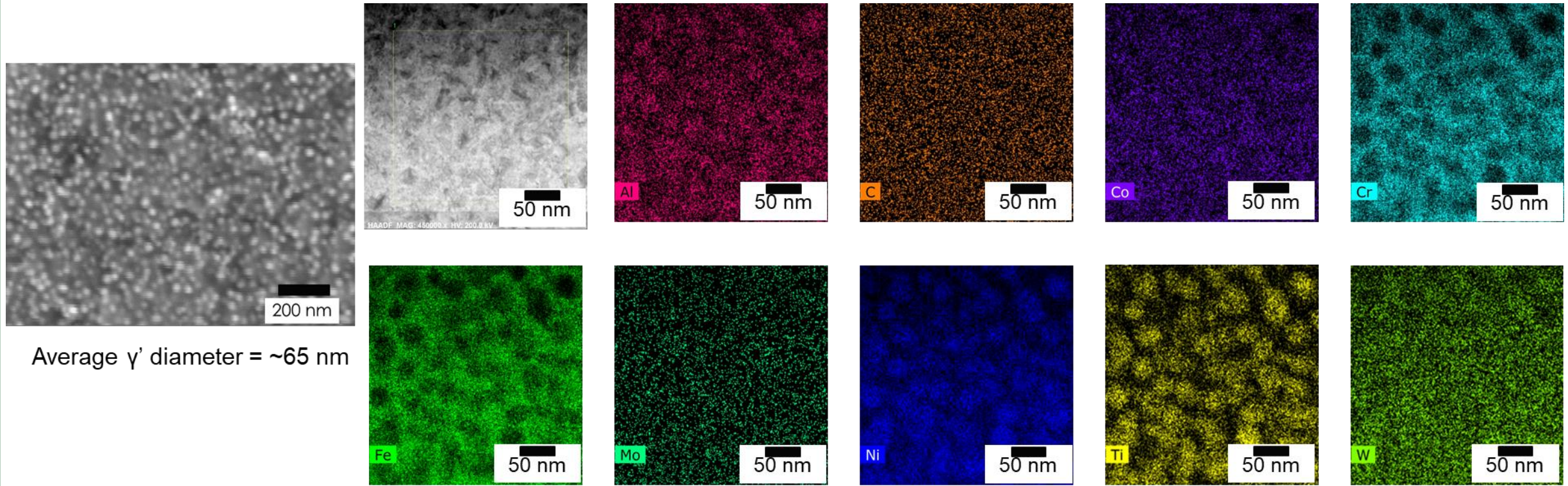


Fatigue testing of M2045 (Scaled up ORNL alloy 161) shows good long-term stability at 900°C



Scale-up is expensive: Need to understand failure mechanisms to help down-select best ORNL alloy for fabrication of exhaust valve

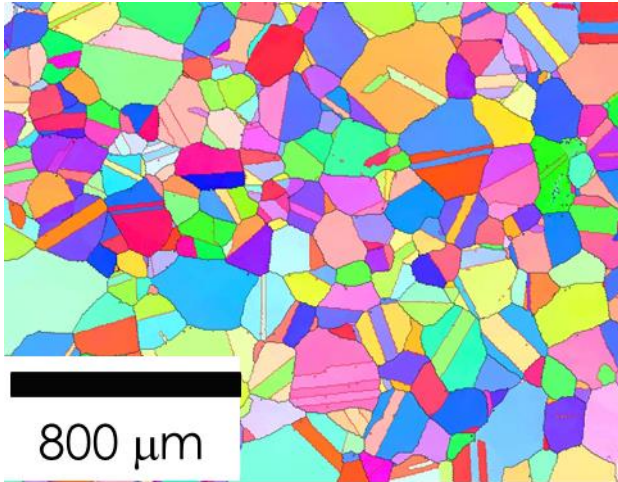
SEM and TEM Studies Show Fine γ' Precipitates in the Aged Condition (800°C) in M2045 (Thrust 4A)



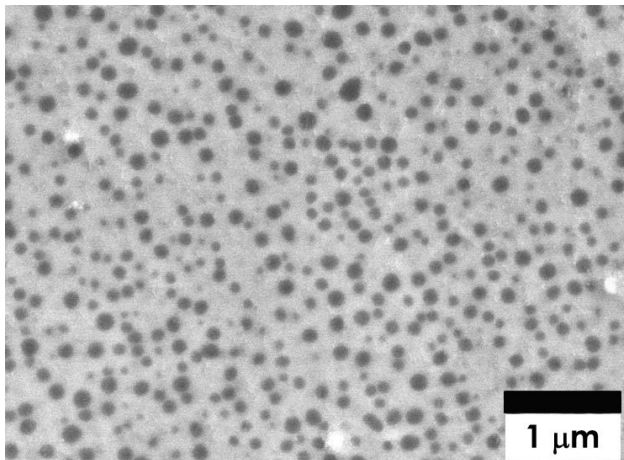
Important to understand evolution of microstructure and strengthening precipitates during long-term fatigue testing at high temperatures

Coarsening of γ' Observed After Fatigue Tests at 900°C in M2045

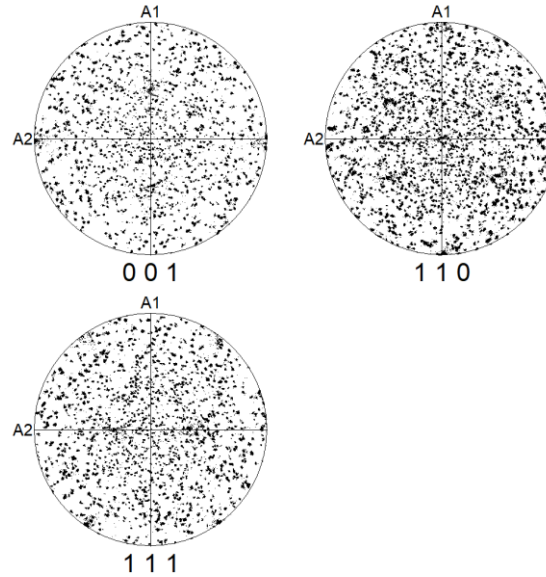
900°C - 175 MPa, 45 hours



grain size = $157 \pm 76 \mu\text{m}$



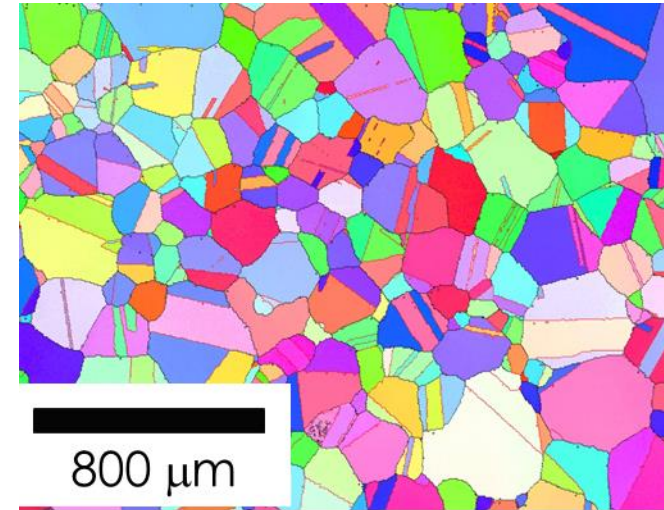
Average γ' diameter = 76 nm



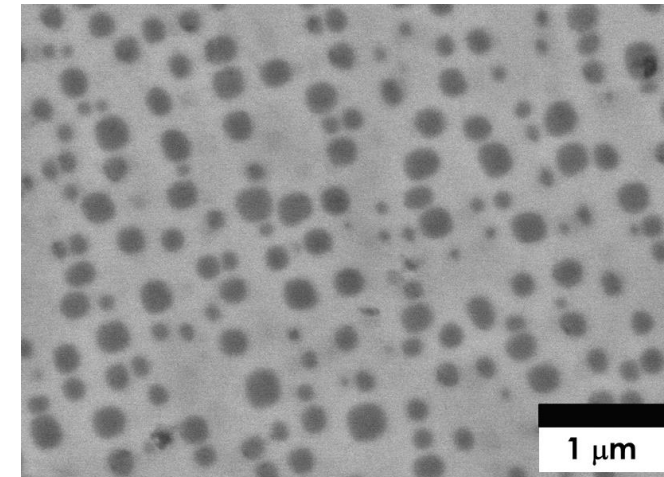
Pole figures show no obvious preferred orientation

