

Overview of Advanced Characterization within the Powertrain Materials Core Program*

*Thrust 4A under the Powertrain Materials Core Program (PMCP)

Thomas R Watkins (PI), Larry Allard, Matt Chisholm, Michael Lance, Donovan Leonard, Jon Poplawsky, Kinga Unocic, **Oak Ridge National Laboratory**

Dileep Singh, Jan Ilavsky, Andrew Chuang, Lianghua Xiong, Matthew Frith, Yang Ren, **Argonne National Laboratory**

Arun Devaraj, Bharat Gwalani, Libor Kovarik, Mathew Olszta, Dalong Zhang, **Pacific Northwest National Laboratory**

2021 DOE Vehicle Technologies
Office Annual Merit Review

June 23, 2021

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

THRUST 1.
Lightweight
Alloys
(200 - 550°C)

THRUST 2.
Cost-
Effective,
Higher
Temperature
Alloys
(550 - 1000°C)

THRUST 3.
Additive
Manufacturing
for Advanced
Powertrains

OAK RIDGE
National Laboratory

Pacific
Northwest
NATIONAL
LABORATORY

Argonne
NATIONAL LABORATORY

TRL 1

Accelerating Development of Powertrain Alloys

TRL 4

Supported by Adv. Characterization & Computation

THRUST 4.

Atom Probe

Synchrotron

Microscopy

Neutrons

High Performance Computing

Thermodynamics

Modern Data Analytics

ICME

\$30M/5 years
launched in
FY19

OAK RIDGE
National Laboratory

Thrust 4A Overview: Advanced Characterization within the Powertrain Materials Core Program

Timeline/Budget

- Task start: October 2018
- Task end: September 2023
- Percent complete: 50%
- **4A Budget**
 - FY20: \$1,050k
 - FY21: \$1,020K

Barriers

- A suite of materials solutions is needed to address specific requirements of advanced engines
- Higher specific strength needed
- Improved strength and fatigue at High pressures and temps
- Materials' data

Partners

- Program Lead Lab
 - Oak Ridge National Lab (ORNL)
 - Center for Nanophase Materials Science (CNMS)
 - Spallation Neutron Source (SNS)
- Program Partner Labs
 - Pacific Northwest National Lab (PNNL)
 - Environmental Molecular Sciences Laboratory (EMSL)
 - Argonne National Lab (ANL)
 - Advanced Photon Source (APS)

Thrust 4. Advanced Characterization & Computation

Foundational support for Thrusts 1, 2 & 3
4A. Advanced Characterization / 4B. Advanced Computation

Task	Title	TRL	FY20	FY21
4A1	ORNL Advanced Characterization	Low	\$450k	\$420k
4A2	Argonne Advanced Characterization	Low	\$300k	\$300k
4A3	PNNL Advanced Characterization	Low	\$300k	\$300k
4B1	Advanced Computation	Low	\$350k	\$400k
4B2	Modeling of Light-Duty Engines	Low	\$125k	\$125k
Subtotals			\$1,525k	\$1,545k

New propulsion materials are needed to address current technology gaps for powertrains in LD and HD vehicles*

- Higher efficiency powertrains: PMCP is addressing some of the current materials technology gaps in the three development thrusts*†
 - Light weight alloys-Thrusts 1 & 3
 - Alloys for higher pressures and temperatures-Thrusts 2 & 3
- Objective of Thrust 4A: Apply advanced materials characterization tools to accelerate the development of the next generation powertrain materials with superior combinations of properties, manufacturability and cost to enable the design of future advanced internal combustion engines and hybrid electric vehicles.

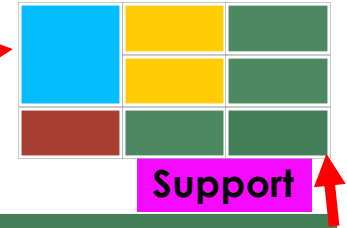
Milestones

Qtr	Thrust 4A: Advanced Characterization	National Lab Ownership
1	Task 1B1: Complete STEM characterization of a low index Al-Al ₃ Ni interface and include in Q1 quarterly. Complete.	
2.1	Task 2A1: Submit a journal paper on characterization of precipitates in Ni-based alloys using TEM, APT, and scattering techniques. Anticipated completion in Q3.	 
2.2	Task 2B1: Submit a paper about APT measurement attempts of oxygen at oxide-alloy interfaces in model oxidized Ni or Ni-Cr alloys. Anticipated completion in Q3.	
2.3	Task 2A2: Complete the Characterization of the type, composition, and spatial distribution of precipitates in HD Piston Steels using STEM/TEM and report in Q2 quarterly. Anticipated completion in Q3.	
3.1	Task 3A1: Complete characterization of intermetallic phases in AM AlCeNi using APT and report in Q3 quarterly. On Track.	
3.2	Task 1A1: Complete APT characterization of Ti free AlCuMnZr and Zr free AlCuMnTi in the as-aged and after 200 hour exposure at 300 C conditions and include in Q3 quarterly. On Track.	
4	Task 3B1: Submit a journal paper on the TEM analysis of the distribution of nano precipitates in HK30Nb steel fabricated by LBPF. On Track.	

Matching programmatic and technical needs, expertise and opportunity to unique NL tools to *accelerate* alloy development

- There are 24 Thrust 4A-Advanced Characterization Projects. Three examples:
- 1. Load transfer within cast and additively manufactured Aluminum-Copper-Manganese-Zirconium (ACMZ) alloys
 - ✳ ORNL's microscopy and ANL's synchrotron support
 - ⌘ **Task 1A1:** Fundamental Studies of Complex Precipitation Pathways in Lightweight Alloys
 - ⌘ **Task 3A1:** Fundamental Development of Aluminum Alloys for Additive Manufacturing
- 2. Measuring dissolved oxygen in Ni-based alloys
 - ✳ ORNL's atom probe tomography supports
 - ⌘ **Task 2A4:** High Temperature Oxidation
 - ⌘ **Task 2B1:** Development of Cast, Higher Temperature Austenitic Alloys
- 3. Validating alumina forming austenitic alloys
 - ✳ PNNL's microscopy and atom probe tomography support
 - ⌘ **Task 2B1:** Development of Cast, Higher Temperature Austenitic Alloys

