Powertrain Core Program: Higher Temperature (>550°C) Alloys--Nickel-/Iron-Based Alloys

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Program Overview

Timeline

- Program start: Oct 2018
- Program End: Sept 2023
- 5% Complete

Budget

- New Powertrain Materials Core Program (PMCP):
  - $30M / 5 years (DOE 100%)

FY19 PMCP Research Thrusts	FY19 Budget
1. Cost Effective LW High Temp Engine Alloys	$1.15M
2. Cost Effective Higher Temp Engine Alloys	$1.55M
3. Additive Manufacturing of Powertrain Alloys	$1.05M
4. Advanced Characterization & Computation	$1.55M
5. Emerging Technologies	$0.7M

Barriers

Barriers Addressed

- Changing internal combustion engine regimes
- Long lead times for materials commercialization
- Cost of the high performance alloys

Targets

- Improve passenger vehicle fuel economy 25%
- Improved commercial vehicle engine efficiency at least 20%

Program Partners

- Program Lead
  - Oak Ridge National Lab (ORNL)
- Program Partners
  - Pacific Northwest National Lab (PNNL)
  - Argonne National Lab (ANL)

Thrust 2: Subtask 2A1 Overview

2A1.Oxidation Resistant Valve Alloys (900- 950°C)

Timeline

- Project start: Oct 2018
- Project End: Sept 2022
- Percent Complete: 10%

FY19 Budget

- **Thrust 2 total:** $1.55M (DOE funds)

FY19 Thrust 2 Subtasks	FY19 Budget
1. Cost Effective LW High Temp Engine Alloys	
2A1.Oxidation Resistant Valve Alloys (900- 950C)	$400k
2A2. Higher Temperature HD Piston Alloys (≥600C)	$250K
2A3. High Temperature Coatings	$175K
2A4. High Temperature Oxidation	$150K
2B1. Development of Cast, Higher Temperature Alloys	$250K
2B2. Advanced Surface Processing of Castings (PNNL)	$300k

Barriers

- Changing internal combustion engine regimes
  - Higher power density engines leading to higher peak exhaust valve temperatures
- Long lead times for materials commercialization
- Cost of high performance alloys

Collaborators

- Lead: ORNL
- Partner Laboratories
  - PNNL
  - ANL
- Industrial Partners:
  - Materials Supplier: Special Metals
  - Valve Manufacturer

Relevance and Objectives

- Exhaust gas temperatures are on the rise and are expected to continue to increase in future higher efficiency advanced engines
  - Temperatures are expected to increase from 870°C to 950°C by 2025 and to 1000°C by 2050* in light-duty vehicles
- There is a critical need to develop materials that meet projected operational performance parameters but also meet *cost constraints*
- **Overall Objectives**: Develop cost-effective exhaust valve alloys suitable for operating at 900 - 950°C for use in advanced future engine concepts
  - Develop cost-effective alloys with
    - High temperature tensile and fatigue strengths: f(cylinder pressure, valve diameter, temp)
    - Oxidation resistance
  - Demonstrate suitability for use in exhaust valves with industrial partners

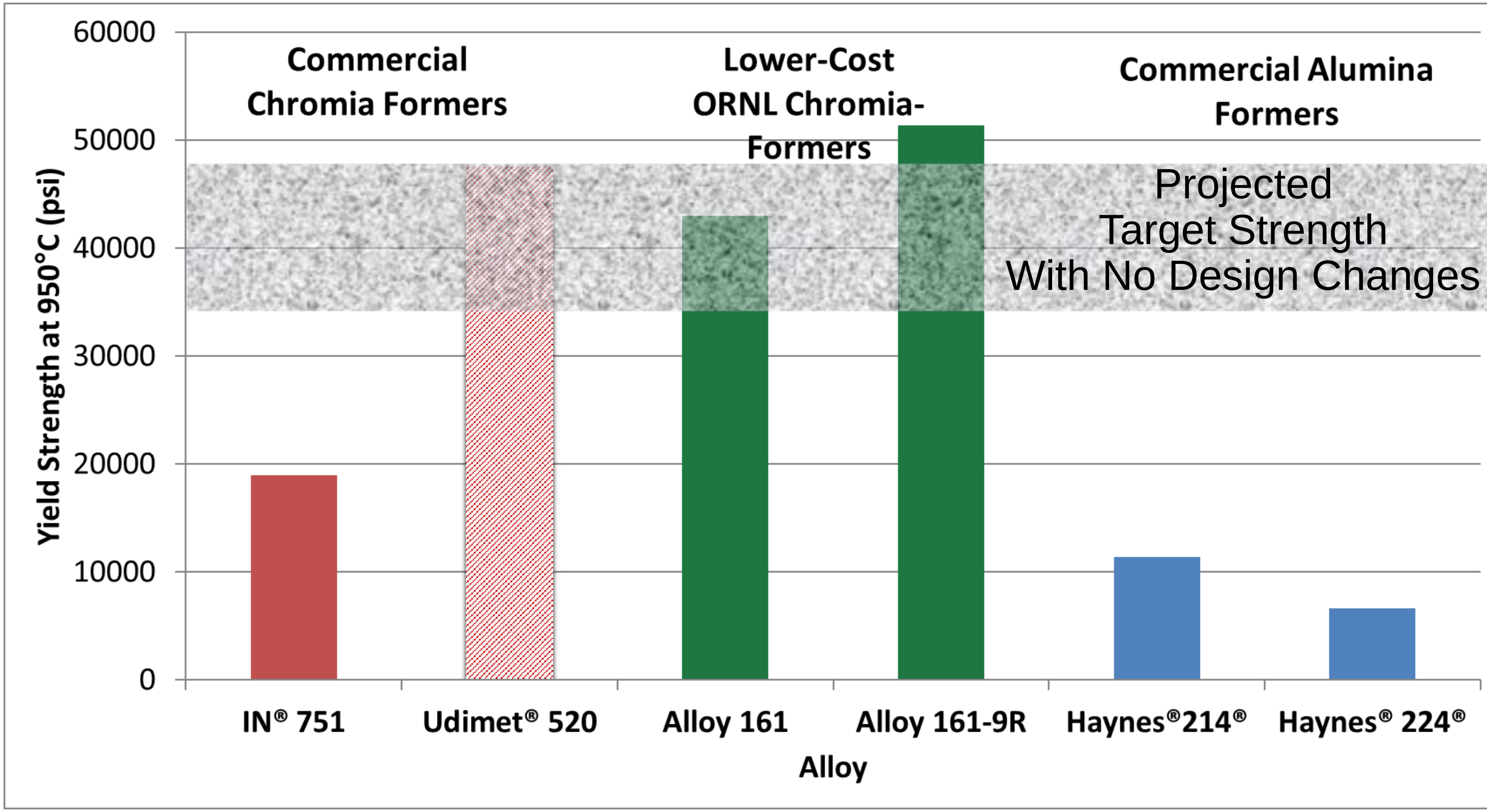
***DOE Vehicle Technologies Workshop report: Light-Duty Vehicles Technical Requirements and Gaps for Lightweight and Propulsion materials, Feb. 2013.**