Initial grain size = $145 \pm 23 \mu\text{m}$
Initial diameter = 65 nm

900°C - 125 MPa, 254 hours



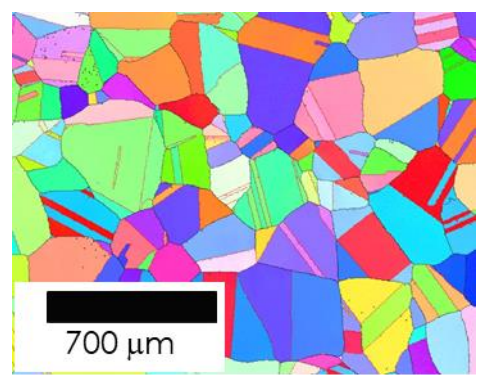
grain size = $166 \pm 75 \mu\text{m}$



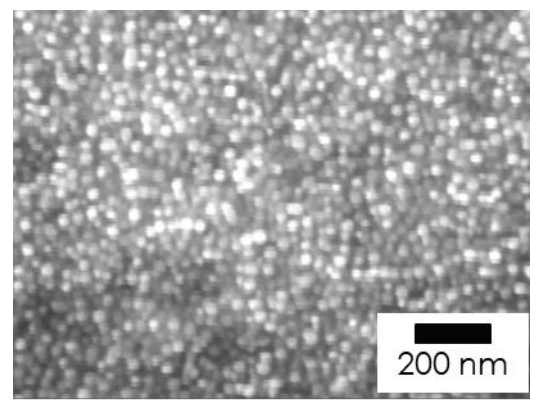
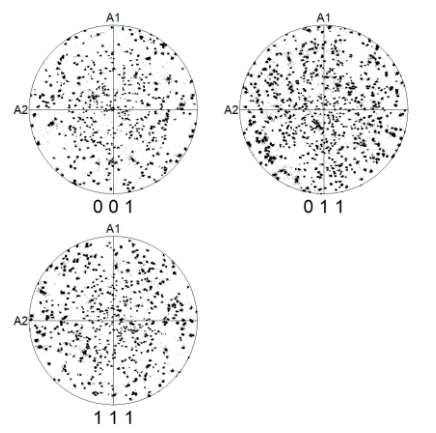
Average γ' diameter = 152 nm

New Industrial Heats Show Challenges in Processing

H2078 →

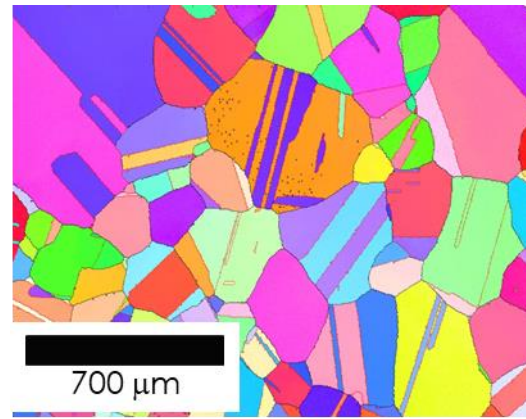


Average grain size = 193 μm

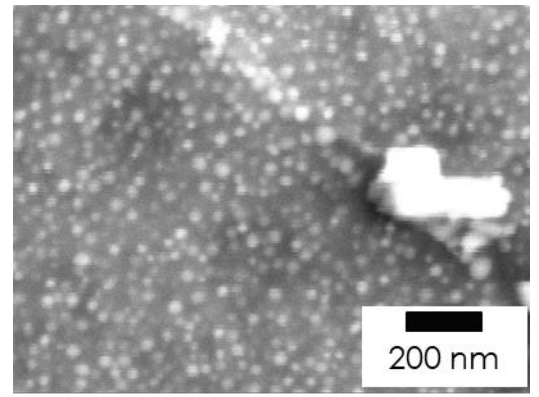
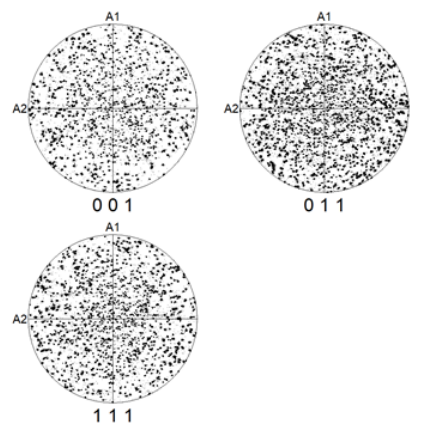


Two new successful scale-ups in FY20
ORNL Alloy 200 (H2078)
ORNL Alloy 163 (H2079)