Approach: Matrix of experts with unique tools that accelerate alloy development



Synchrotron X-Rays
Diffraction, SAXS

Electron Microscopy

Electron Microscopy

Atom Probe

Atom Probe

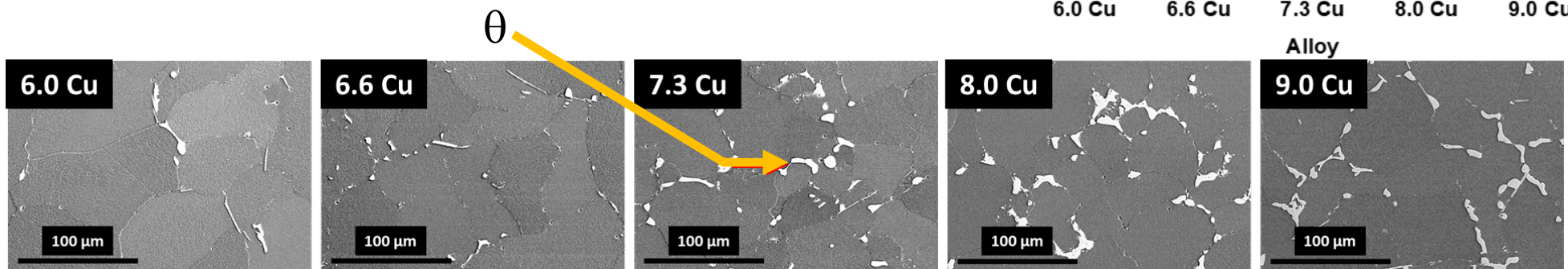
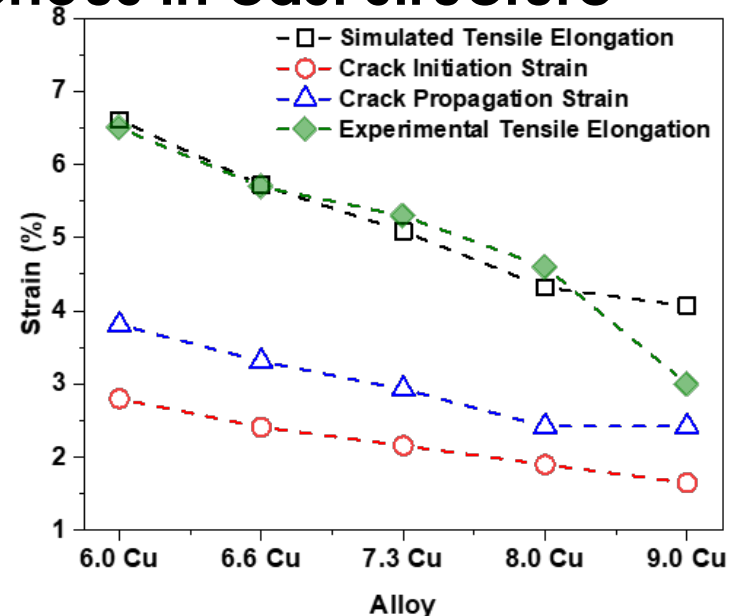
In-situ stages, environments

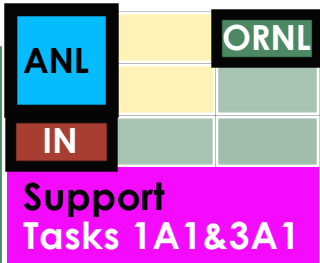
Neutrons & X-Rays
Diffraction
Non-Ambient
Tomography

Electron MicroProbe

Example 1. Cast ACMZ alloys for engine heads: Properties are controlled by precipitates, θ' is beneficial but θ is deleterious in cast structure

- θ phase fraction increases at grain boundaries with increasing Cu content
- Experiments and models agree, failure strain decreases



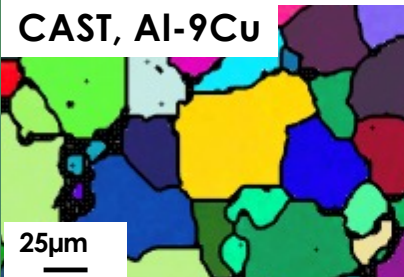


ORNL
S.Bahl
X.Hu
J.Cheng
A.Shyam
A.Plotkowski
ANL
A.Chuang
Y.Ren

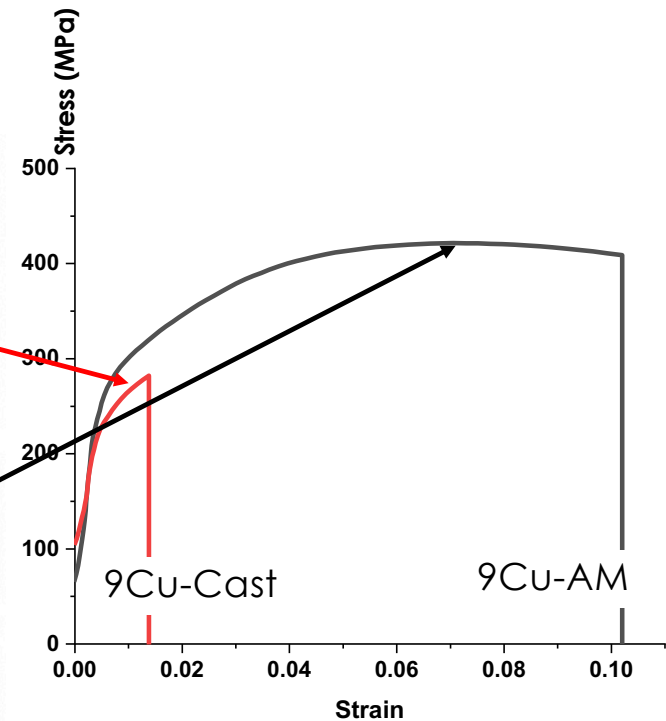
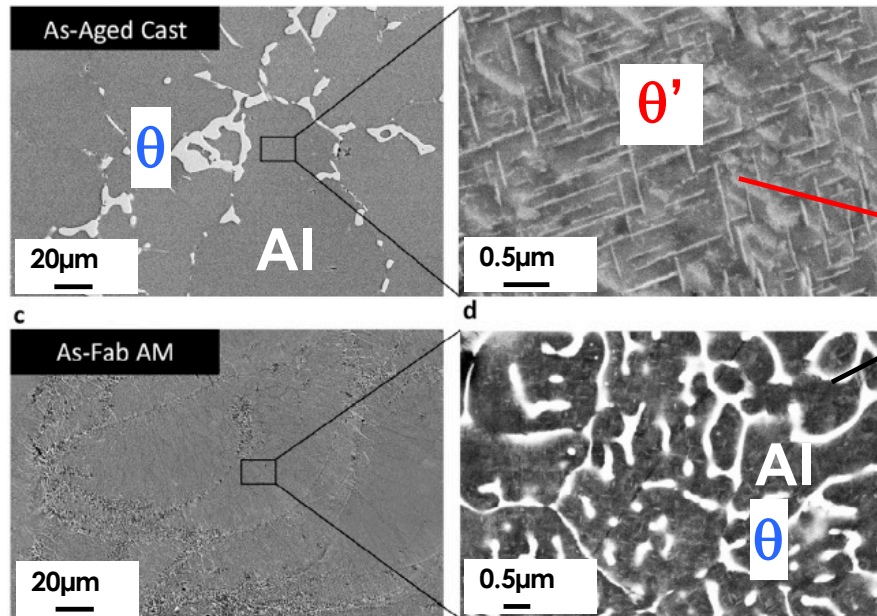
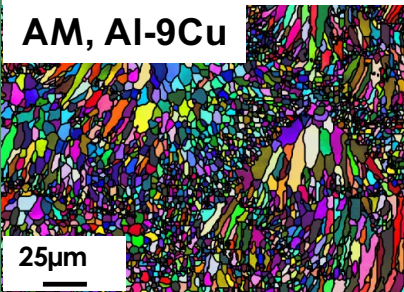
Yet, additive manufacturing (AM) of the same alloy produces a unique fine microstructure where properties of the AM are much better than the cast!