Commercial Alloys of Interest are Ni-Based

- Ni-based alloy IN®751 is used in high performance exhaust valves
  - Other alloys have greater strength but can be expensive due to high levels of Ni + Co and manufacturing challenges (example: Udimet®520)
- Oxidation resistance achieved through *in-situ* formation of
  - chromia-scale (limited to < ~ 850-900°C)
  - alumina-scale (desirable for ≥ ~900°C in water vapor containing environments)

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

Use of Commercial Alumina-Forming Alloys is Limited by their Lower Strength Compared to Chromia-Forming Alloys at Higher Temperatures



Chromia forming alloys have high strengths at 900-950°C but need coatings for oxidation resistance

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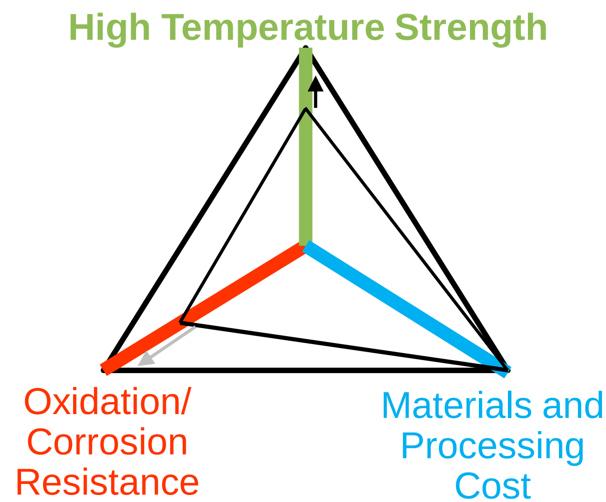
Overall Approach

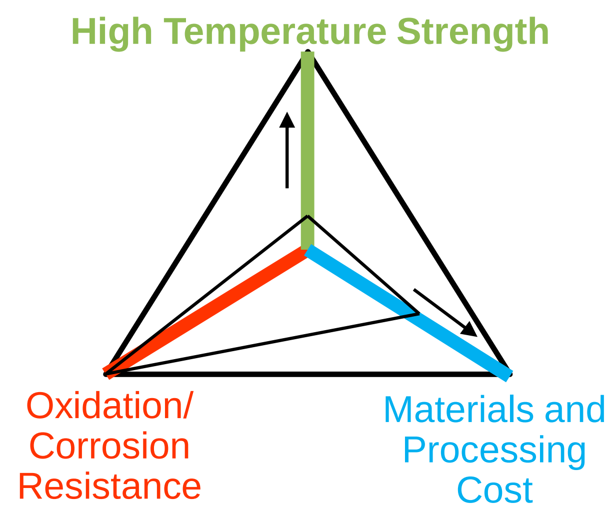
- Current state-of-the-art commercial valve alloy 751, a chromia-forming alloy is
  - Primarily strengthened by coherent, intermetallic precipitates- γ' ($Ni_3(Al,Ti,Nb)$)
  - Does not have significant strength above ~850°C due to dissolution of strengthening phase
  - Chromia-containing oxide forms *in-situ* and provides oxidation resistance only up to ~850°C

Chromia-forming alloys

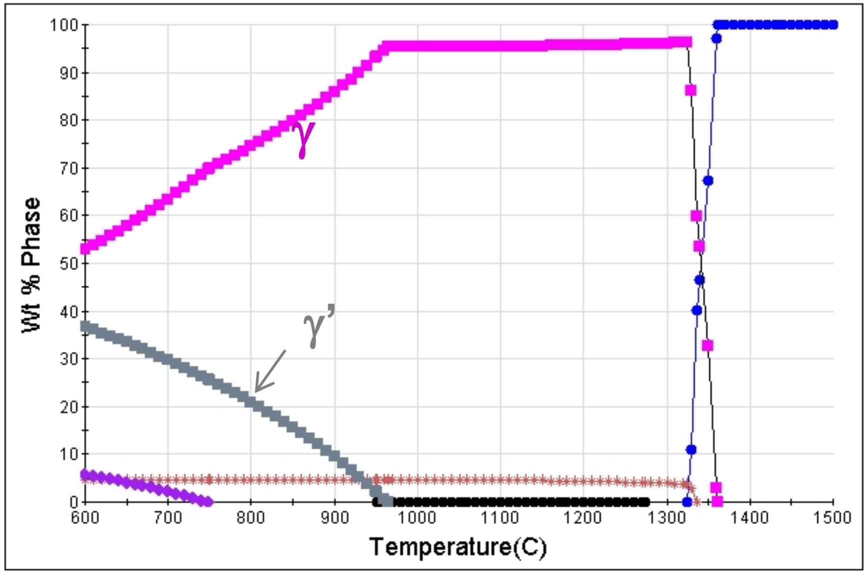


- Two parallel approaches to develop materials for 900-950°C operation
  - Identify suitable ORNL low- cost, high-strength chromia-forming alloys for 900-950° for use with coatings (developed in Sub-task 2A3)
  - Develop new stronger, low- cost, alumina-forming alloys