H2079 →



Average grain size = 155 μm



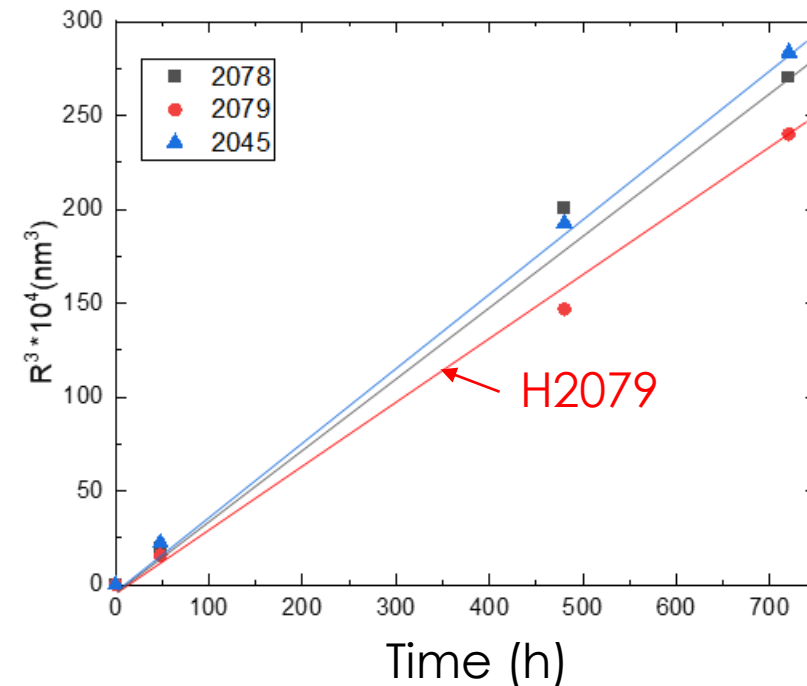
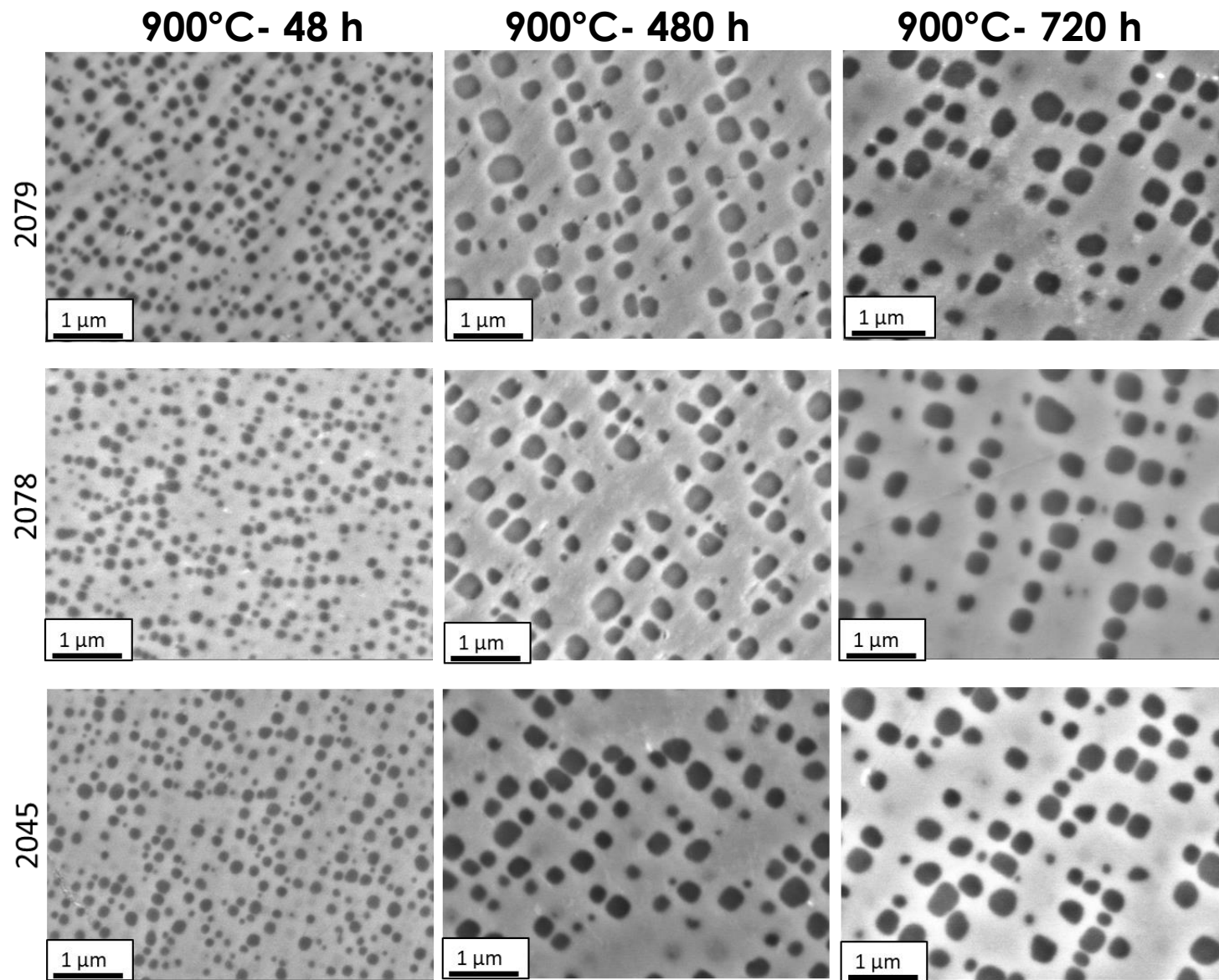
MV2045 grain size = 145 μm

Pole figures show no obvious preferred orientation

Fine γ' produced by aging

H2078 and H2079 show larger grain size (undesirable for strength and ductility) than M2045: Need to modify heat-treatment and future rolling process

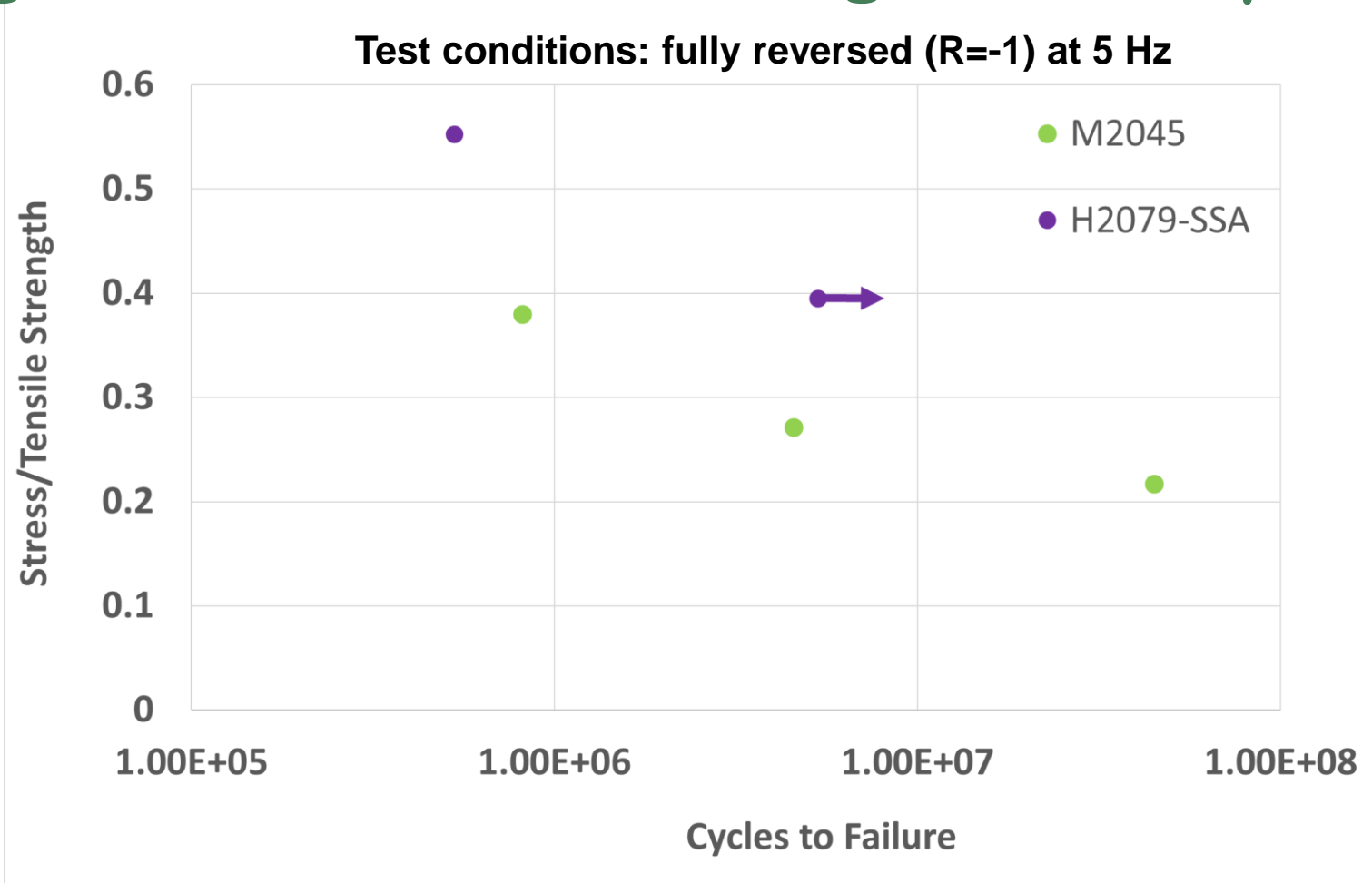
Coarsening Kinetics of γ' is Slower in HV2079 at 900°C



$(R^3 - R_0^3)$ vs. Time plot shows lower coarsening rate of H2079

Strength will be higher at longer times in HV2079 potentially improving fatigue properties

On-going Fatigue Testing of H2079 Suggests Potential Advantage of Slower Coarsening Rates of γ' Precipitates