Example: Aluminum with 9wt% Cu

CAST, Al-9Cu



AM, Al-9Cu



ANL

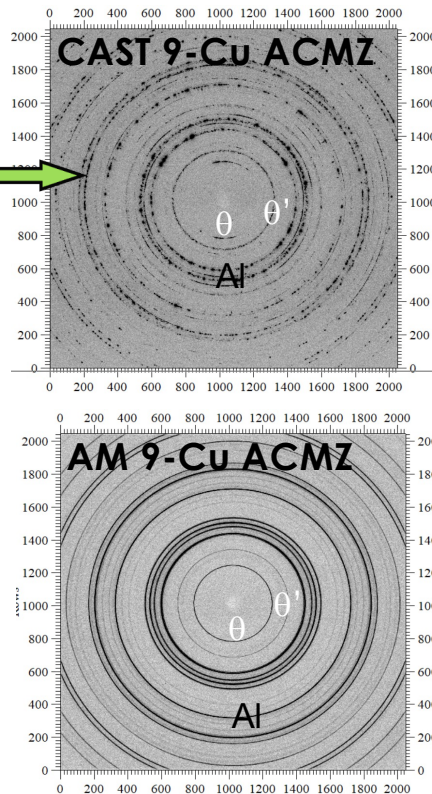
ORNL

IN

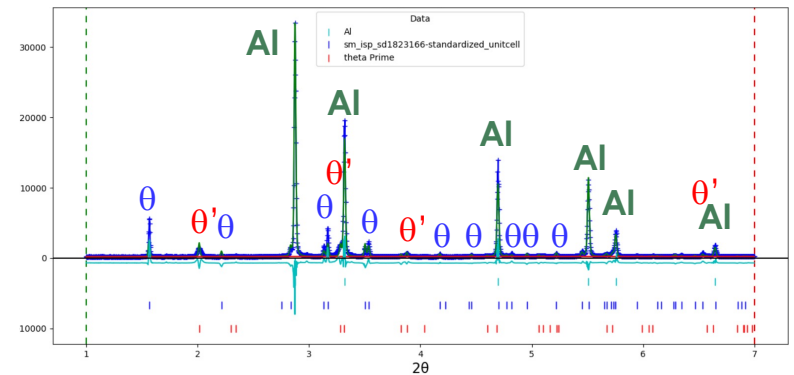
Support
Tasks 1A1&3A1

ORNL
S.Bahl
X.Hu
J.Cheng
A.Shyam
A.Plotkowski
ANL
A.Chuang
Y.Ren

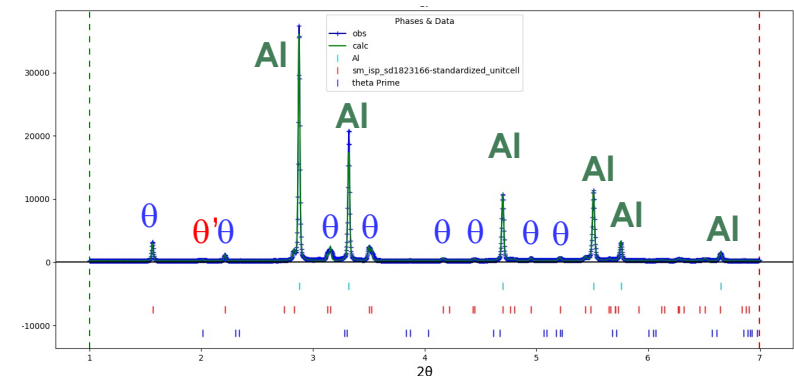
ANL's Advanced Photon Source synchrotron provides 1,000,000 more x-rays than a standard x-ray tube allowing quantification of the θ and θ' (trace) phases within minutes

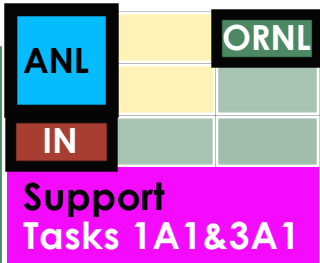


Diffraction patterns showing Al matrix, θ and θ' phases

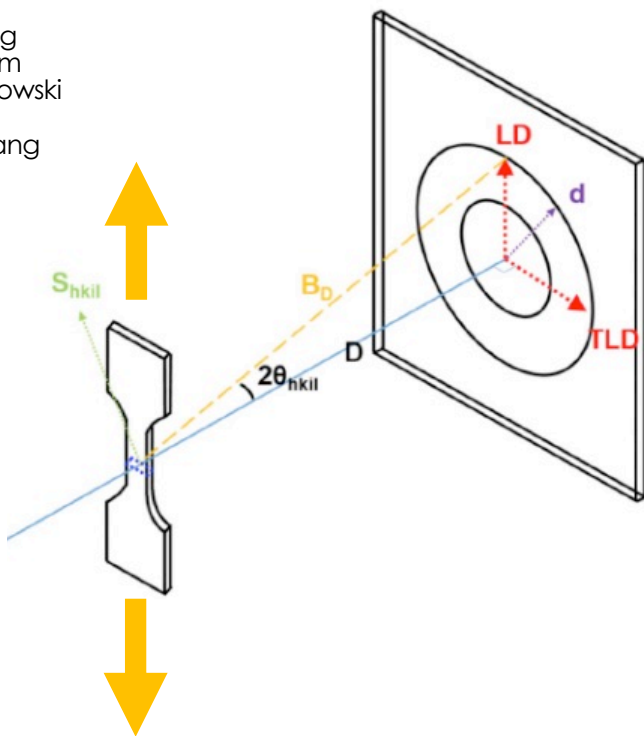


Rietveld refinement shows:
9Cu-Cast ACMZ: θ 8 wt%; θ' 4.0 wt%
9Cu-AM ACMZ: θ 9 wt%; θ' 0.3 wt%

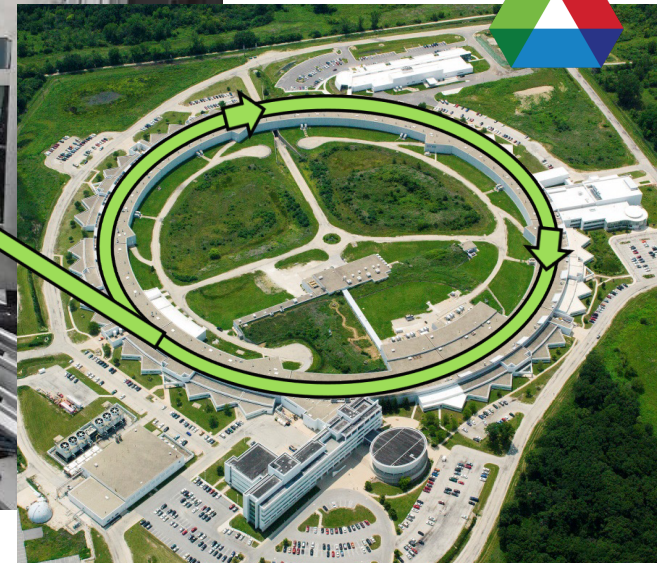
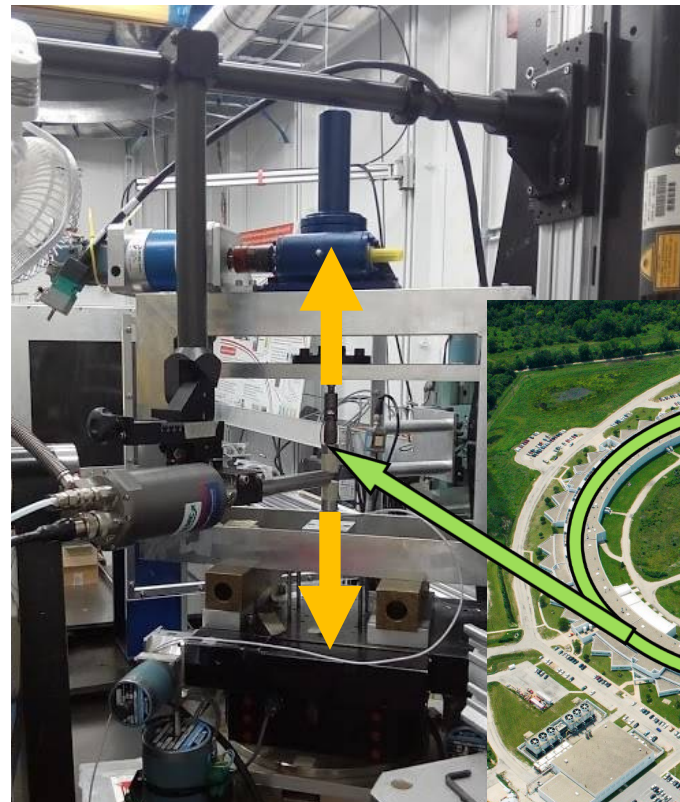




ORNL
S.Bahl
X.Hu
J.Cheng
A.Shyam
A.Plotkowski
ANL
A.Chuang
Y.Ren



CAST and AM ACMZ alloys studied with *in-situ* loading in High Energy X-ray Diffraction at the APS to observe load transfer amongst matrix and precipitate phases