Alumina-forming alloys

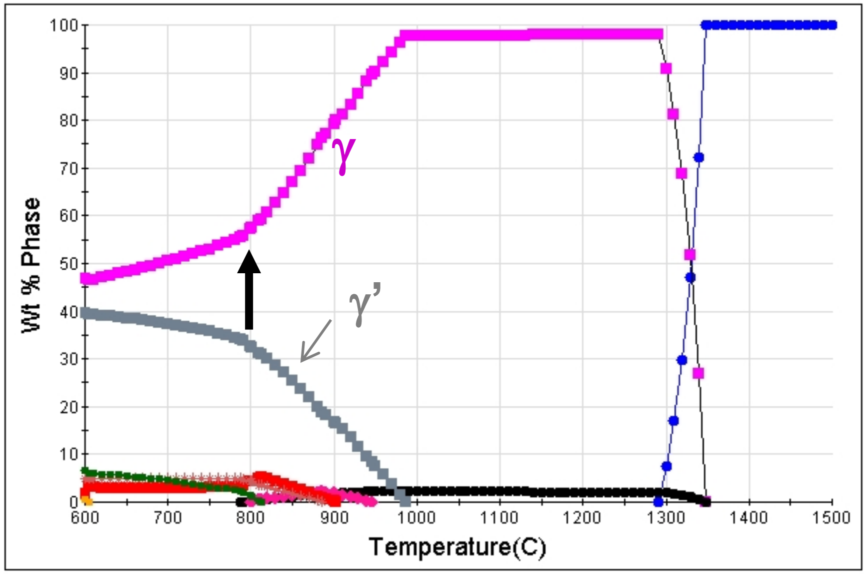


Alloy Development Approach: New Generation of Alloys Are Designed with Increasing Fractions of γ’ For Higher Strengths