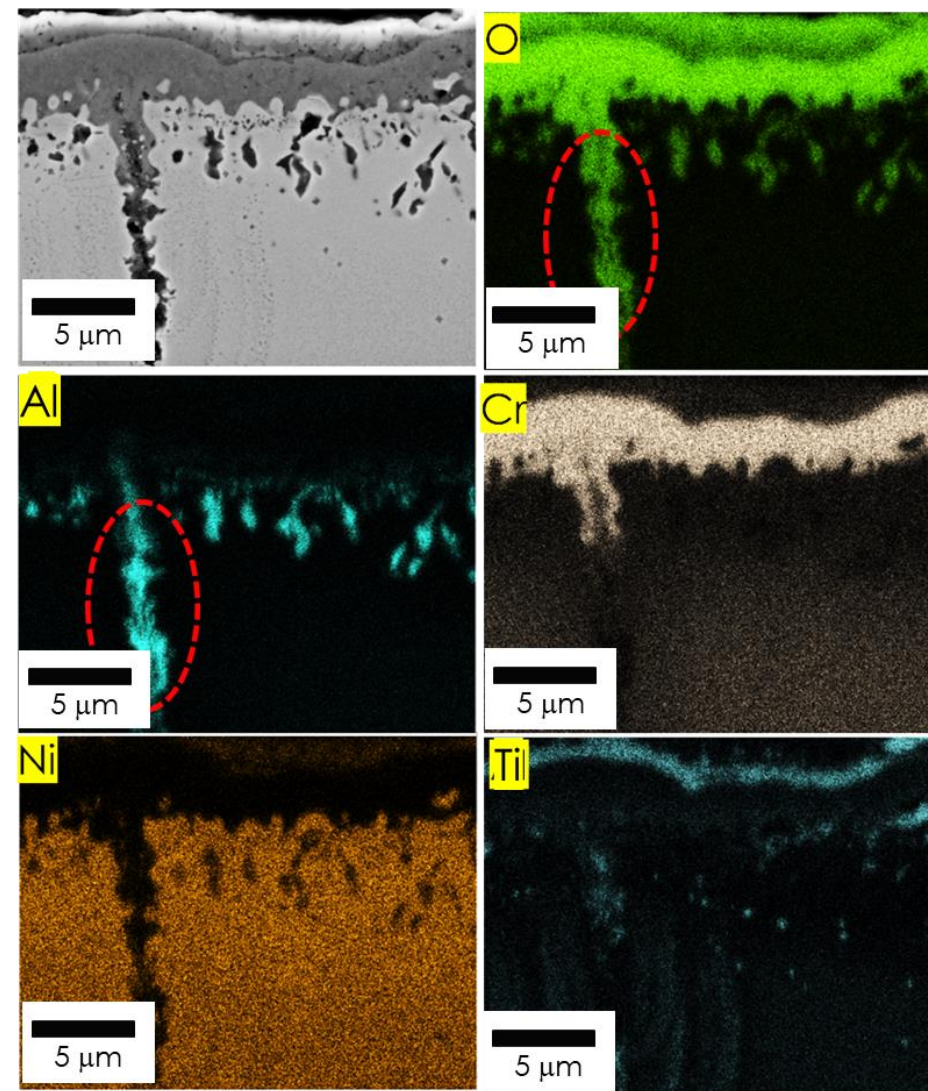
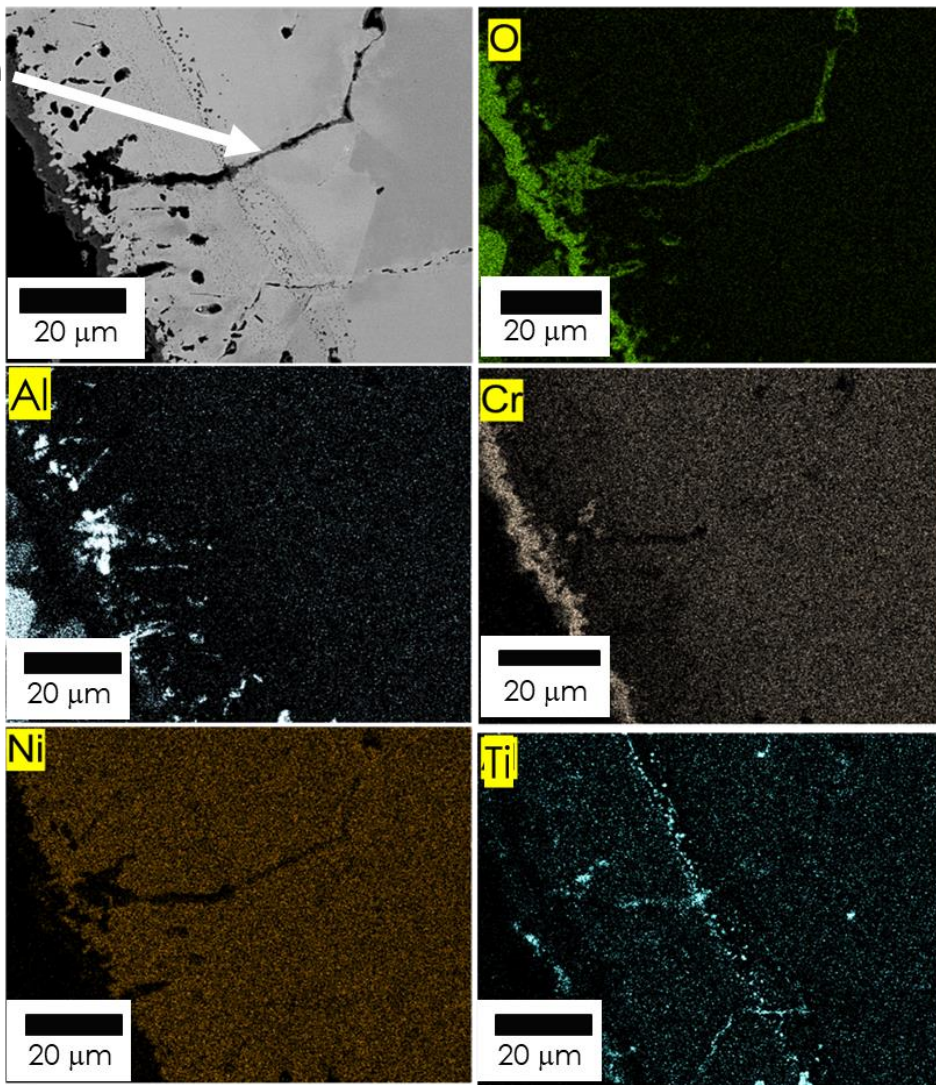


→ Indicates running test

Machined specimens of H2078 and H2079 have been sent to Tenneco Powertrain for *rotating beam fatigue tests*