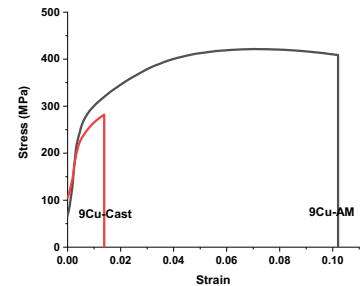
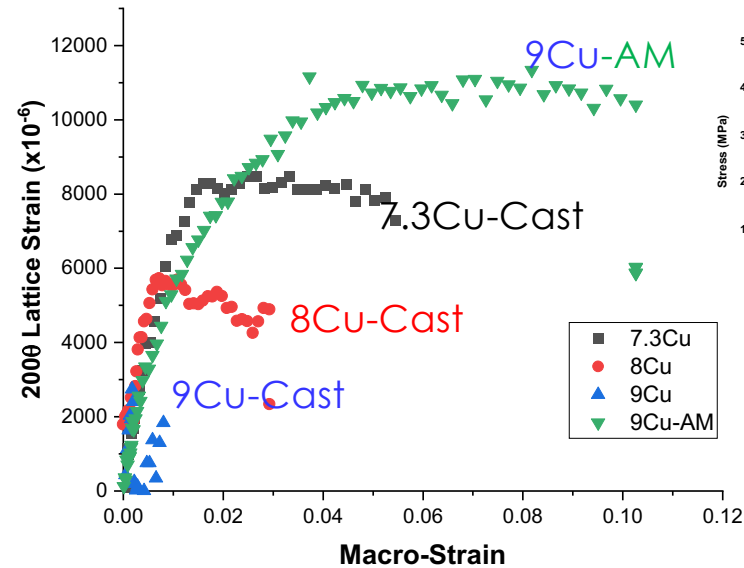
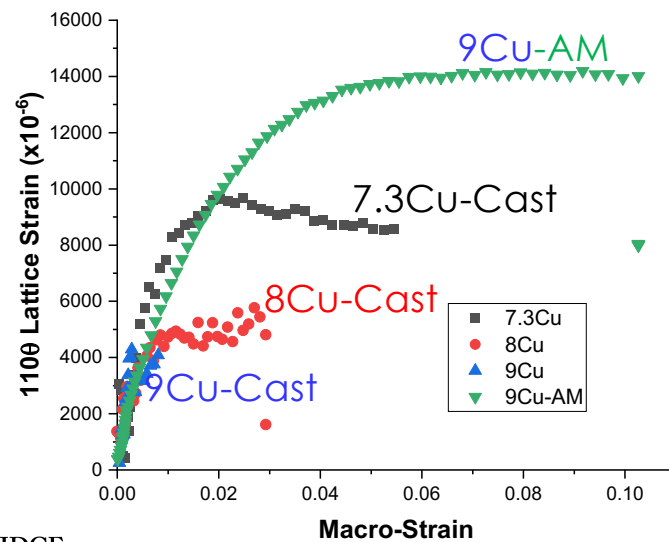




ORNL
S.Bahl
X.Hu
J.Cheng
A.Shyam
A.Plotkowski
ANL
A.Chuang
Y.Ren

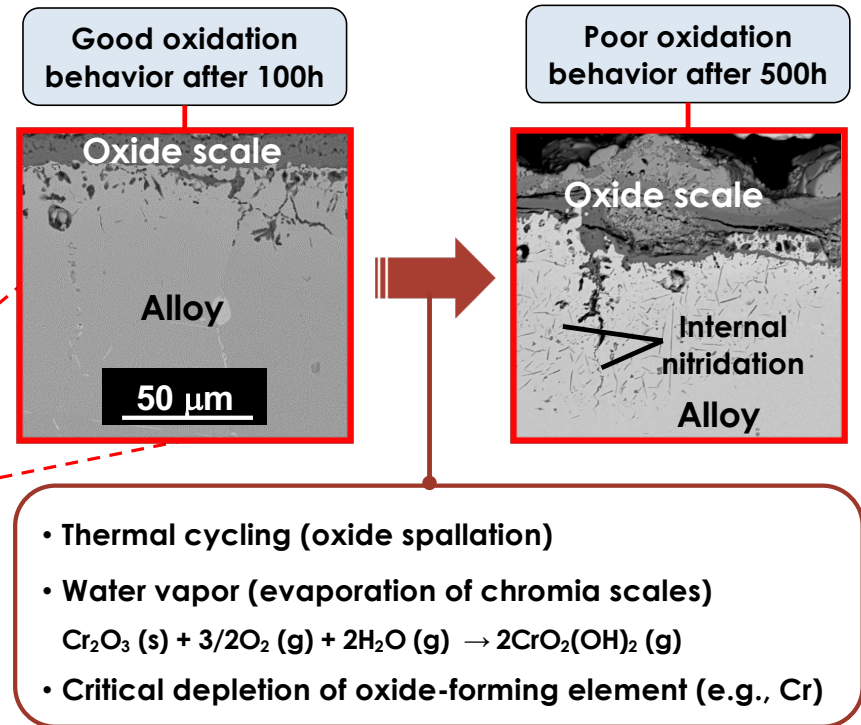
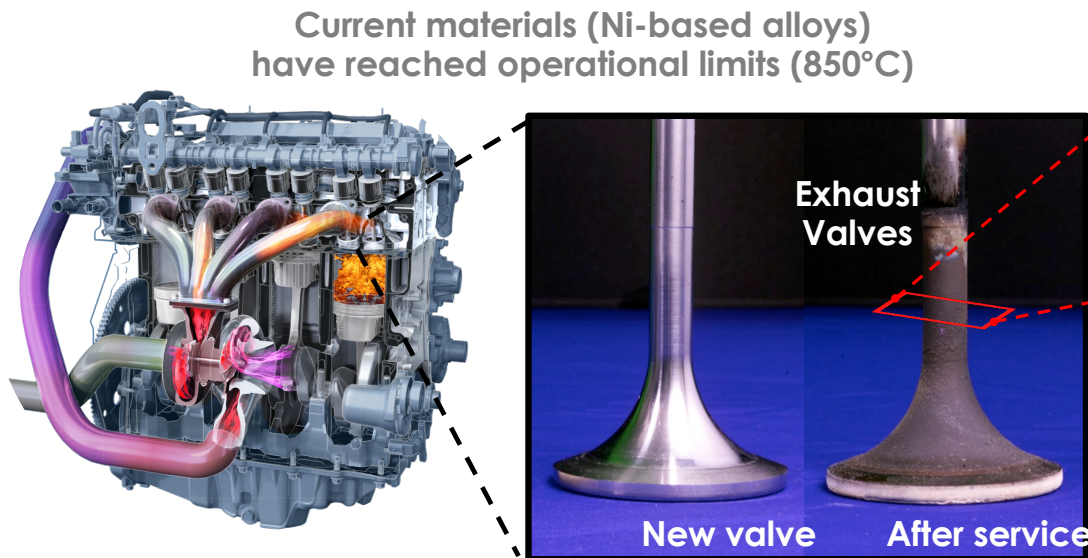
Dispersed fine θ precipitates stronger and stiffer than θ' which both strengthen and increase ductility in the ACMZ alloys

- θ Lattice Strain decreases substantially with increasing Cu content, indicating decreasing fracture stresses in cast.
- Fine θ in AM 9Cu ACMZ alloy can sustain much higher stresses and might be deformable.