Example 1

Wt. % γ’ at 950°C: **~ 2.5 wt. %**
Ni: 60-70 wt. %



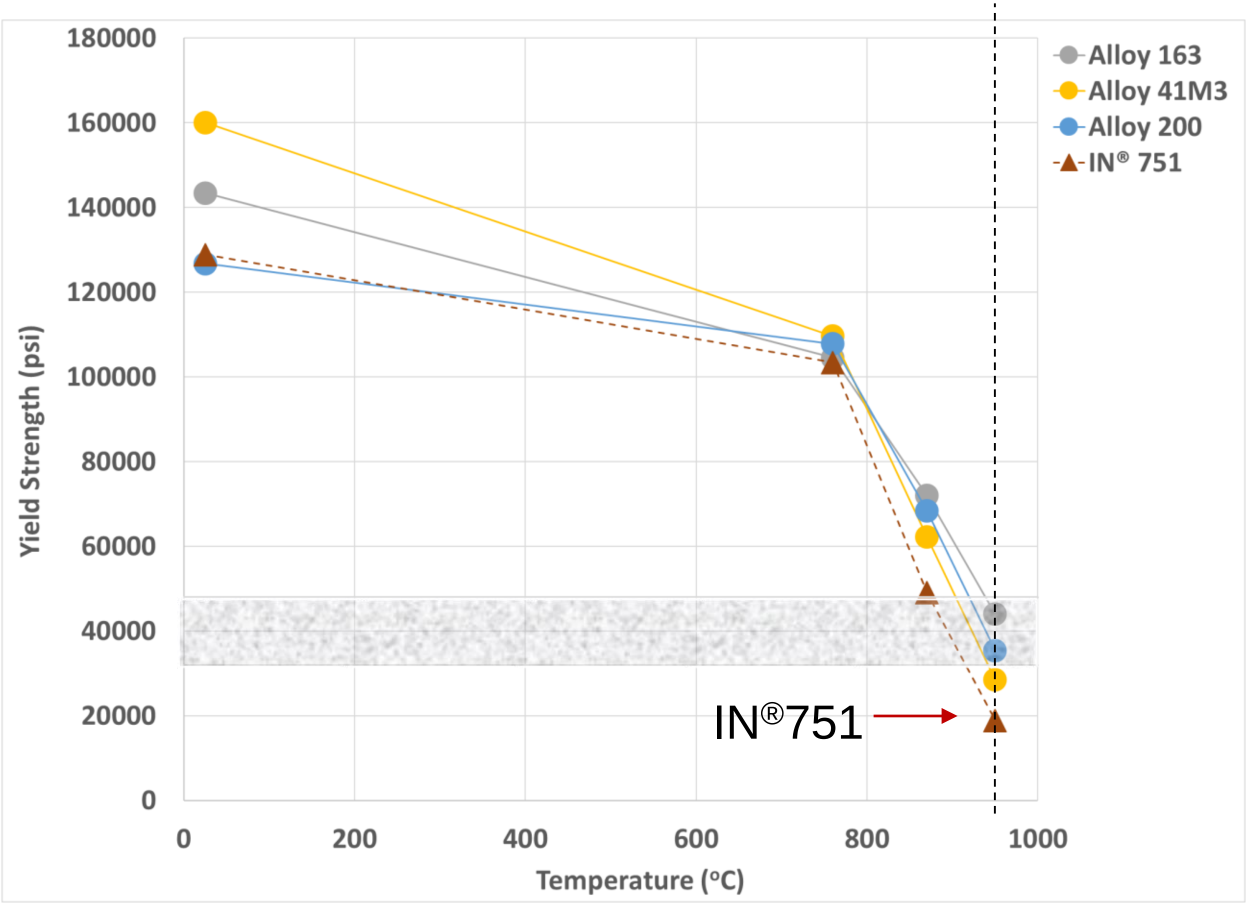
Example 2

Wt. % γ’ at 950°C: **~ 7.5 wt. %**
Ni: <60 wt. %

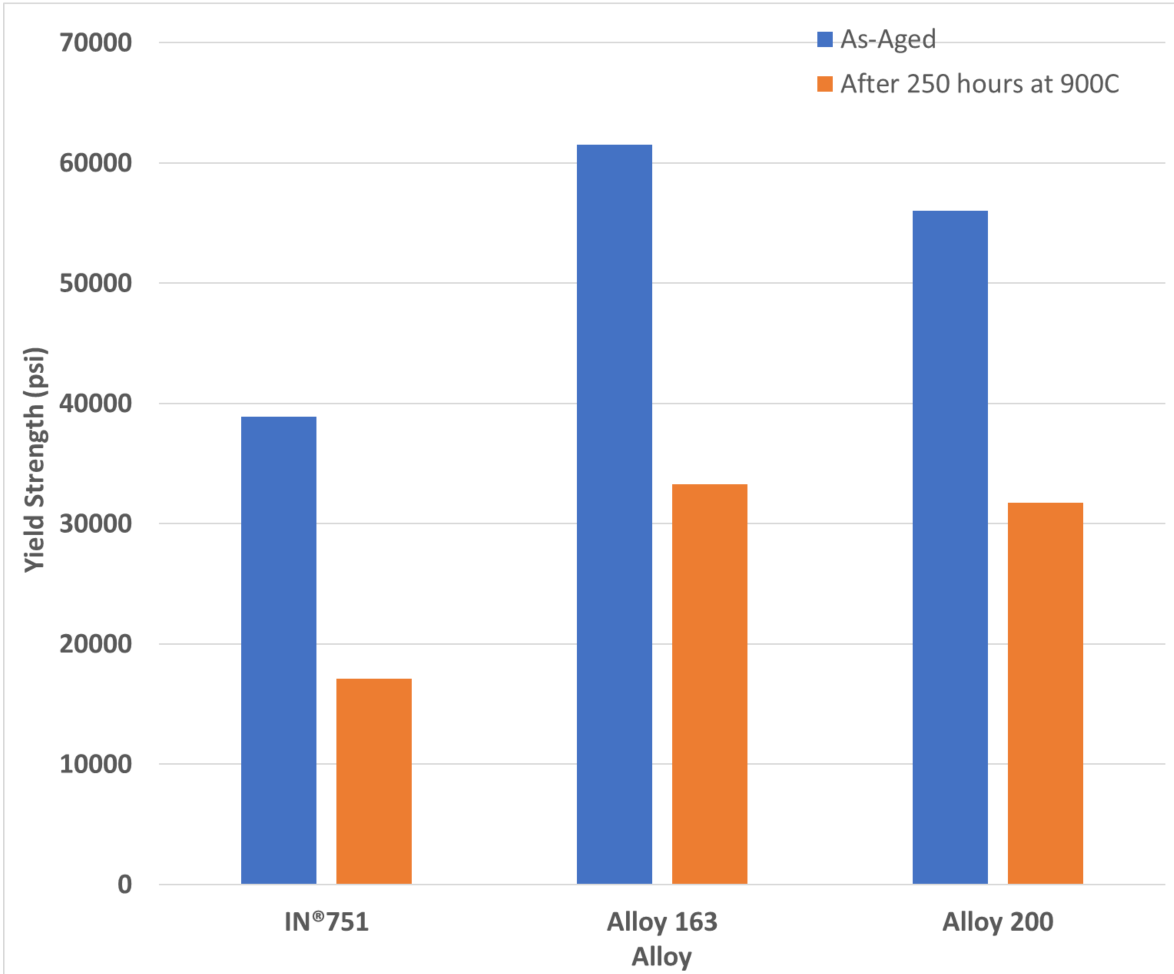
FY19-FY20 Milestones

Month/ Year	Milestone Description	Status
Dec. 2018	Evaluate the effect of long term exposure (250 hours) at 900°C on the tensile properties of four down-selected, chromia-forming ORNL alloys	**Complete**
Mar. 2019	Computationally design and fabricate laboratory scale heats of alumina-forming alloys (Target yield strength: ≥30 Ksi at 950°C)	**Complete**
Jun. 2019	Evaluate high cycle fatigue life of downselected alloys **Go/No-Go:** Fatigue life of new alloys > fatigue life of alloy 751) at 900°C at relevant stress level	**On-track**
Sep. 2019	Identify pathways to improve yield strength of alumina-forming valve alloys (Target yield strength: ≥35 Ksi at 950°C)	**On-track**

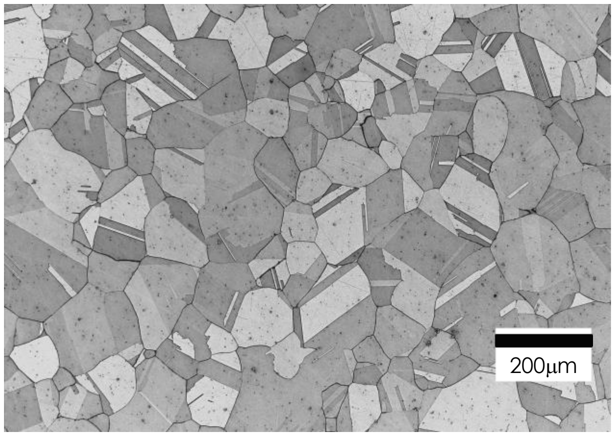
Accomplishments: ORNL Chromia-Forming Alloys With Lower Ni Have Higher Strengths than IN®751 at 900-950°C