900 °C -125 MPa

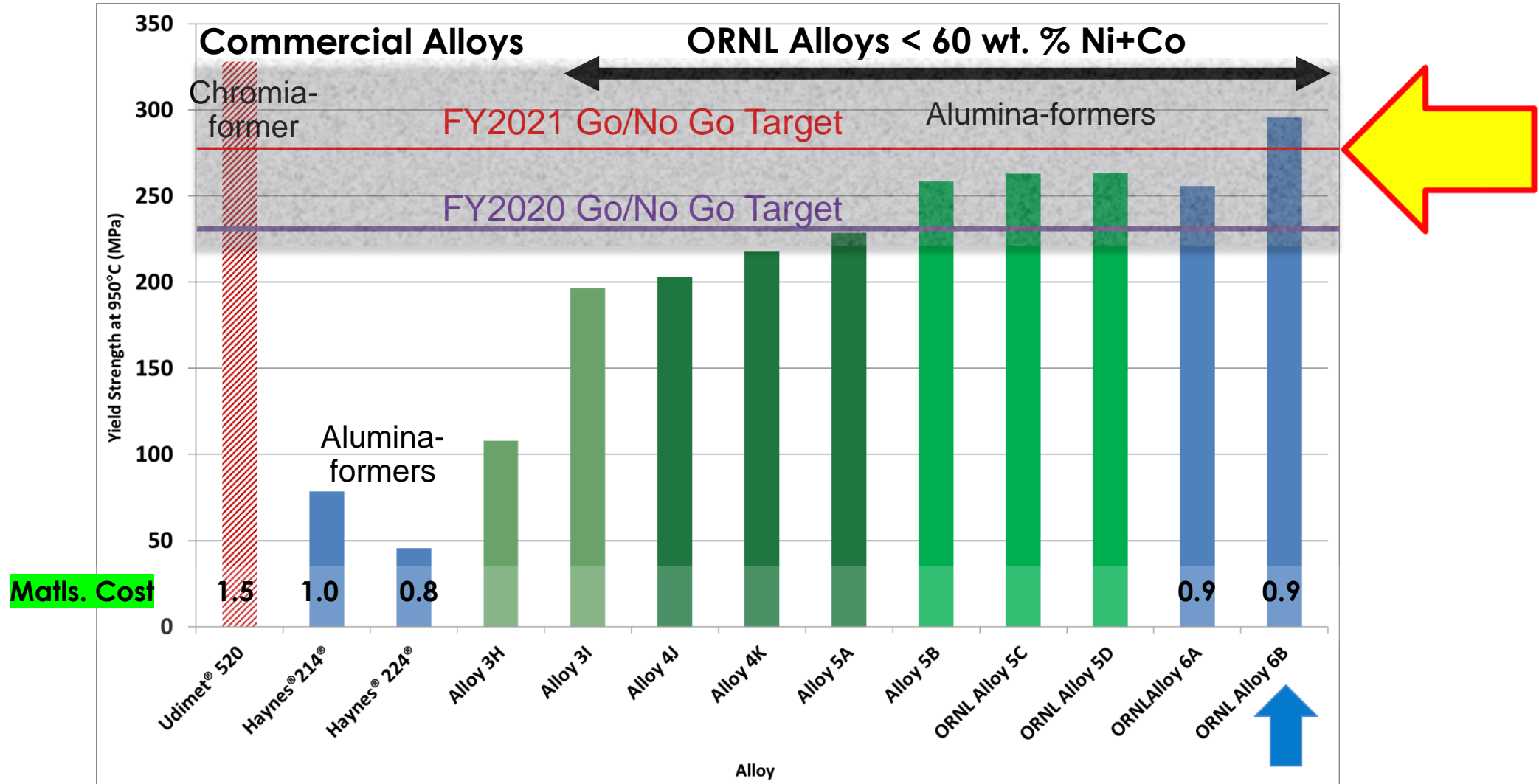
Oxidation along grain boundary



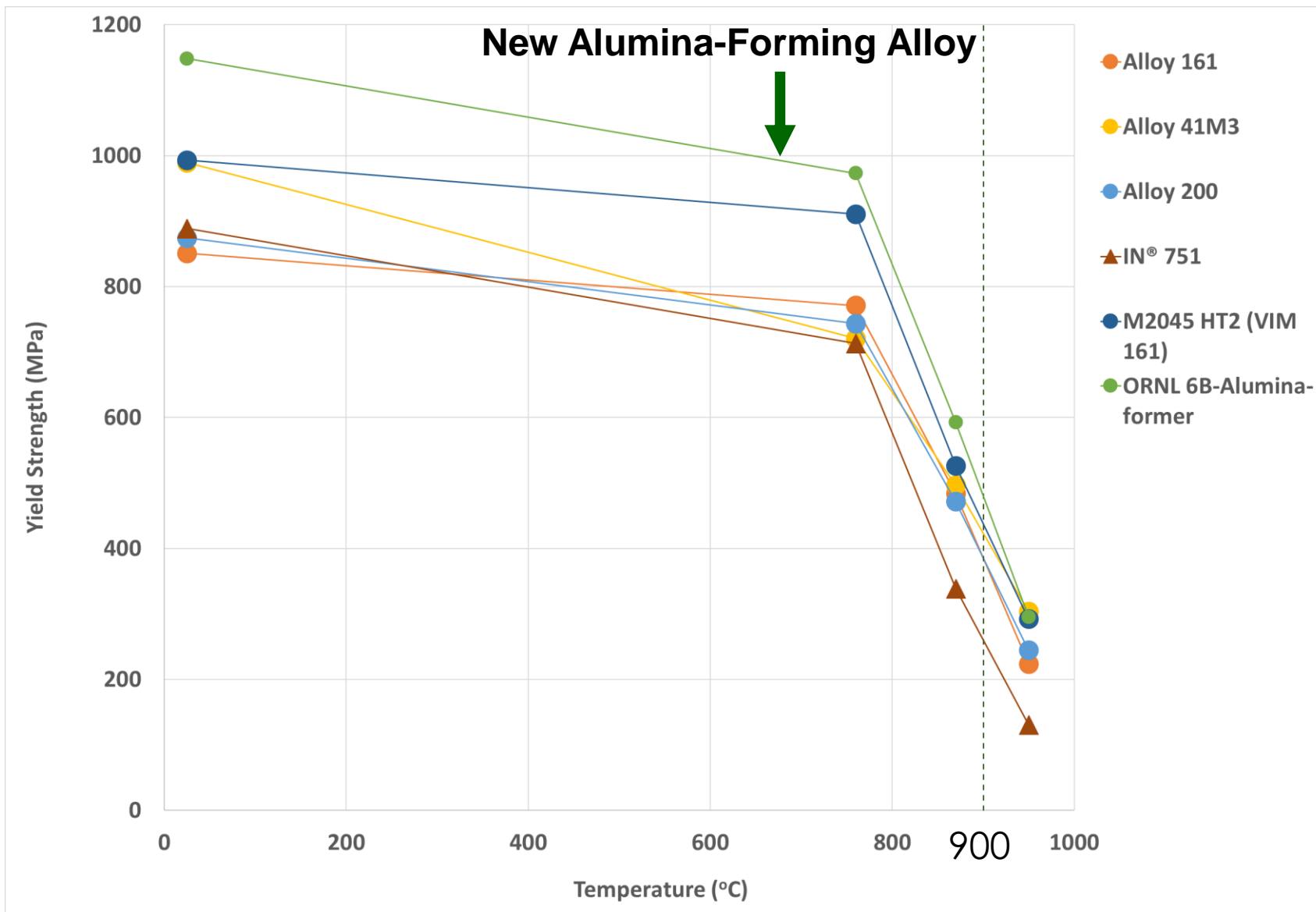
Oxidation resistant coatings may be needed to improve fatigue life OR
Higher strength alumina-forming alloys will be required