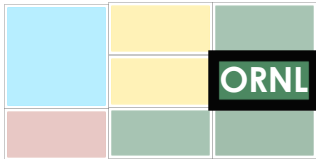


Example 2. Increasing efficiencies of ICEs will require increasing operating temperatures and pressures. Existing alloys have poor strength & corrosion resistance at higher temperatures (>870°C)



Overall Goal:

Design oxidation-resistant high temperature alloys to minimize metal loss (structural integrity), balance mechanical properties and maximize component lifetime at temperatures > 850°C



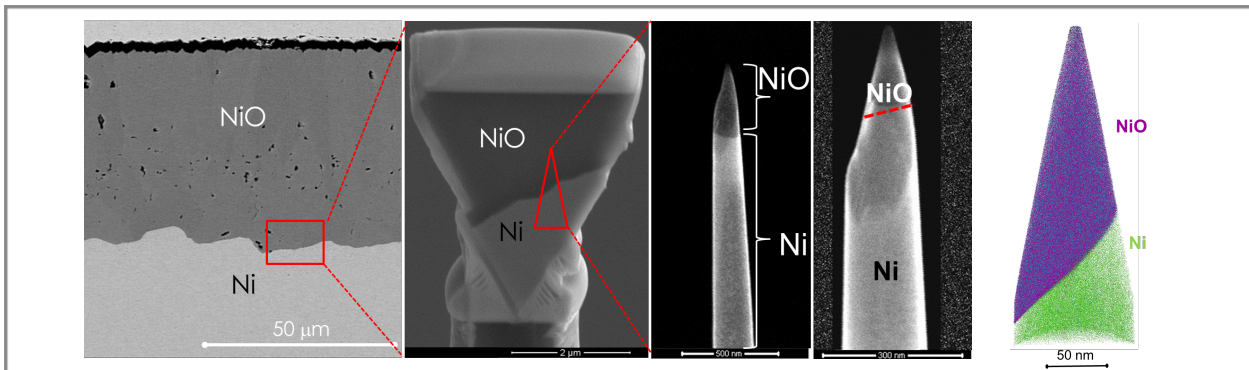
Support
Tasks 2A4&2B1

ORNL
R.Pillai
J.Poplawsky
A.Haynes
B.Pint
Y.Yamamoto
M.Brady

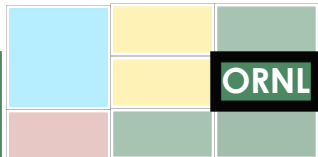
Key challenge: Lack of predictive models to describe high temperature oxidation behavior of multicomponent and multiphase alloys as a function of environment, alloy composition, microstructure and operating conditions.
Key need: Experimental measurement of oxygen concentration in practical alloys

- **Start: Validate/replicate prior measurements on pure Nickel/NiO (*Park and Altstetter, Met. Trans. 1987*).**
- Atom probe tomography is the **ONLY** tool suitable for measuring concentrations with a sensitivity of ~10 ppm and 3Å resolution

- High purity Ni (total Impurities < 10 ppm) specimens (post 600-grit finish) sealed in a quartz ampoule (pressure controlled to be ~ 1 atm.)
- Exposure conditions:
1000°C, 48 h in O¹⁸ gas (to avoid ambiguity in identification due to O¹⁶ (air) background)
- **Specimen:** 10 x 10 x 1.50 mm

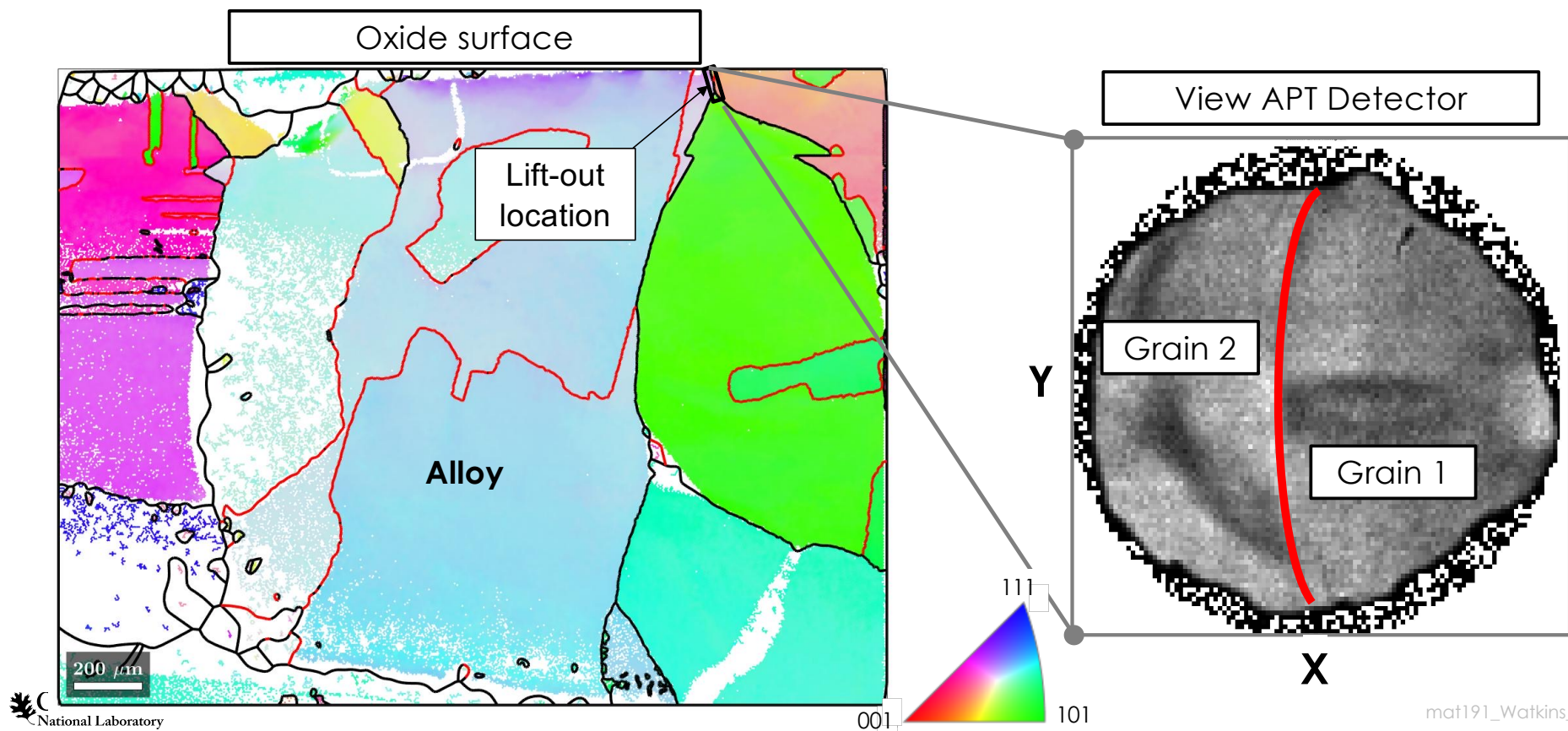


Key takeaways 1) APT was essential to be successful in measuring oxygen in the metal near oxide metal interfaces in oxidized alloys, 2) but that the measured levels of oxygen in the bulk nickel grains were unexpectedly lower than predicted by oxidation theory. So...