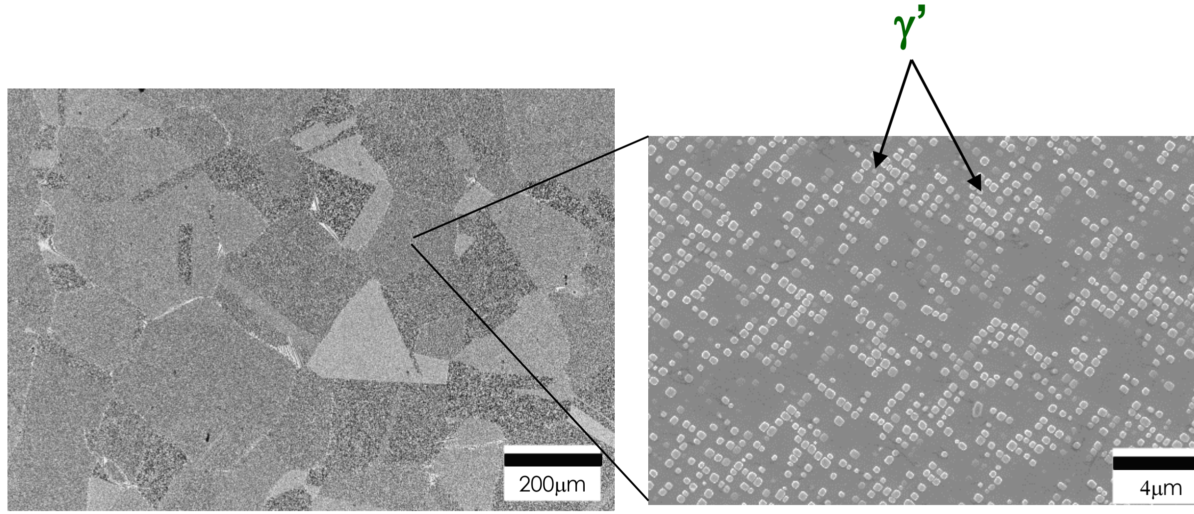
Accomplishments: New ORNL Chromia-Forming Alloys Have Higher Yield Strength than IN®751after 250 hours at 900°C



Accomplishments: Microstructural Evaluation of Chromia-forming ORNL Alloy ORNL 163 Confirms γ' Strengthening after 250 hour Exposure at 900°C



As-aged



After 250 hours at 900°C

Average γ' size= ~275 nm

γ' Content: ~15 vol. % vs ~ 4% vol. % for IN®751)

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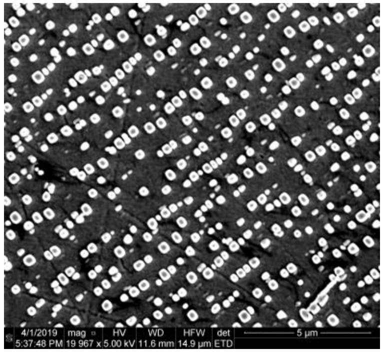
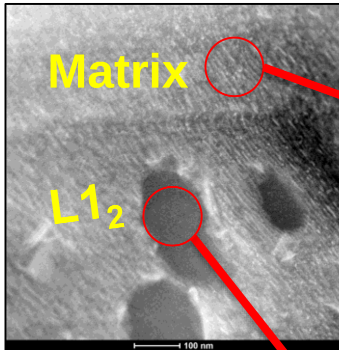
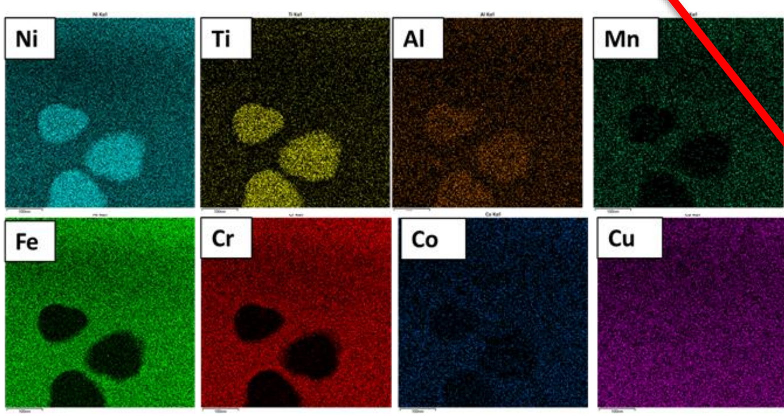
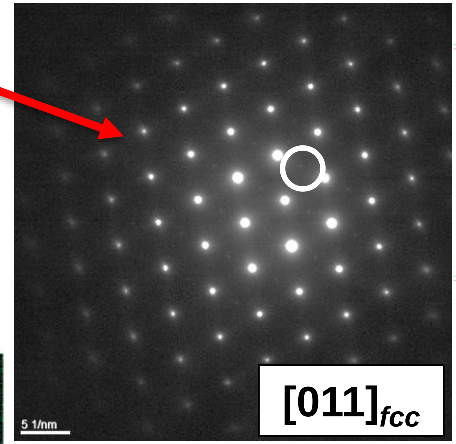
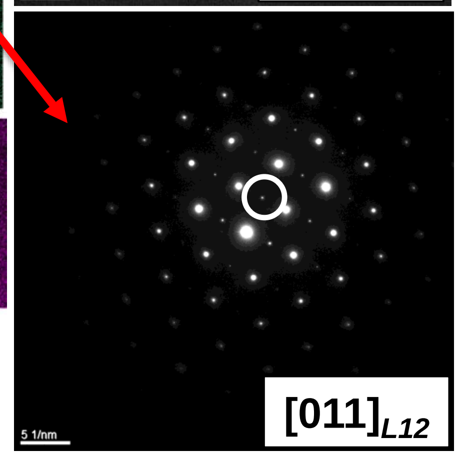
TEM/APT Characterization on Alloy 163: Aged+ 900°C/250h is on-going at PNNL*



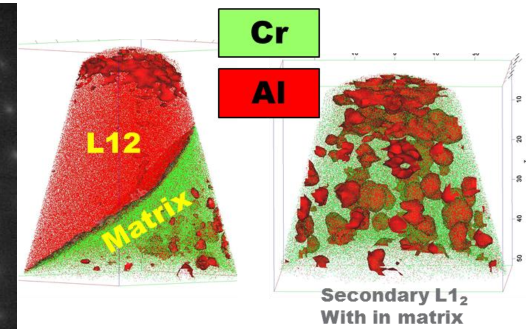


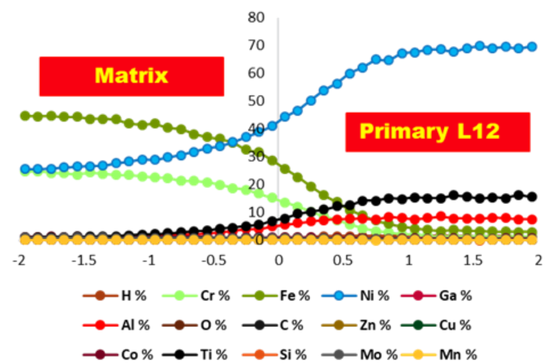






Atom-Probe Tomography





Faint $L1_2$ super-lattice spots seen in matrix as well.