Development of Higher-Strength, Alumina-Forming Alloys

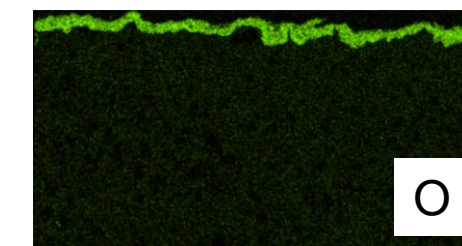
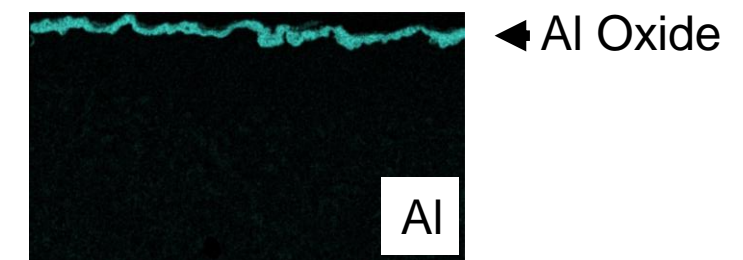
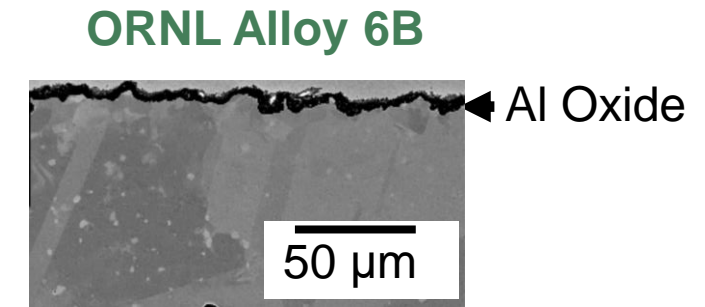
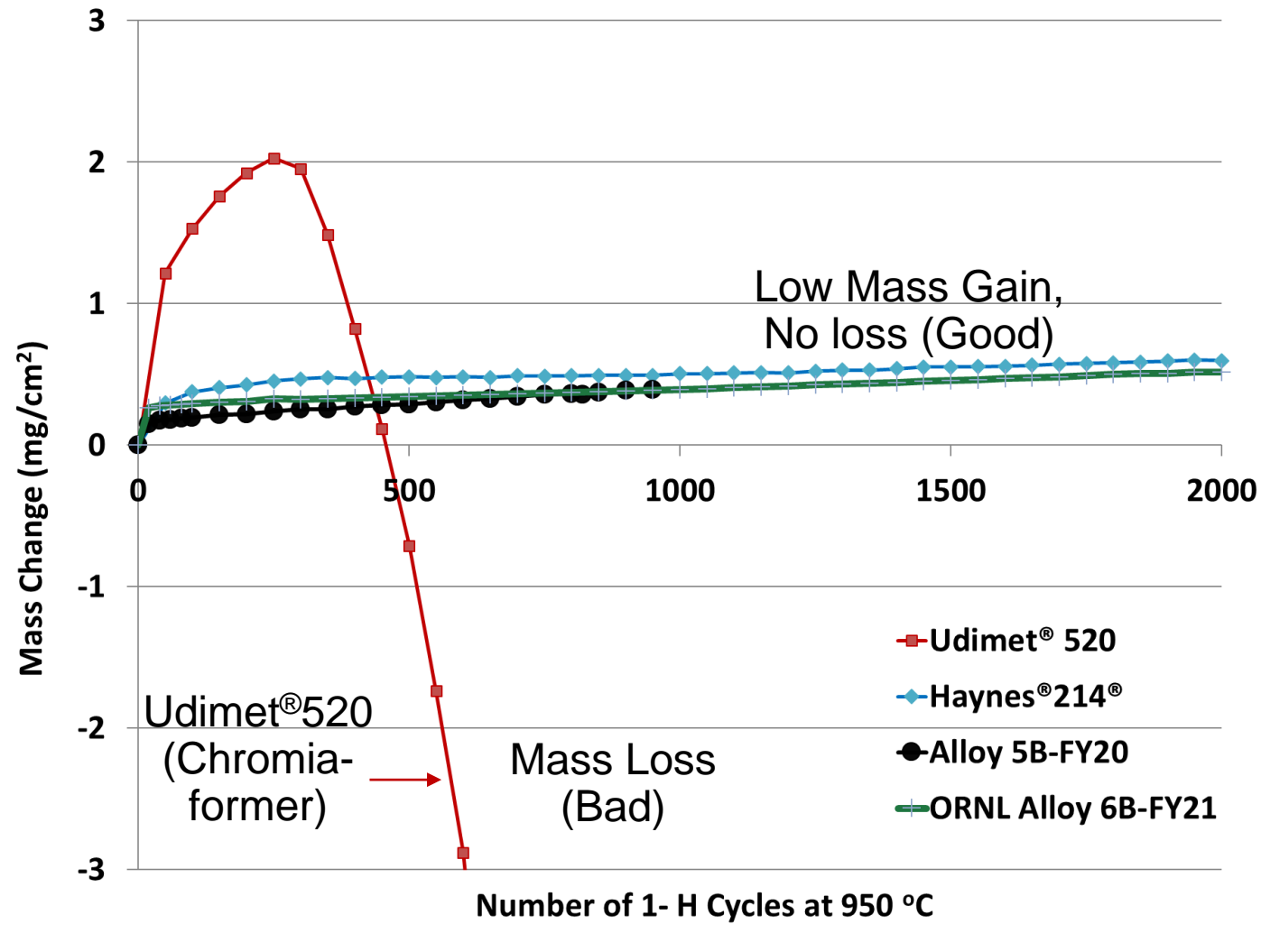
New Alumina-Forming Alloys Have Exceeded 2021 Target Yield Strengths at 950°C



New Laboratory-Scale Alumina-Forming Alloys Show Better Strength Than Chromia-Formers at 900°C



New Generation of ORNL Alumina-forming Alloys Shows Very Good Oxidation Resistance at 950°C, Air+ 10% Water Vapor



Yield strength at 950°C >276 MPa (40 Ksi), and Lower Ni levels

Response to Reviewers Comments

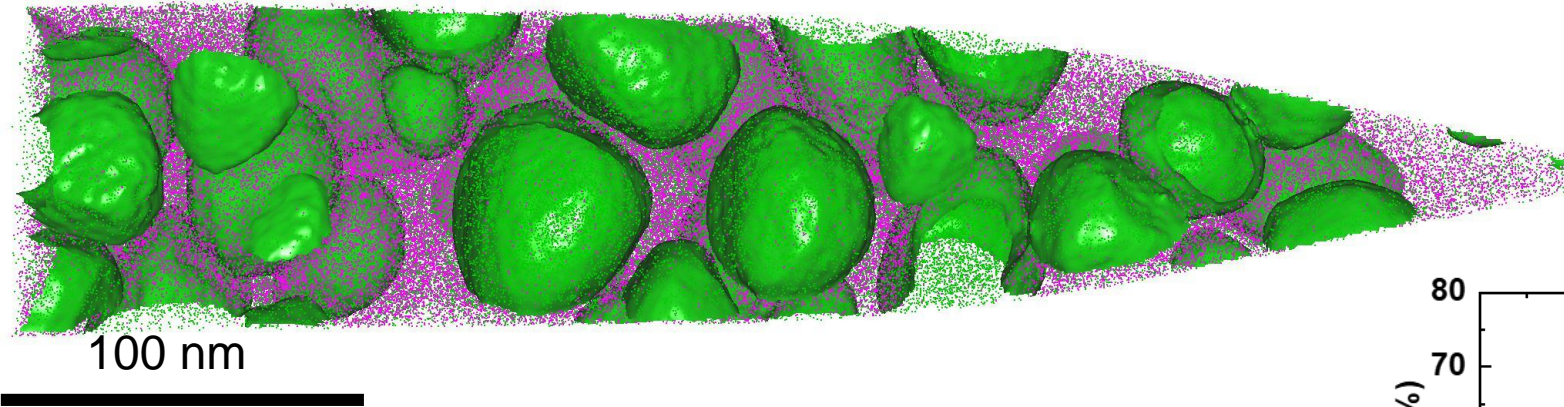
- We thank the reviewer for the many positive comments on the project
- **Comment 1:** Some cost factors are listed but the reviewer cannot tell how they were developed
 - **Response:** Cost factors were assessed through discussions with OEM and CRADA partner
- **Comment 2:** Challenges of scaling up vacuum induction melting process may create a significant risk
 - **Response:** We agree that scaling up heats are a significant risk. However, scaling up of the heats using vacuum induction melting is required for providing enough material for fatigue testing, technology implementation, and successful technology transfer to the CRADA partner, Tenneco. Some of this risk is off-set by input from the CRADA partner.