ORNL
R.Pillai
J.Poplawsky
A.Haynes
B.Pint
Y.Yamamoto
M.Brady

Lift-out location for grain boundary in the metal identified using electron backscatter diffraction (EBSD)

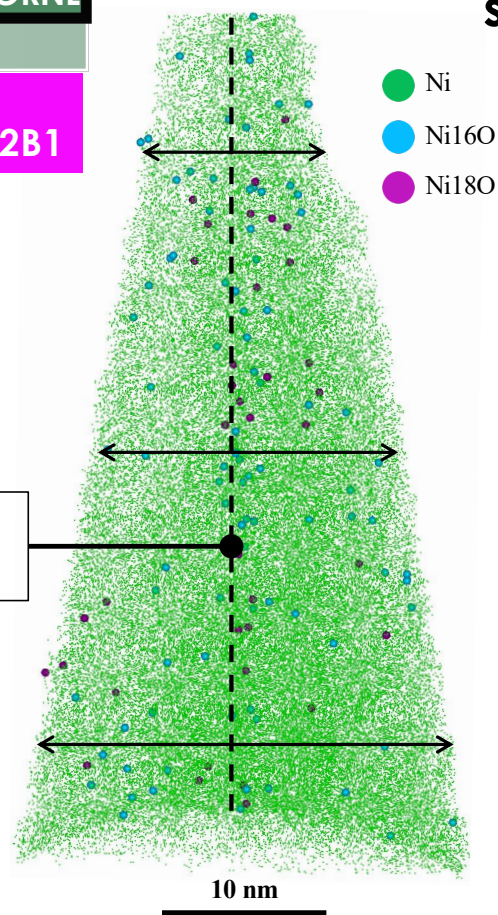


mat191_Watkins_2021_0

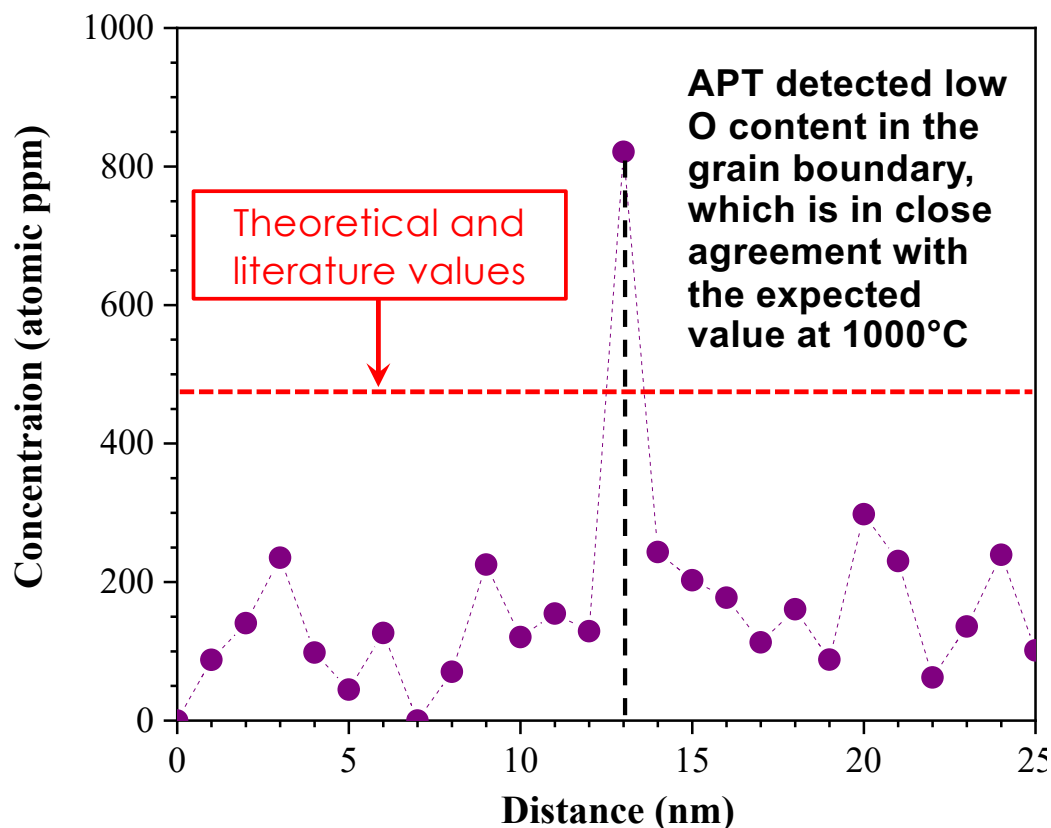


Support
Tasks 2A4&2B1

ORNL
R.Pillai
J.Poplawsky
A.Haynes
B.Pint
Y.Yamamoto
M.Brady



This is a first of its kind outcome that will enable key future studies of oxygen solubility in more complex alloys

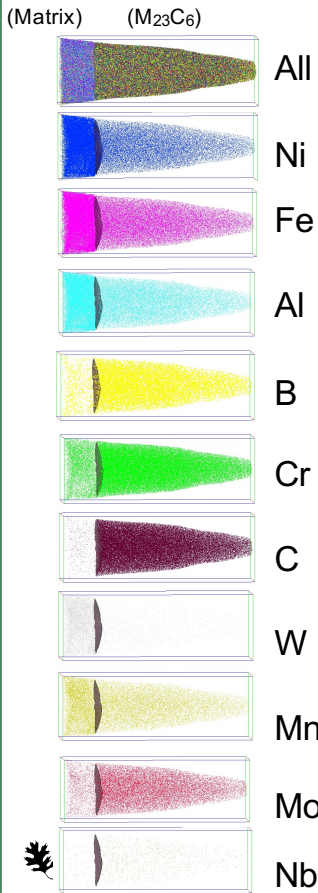


Key take away 3) oxygen enrichment was found at metal grain boundaries. **Unique, new data not previously reported**; will aid in better understanding of alloy oxidation behavior; guide development and lifetime prediction models of higher temperature capable alloys.

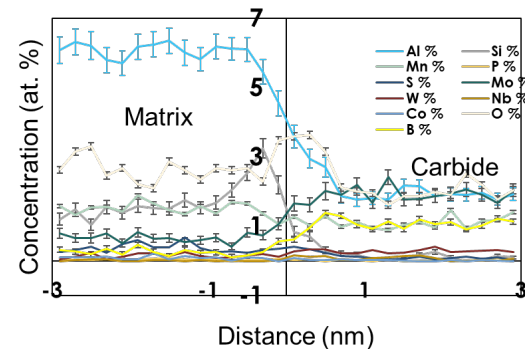
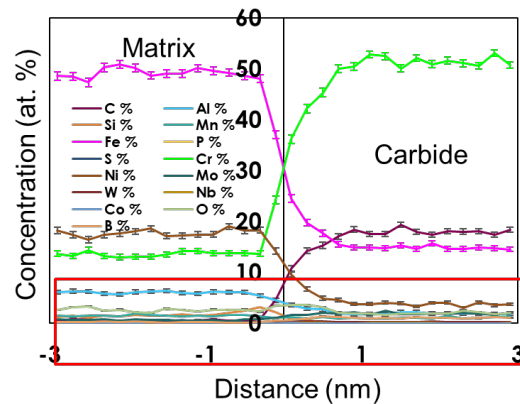


A.Devaraj, PNNL
B.Gwalani, PNNL
L.Kovarik, PNNL
Y.Yamamoto, ORNL
M.Brady, ORNL

Support Task 2B1



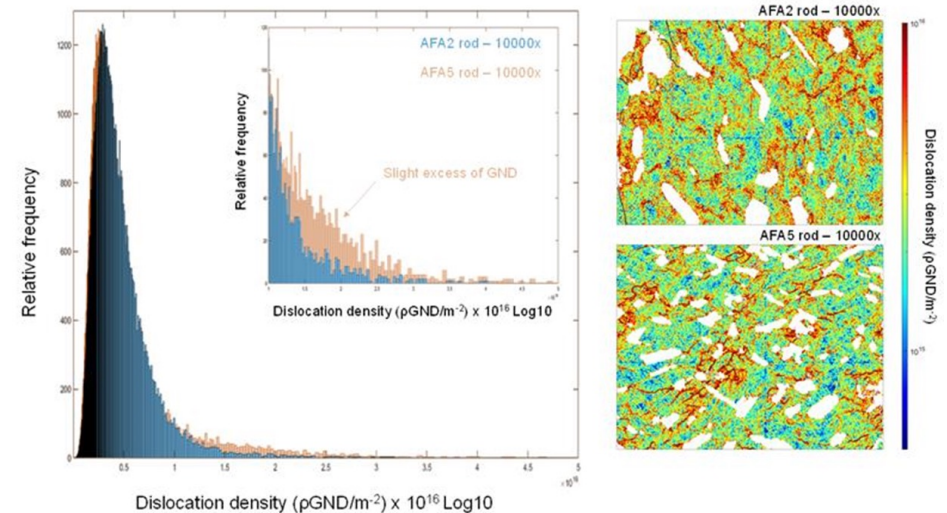
Elemental distribution across the matrix-carbide interface (APT)