*Collaboration with Bharat Gwalani, Libor Kovarik, Arun Devaraj, PNNL

- **TEM diffraction, and STEM-EDS revealed the structure and composition of primary γ’ and γ matrix**
- **APT helped to quantify of composition of primary and secondary γ’ and γ matrix**

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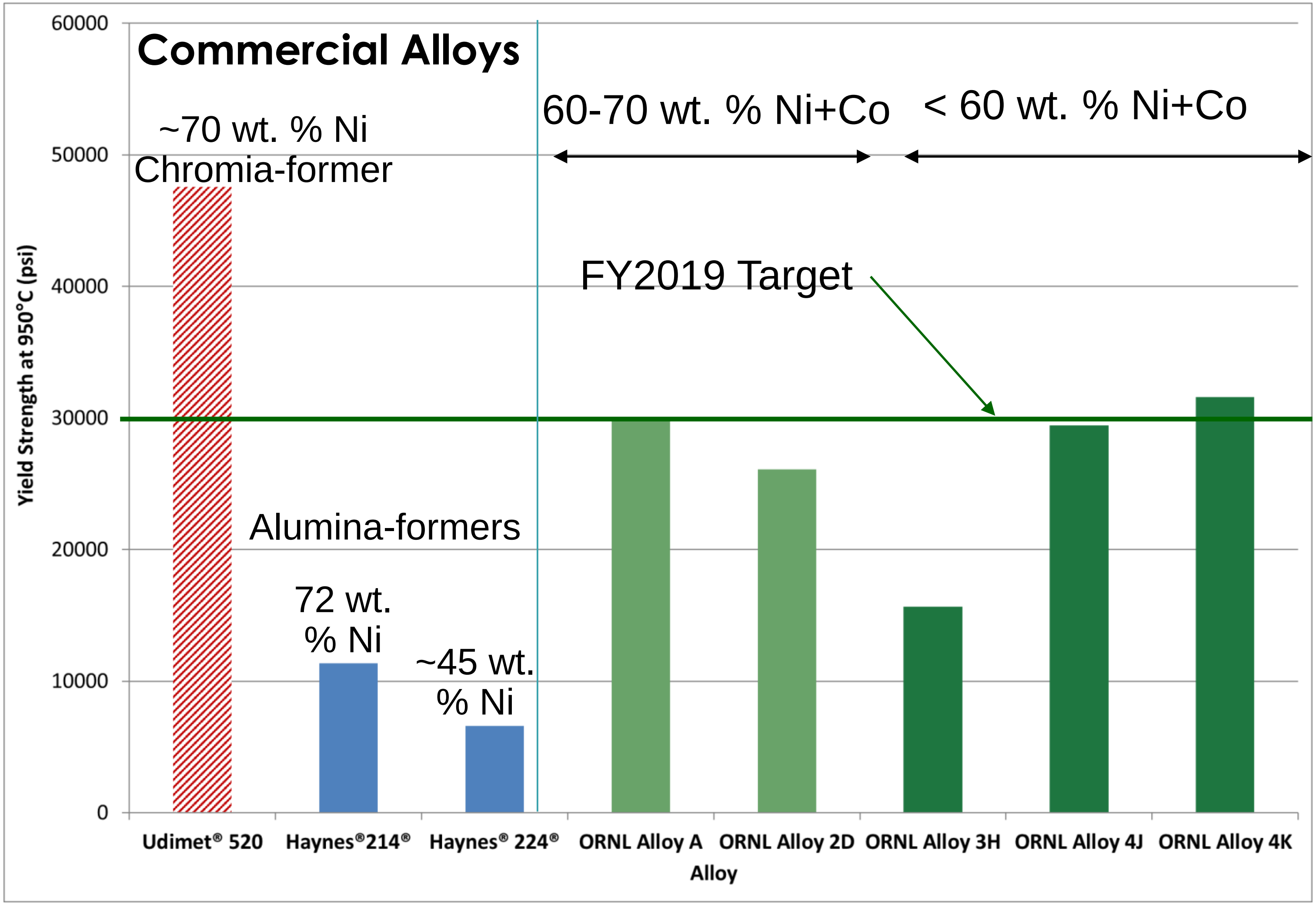
Accomplishments: New Alumina-Forming Alloys Have Achieved Target Yield Strengths at 950°C