Collaborations and Coordination with Other Institutions

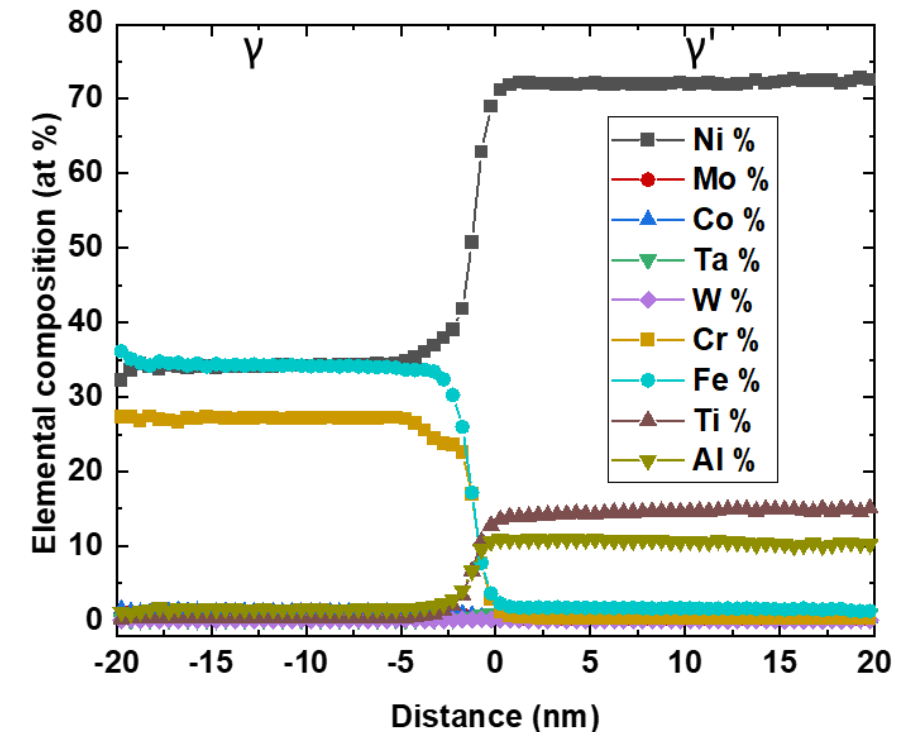
- Collaborations within **ORNL Task 2A3, and Task2A4**
- Collaborations within **ORNL** on characterization (**Thrust 4A**)
- Collaborations with **Argonne National Laboratory** are on-going (**Thrust 4A**)
 - Extended range Ultra Small-angle, Small-angle, and Wide-angle X-ray scattering facility to understand role of precipitation on strengthening
 - Powder diffraction facility for structure characterization
- Collaborations with **Pacific Northwest National Laboratory** are on-going (**Thrust 4A**)
 - Advanced microstructural characterization to understand microstructure-mechanical properties link
- Collaborations with **Special Metals Corporation**
 - Fabricator of industrial heats
- **CRADA with Tenneco/Federal Mogul**



Advanced Characterization: Atom Probe Tomography Measurements Are Used To Understand γ' Size, Shape, and Chemistry in H2079 (Thrust 4A)



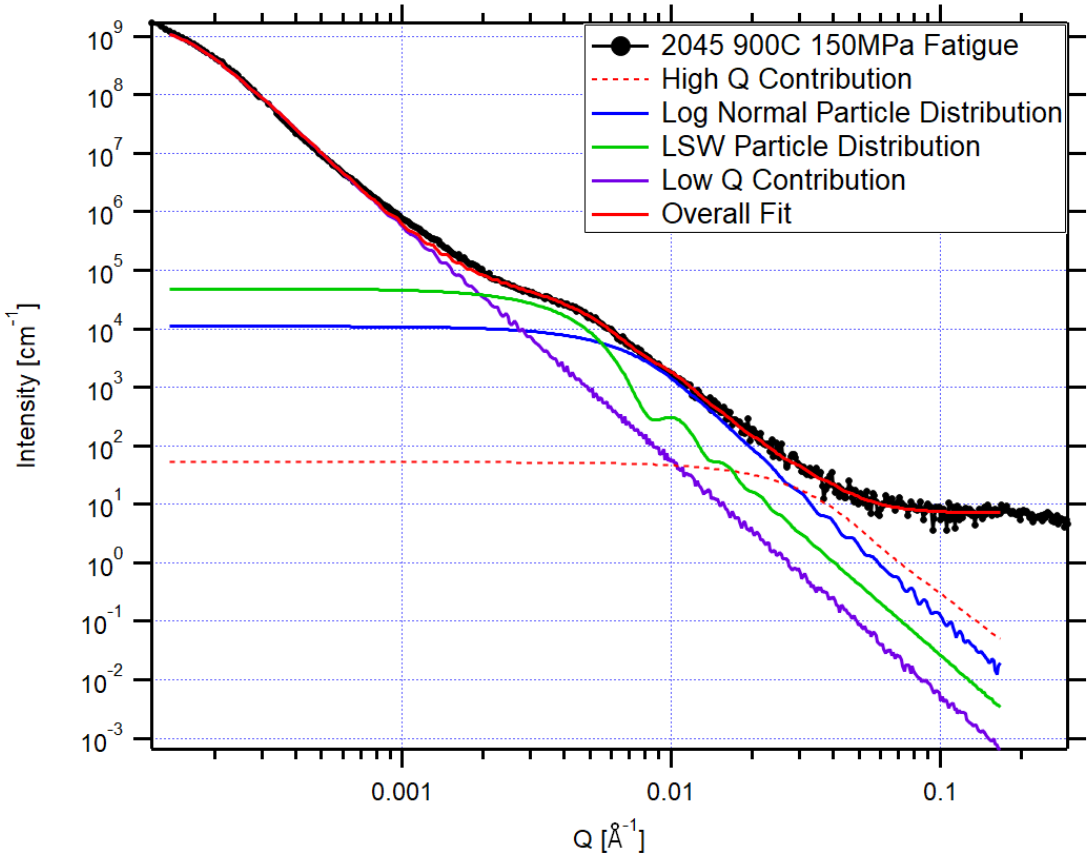
Compositions of precipitate and matrix are being obtained for comparison between alloys and correlation with strength and fatigue properties



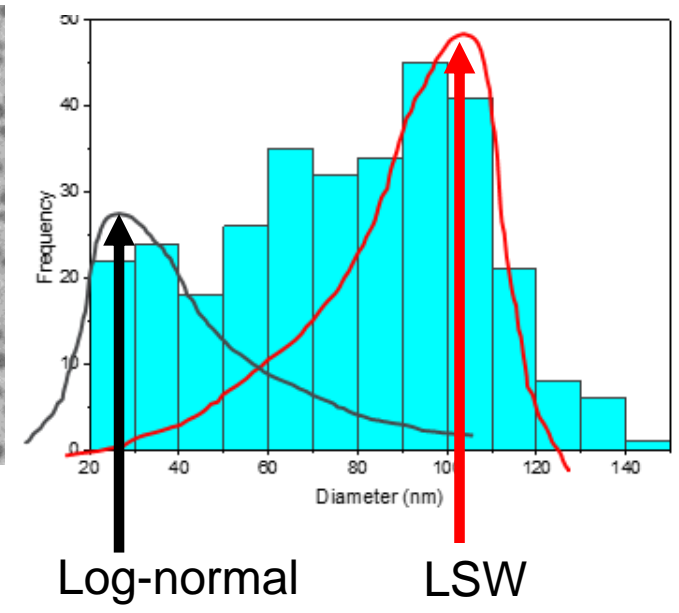
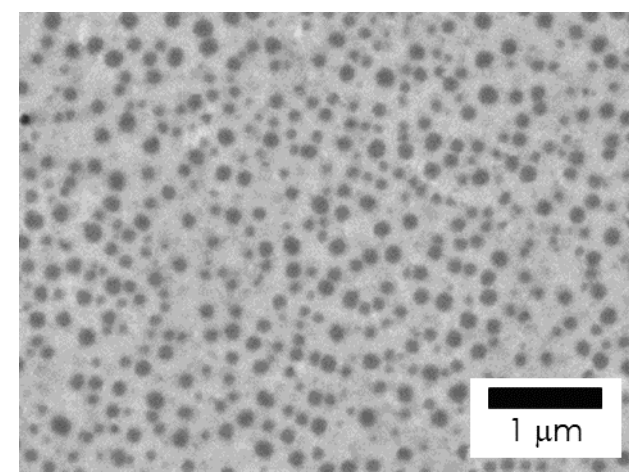
Advanced Characterization: Particle Size Distributions After Fatigue Testing are Being Evaluated using Ultra Small-Angle Scattering (USAXS)