• Segregation of B and Mo in $M_{23}C_6$

Example 3. PNNL's Adv. microscopy & APT revealed dislocations & composition of primary precipitates & verified the design of ORNL's newly developed alumina forming austenitic, AFA, alloy

Estimated GND in creep-ruptured cast AFA (SEM-EBSD)



- AFA5 alloy has higher density of "Geometrically Necessary Dislocations, GND" compared to AFA2
- **IMPACT: Lower cost (Fe-based) experimental alloy with improved HT creep strength for turbo housings and exhaust manifolds**
- ***Alumina-formers may also offer enhanced resistance of attack from alternative fuels, such as natural gas/bio-fuel/hydrogen***

Collaborations and coordination with other institutions



Synchrotron X-Rays

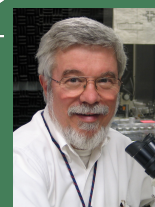
Diffraction, SAXS



Electron Microscopy



Electron Microscopy



Atom Probe



Atom Probe



In-situ stages, environments



Neutrons & X-Rays



Diffraction
Non-Ambient
Tomography



Electron MicroProbe



Responses to Previous Year Reviewer's comments

- Reviewer's responses were generally positive
- It was posed that "Each National Laboratory was autonomous..."
 - Most Tasks have regular meetings where each researcher is invited in turn to present and discuss their results. The collaborative information exchange drives and informs all researchers work.
 - S.Bahl et al. **Materials & Design** (journal cover article) 198 (Jan 2021) 109378 (ORNL & ANL)
 - B.Gwalani et al. "Understanding the microstructural stability in a γ' -strengthened Ni-Fe-Cr-Al-Ti alloy" submitted to **Journal of Alloys and Compounds**, April 2021. (PNNL & ORNL)
- Another posed the lack of a link to ICME
 - Please see slides 23.
 - M.F. Chisholm et al. Acta Mat. accepted April 2021
- Another wanted to see synchrotron x-rays used in addition to neutrons
 - Please see slides 8-11.

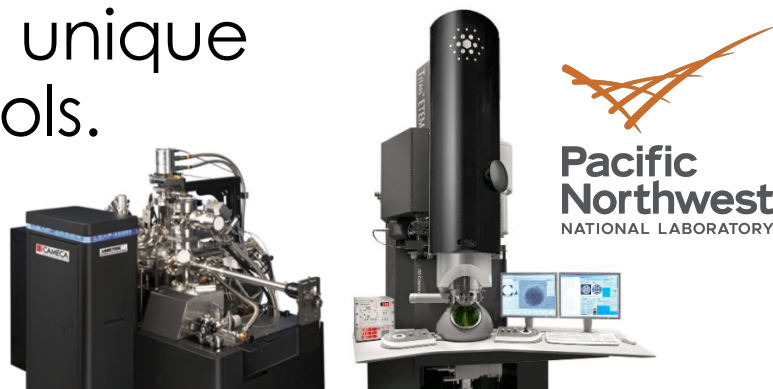
Remaining Challenges and Barriers

- Demand high for tools limits access, e.g., APT, synchrotron
- Integrating characterization data with ICME and advanced analytics with Thrust 4B

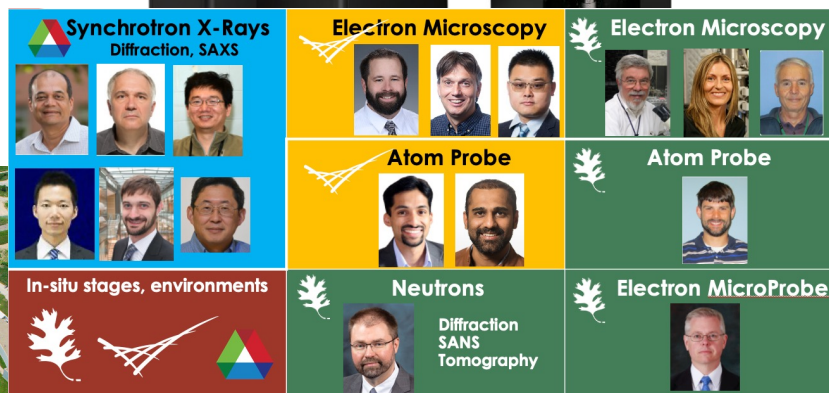
Proposed Future Research

- Study microstructural features to understand the co-optimization of material properties
 - ORNL & PNNL: STEM and APT at nano scale and atomic scales
 - Structure, composition, shape, size and size distributions
 - High strength Ni-based super alloys
 - Carbides in AM austenitic steel
 - Alumina Forming Austenitic (AFA) alloys
 - ANL Synchrotron: Diffraction, Small Angle X-Ray Scattering bulk view at nano scale
 - Phase, distribution, sizes
 - Ni-based alloys
 - AFA Alloys
 - In-situ coarsening behavior in advanced martensitic steels
- ORNL: Electrical and thermal measurements for EV materials
- ORNL: Neutrons in-situ creep of precipitate strengthened ACMZ alloys

Summary: Accelerating alloy development via scientific understanding with unique characterization tools.



Argonne
NATIONAL LABORATORY



**OAK
RIDGE**
National Laboratory



**Matrix of
17+ experts w/
Unique tools**

Technical Back-Up Slides

ANL

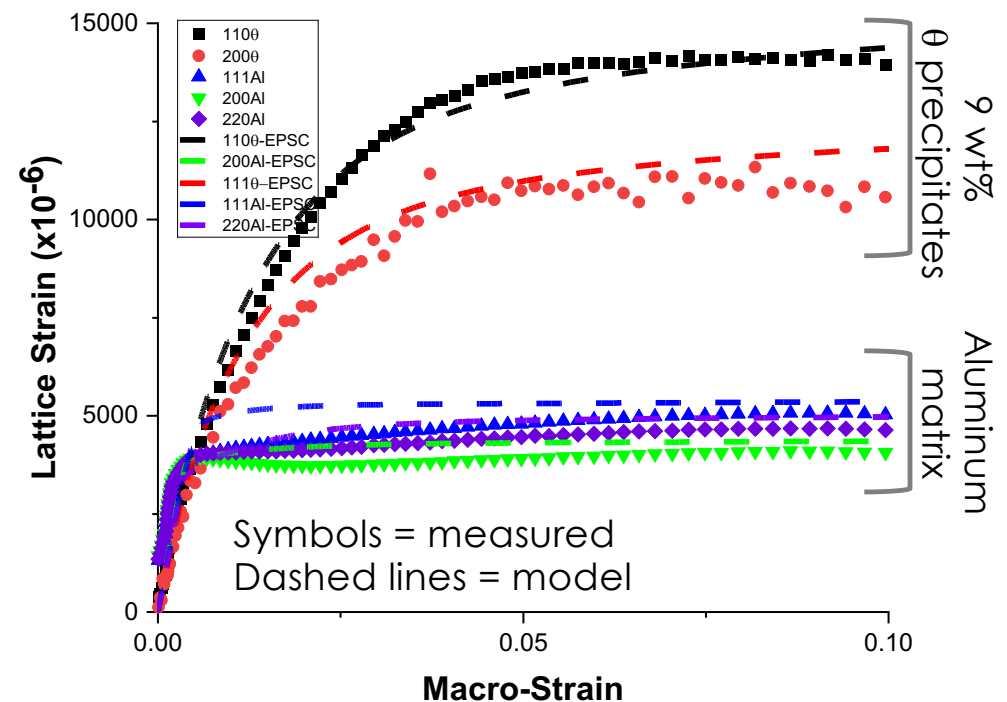
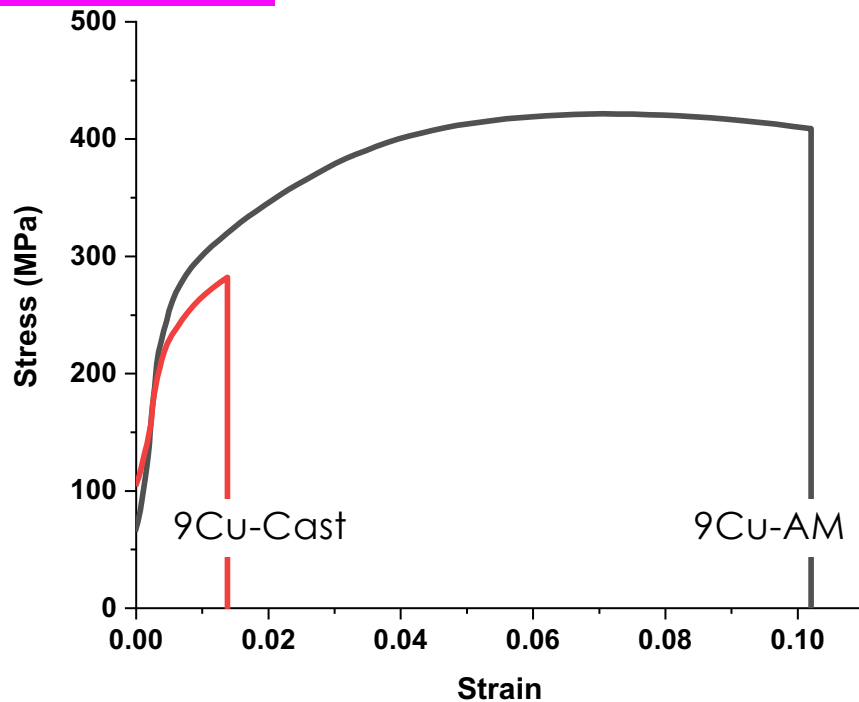
IN