2019 Milestone target of 30 ksi at 950°C has been achieved at lower Ni-levels

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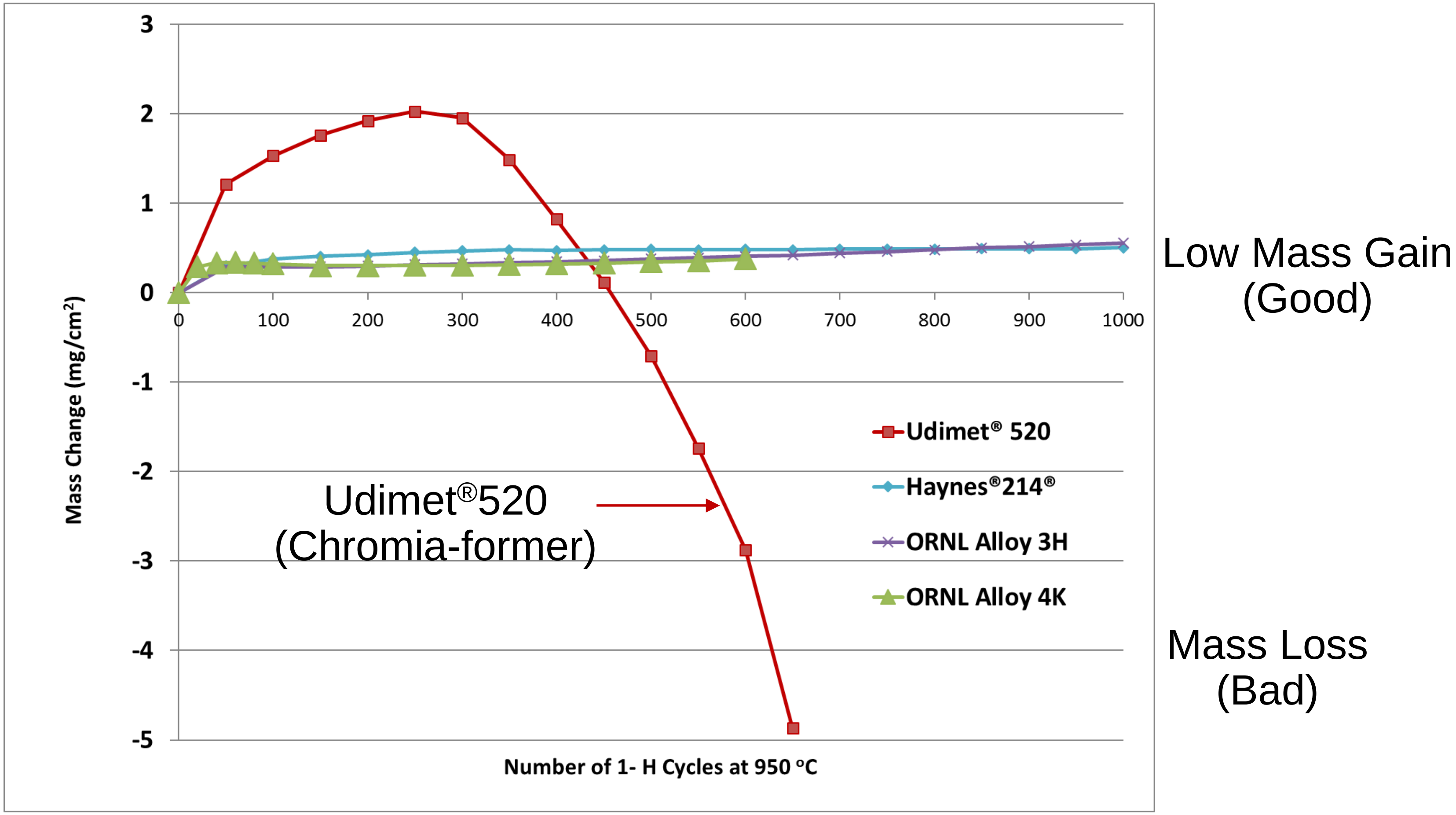
New Generation of ORNL Alumina-forming Alloys Show Good Oxidation Resistance at 950°C, Air+ 10% Water Vapor*

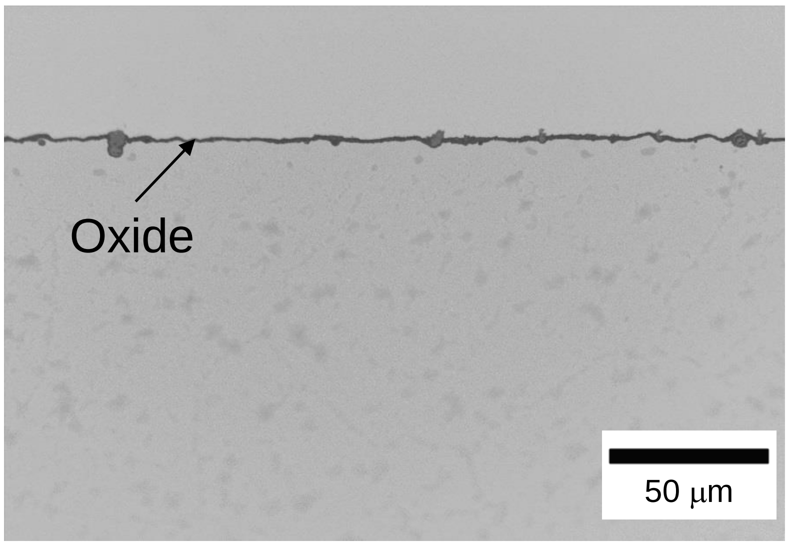


ORNL Alloy 4K Has >30 Ksi yield strength, good oxidation resistance at 950°C, and is lower in Ni levels compared to commercial alumina-formers

***collaboration with Bruce Pint, ORNL**

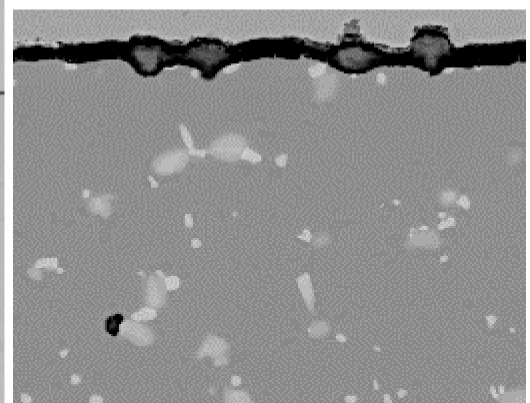
Cross-Sections of New Higher Strength Alumina-Forming Alloy Show Presence of Aluminum-rich Oxide