Two particle size distributions were required to fit the USAXS data

M2045 fatigue tested at 900°C, 150 MPa



SEM size analysis

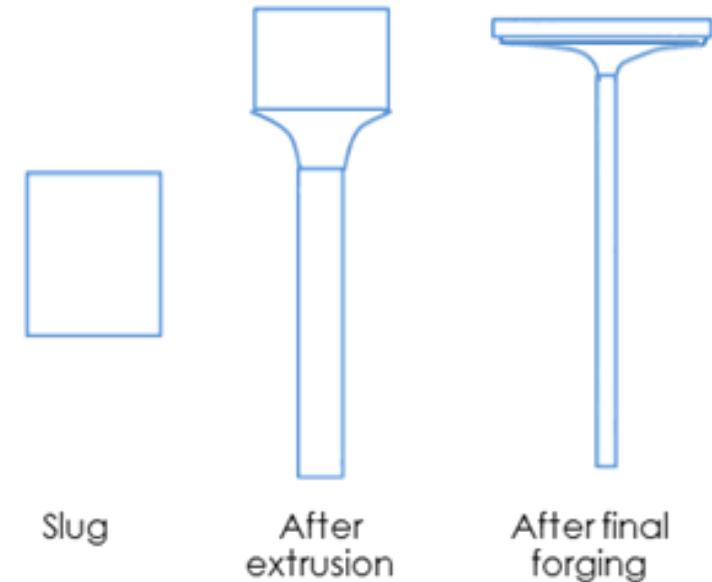


Particle Size Distributions Used to Fit USAXS data

Type of Distribution	Diameter
Log-Normal Population	26 ± 2 nm
LSW Population	110 ± 2 nm

Remaining Challenges and Barriers

- Additional heats of chromia-forming alloys must be fabricated and fatigue-tested to down-select alloy for valve fabrication
- Large industrial scale Vacuum Induction Melted/Vacuum Arc Refined (VIM/VAR) heat of alumina-forming alloy must be fabricated
- Fatigue properties of chromia-forming and alumina-forming alloys must be compared
- One or more alloys (as determined by CRADA partner) must be down-selected
- Valve must be fabricated using down-selected alloy
- Engine testing must be performed and valve performance validated



**Valve Manufacturing
Process Development**

Proposed Future Research

- Compositions of 2078 and 2079 were modified and two new VIM heats fabricated by Special Metals
 - High temperature fatigue properties will be measured at ORNL using **uniaxial fatigue testing**
 - **Rotating beam tests** will be performed by Tenneco
- Additional heats of ORNL alloys will be scaled-up in collaboration with CRADA partner Tenneco
 - **Two chromia-forming alloys**
 - **One ORNL alumina-forming alloy**
- Microstructural stability of scaled-up alumina-forming alloy will be evaluated at 900°C
- High temperature fatigue properties of scaled alumina-forming heat will be measured at ORNL using uniaxial fatigue testing and by Tenneco using rotating beam tests

New heats fabricated in FY21



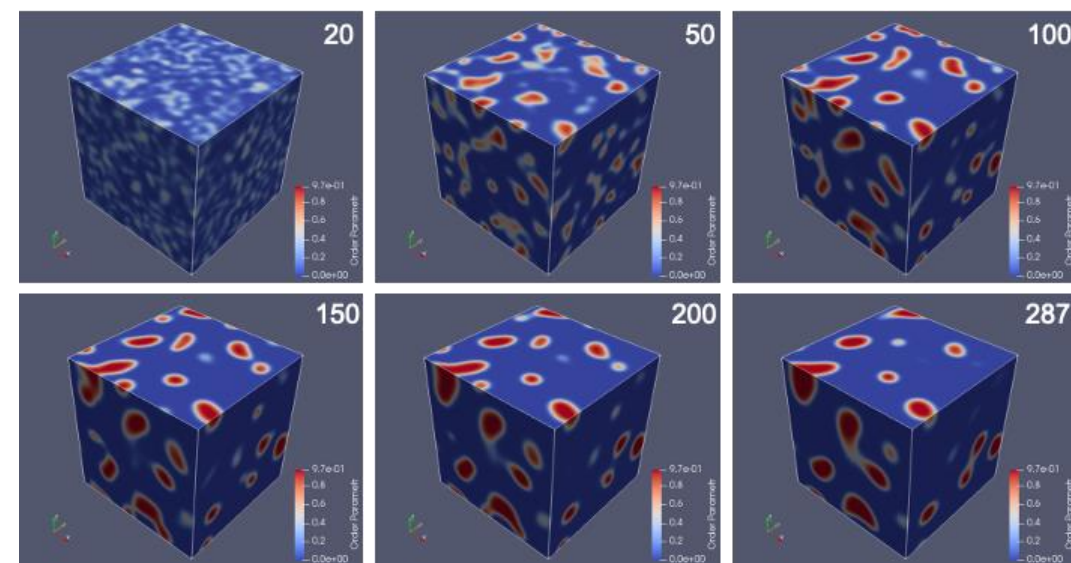
Summary

- **Relevance:**
 - Current valve alloy cannot meet strength, oxidation, and cost requirements for use with increasing exhaust gas temperatures (from 870°C to 950°C in 2025 and to 1000°C by 2050).
- **Approach/Strategy:**
 - Lower cost-effective chromia-forming alloys developed at ORNL will be commercialized for use at $\leq 900^\circ\text{C}$ as exhaust valve alloys
 - New higher strength alumina-forming alloys are being developed for use at 900-950°C
- **Accomplishments:**
 - Industrial heats of ORNL patented chromia-forming alloy shows **good tensile & fatigue properties at 900°C.**
 - **New alumina-forming alloys have achieved target yield strength of ≥ 267 MPa (40 Ksi) at 950°C** in laboratory scale heats (comparable to ORNL chromia-formers) while maintaining good oxidation resistance and comparable cost.
- **Collaborations:**
 - Collaborations are on-going with Tenneco Powertrain/Federal Mogul, Special Metals, Thrust 4A: ANL and PNNL, and Thrust 4B.
- **Proposed Future Work:**
 - Evaluate fatigue properties of industrial scale heats of ORNL patented chromia-forming alloys to down-select best alloys
 - Scale-up one alumina-forming alloy and evaluate long-term microstructural stability and fatigue resistance at 900°C

Technical Back-up Slides

Advanced Modeling: Phase Field Modeling Initiated to Understand γ' Nucleation, Growth and Coalescence

- Simulation volume $252 \times 252 \times 252 \text{ nm}^3$
 - Model Alloy: Ni-0.037Mo-0.056Nb (at. Frac.)
- Nucleation through Langevin noise to perturb order parameter
- Simulations able to capture the nucleation, growth and coalescence stages
- Future work will involve simulations on Ni-Al-Nb system to investigate
 - the effect of variation in elastic energy and interfacial energy on coarsening
 - Effect of bimodal distribution of γ' on coarsening and coalescence



Temporal evolution of γ' in a Ni-Mo-Nb ternary alloy using MEUMAPPS-SS phase field code developed at ORNL with support from the Exascale Computing Project (ECP). Evolution time = $250 \times$ step number (shown in each frame)