ORNL

Support
Tasks 1A1&3A1

ORNL
 S.Bahl
 X.Hu
 J.Cheng
 A.Shyam
 A.Plotkowski
ANL
 A.Chuang
 Y.Ren

The monochromatic and deeply penetrating synchrotron x-rays enabled the determination of phase loading in-situ



Standard tensile test compared to the combined phase specific loading behavior of HEXRD and EPSC CP* modeling of 9Cu ACMZ-AM showing the applied load distribution amongst the phases. **IMPACT:** Expedited understanding and models facilitate design of ICEs. *EPSC CP=Elastic Plastic Self Consistent Crystal Plasticity



A.Devaraj, PNNL
 B.Gwalani, PNNL
 L.Kovarik, PNNL
 Y.Yamamoto, ORNL
 M.Brady, ORNL

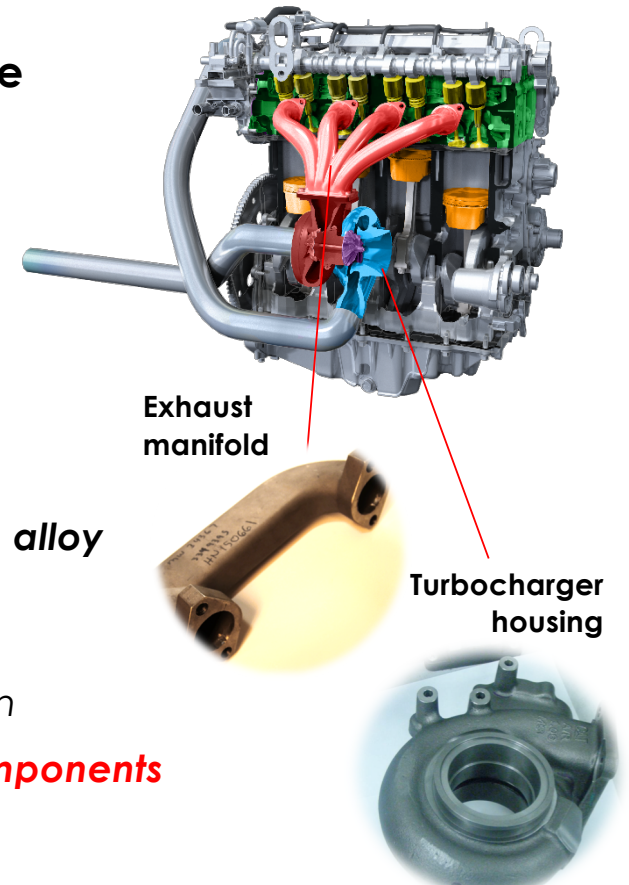
Support Task 2B1

- Driver: Demands of **higher exhaust gas temperature/pressure**
 - Heavy duty: $\geq 800\text{-}900^{\circ}\text{C}^*$, $>260\text{bar}$
 - Light duty: $\geq 950\text{-}1000^{\circ}\text{C}^*$, $>103\text{ bar}$ (*targets in 2050)
- Targets: Higher-temperature capable structural materials
- Components: Exhaust manifold, turbocharger housing

Objective: Develop “Fe-base alloys” for “ $\geq 900\text{-}950^{\circ}\text{C}$ ”

- Improved oxidation resistance by utilizing protective Al_2O_3 scale formation → **newly developed alumina-forming austenitic (AFA) alloy**
- **Increased strength and creep resistance by nano-precipitation**
- Low cost by use of Fe-base cast component with $\text{Ni} \leq 25\text{ wt.}\%$
- Also target scale-up from lab-scale heats to industrial production

→ **Possible electrification-related applications: HT-SOFC/SOEC components**



Exhaust manifold

Turbocharger housing

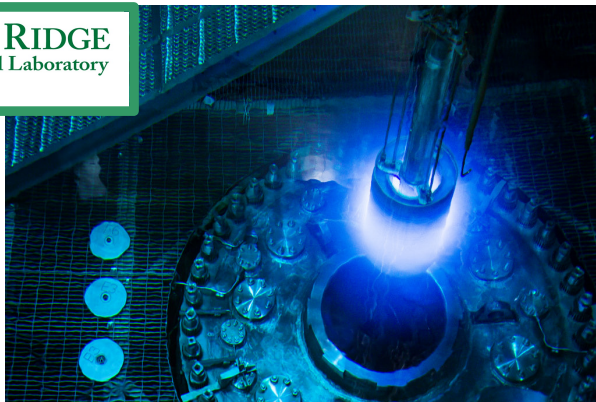
mat191_Watkins_2021_0



OAK RIDGE
National Laboratory

Spallation Neutron Source (SNS)

Neutron characterization



High Flux Isotope Reactor (HFIR)

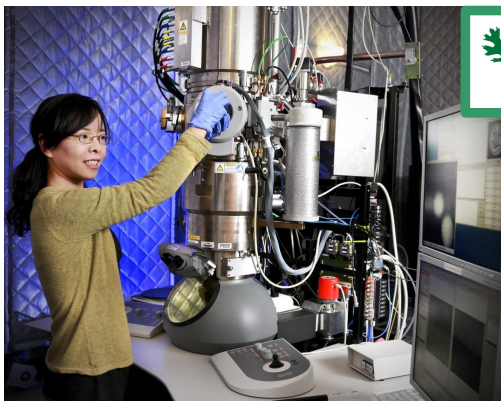


Argonne
NATIONAL LABORATORY

Advanced Photon Source (APS)

Synchrotron characterization

Summary Thrust 4A: Leveraging powerful, unique science tools & expertise at three National Labs accelerate powertrain materials research



OAK RIDGE
National Laboratory



Advanced Microscopy Laboratory (AML), Center for Nanophase Materials Science (CNMS) Advanced electron microscopy facilities

Pacific Northwest
NATIONAL LABORATORY



Environmental Molecular Science Laboratory (EMSL) Advanced electron microscopy facilities