950°C, Air+ 10% Water Vapor, 600 Hours

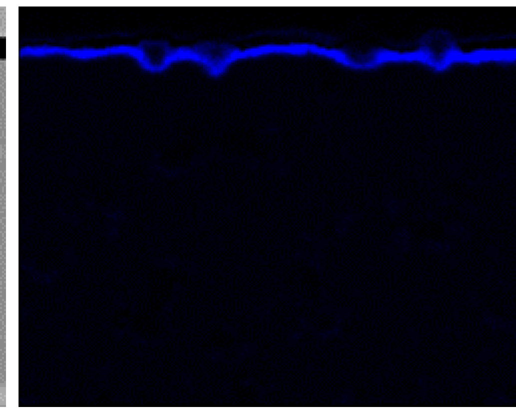


ORNL Alloy 4K

SE Image

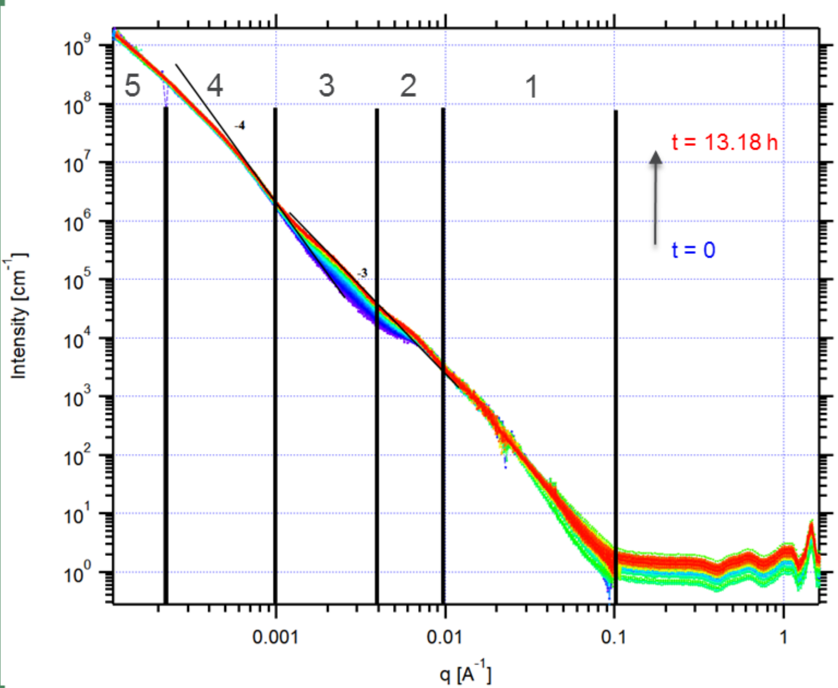


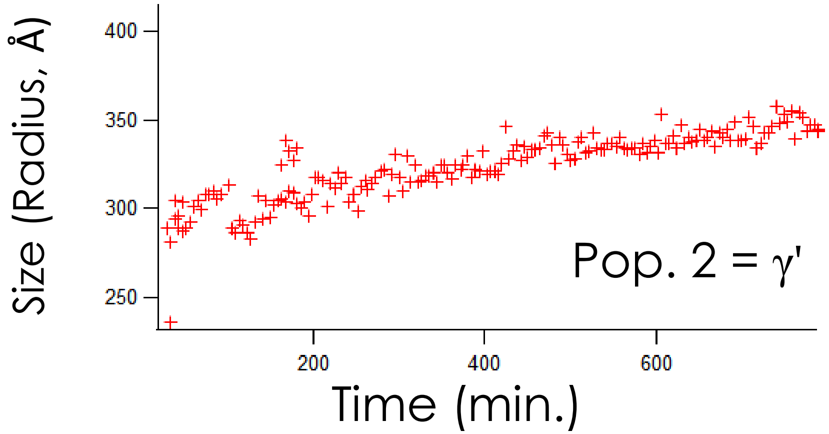
Al Map

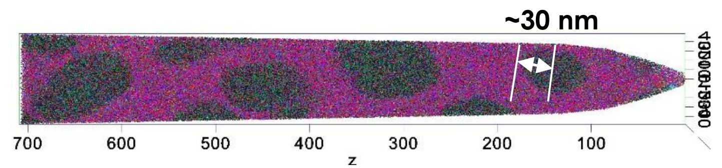


USAXS/SAXS/APT Provides Particle Size Information for Heat-Treatment Optimization of Alumina-forming Alloys*

- *In-situ* Extended range Ultra Small-angle Scattering, and Small-angle scattering (USAXS/SAXS) is used to characterize γ' precipitate size after heat-treatment and its evolution during use
- USAXS data suggests the presence of two populations of strengthening precipitates (smaller size pop 2 and larger sized pop. 3)
  - Size of precipitates being evaluated by APT and TEM







Atom Probe Tomography provides complementary information to USAXS (Jonathan Poplowsky, ORNL)

*Collaboration with Matt Frith, Jan Ilavksy, and Saul Lapidus, Argonne National Laboratory

Collaborations and Coordination with Other Institutions

- Collaborations with **Special Metals Corporation**
  - Larger sized heats are being fabricated
- Collaborations with **Valve Manufacturer**
  - A CRADA is being initiated for development and commercialization of exhaust valves
- Collaborations with **Argonne National Laboratory** are on-going
  - 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
  - Advanced microstructural characterization to understand microstructure-mechanical properties link

Remaining Challenges and Barriers

- High strength chromia-forming ORNL alloys must be successfully produced in industrial scale heats
- Fatigue strength and oxidation resistance must be evaluated and improvements over current valve alloy must be verified
- Long term alloy stability must be demonstrated
- Valve fabrication methods must be developed
- Valve performance must be proven using engine testing

Image of 50 lb heat of ORNL chromia-forming alloy being successfully hot rolled at Special Metals

Proposed Future Research

FY19/ FY20

- Trial heats will be produced in industrial scale in collaboration with industrial adviser/industrial partner
- High temperature fatigue properties of industrial scale heats will be measured
- Long-term microstructural stability at high temperatures will be evaluated

Any proposed future work is subject to change based on funding levels

Summary

- **Relevance:**
  - Temperatures are expected to increase from 870°C to 950°C in 2025 and to 1000°C by 2050 in light-duty engines. Current valve alloy cannot meet strength, oxidation, and cost requirements for use at the higher temperatures and new cost-effect materials are needed for use at these temperatures.
- **Approach/Strategy**:
  - High temperature strength and fatigue properties of cost-effective chormia-forming alloys developed at ORNL are being evaluated for use in exhaust valves at 900-950°C.
  - A computationally guided approach is being used to develop new higher strength alumina-forming alloys for use at 900-950°C.
- **Accomplishments:**
  - ORNL alloys having higher strength than IN751 at 900-950°C have been down-selected
  - New alumina-forming alloys have achieved target yield strength of ≥30 Ksi at 950°C while maintaining good oxidation resistance.
- **Collaborations:**
  - Collaborations are on-going with ANL, PNNL, Special Metals, and a valve manufacturer
- **Proposed Future Work:**
  - Alloys will be produced in larger heats for high temperature fatigue property measurements
  - Pathways to developing alumina-forming alloys with higher yield strength (target 35 Ksi) will be identified