High Temperature Materials for High Efficiency Engines

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Project ID # PM053

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start: September 2013
- Project end: September 2016
- Percent complete: 80%

Budget

- Total project funding Received
  - DOE 100%
- FY15 Funding: $ 190K
- Funding anticipated

  FY16: $ 0 K (carryover only)

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 by 25%
- Improve commercial vehicle engine efficiency at least 20%

Partners

- Lead: ORNL

Interactions/Discussions with:

- Carpenter Technologies- Materials Supplier
- Argonne National Laboratory

Relevance

- Exhaust gas temperatures are expected to increase in future high efficiency engines
  - Temperatures are expected to increase from 870°C to 950°C in 2025 and to 1000°C by 2050* in light-duty vehicles and from 700°C to 900°C by 2050 in heavy duty vehicles**
- Nickel based alloys (~ 70% Ni + Co wt. %) are candidate alloys for use in exhaust valves
  - Alloy 751 (current alloy) loses strength above 850°C
  - Other high strength alloys such as Udimet®520 are expensive

Alloy	C	Si	Mn	Al	Co	Cr	Cu	Fe	Mo	Nb	Ni	Ta	Ti	Ni+Co
IN 751	0.03	0.09	0.08	1.2	0.04	15.7	0.08	8.03	-	0.86	71.32	0.01	2.56	71.32
Udimet 520	*0.04*	*0.05*	*0.01*	*2.0*	*11.7*	*18.6*	*0.01*	*0.59*	*6.35*	*-*	*57.65*	*-*	*3.0*	*69.35*

- Lower cost alloys with high strength and good oxidation resistance are needed at 950°C
- Overall objectives: Develop cost-effective exhaust valve materials suitable for operating at temperatures up to 950°C for use in advanced future engine concepts
- Objective in FY2016:
  - Improve strength of new alloys at 950°C
  - Evaluate oxidation resistance at 950°C and identify strategies for improvement

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

FY15-FY16 Milestones

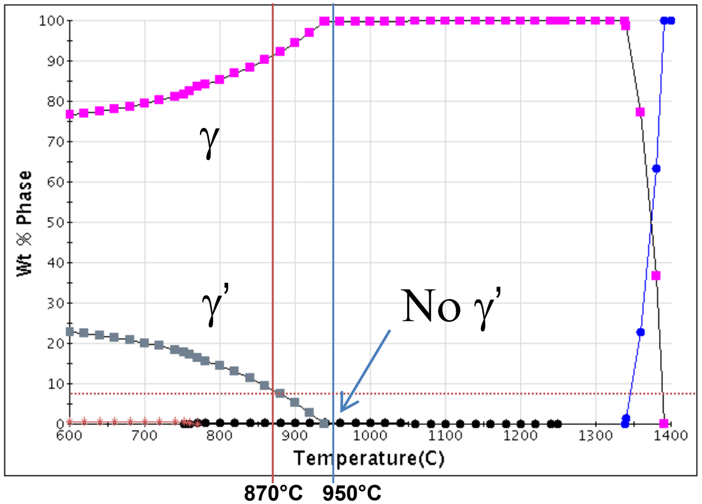
Month/ Year	Milestone Description	Status
March 2015	Identify initial target composition range of new alloys for desired oxidation resistance	Complete
June 2015	Complete oxidation testing and tensile testing of alloys prepared in laboratory scale at temperatures up to 950ºC	Complete
Sept. 2015	Down-select one promising alloy with strength and oxidation resistance at 950ºC comparable to commercial alloy and lower cost	Complete
Sept. 2016	Evaluate strength and oxidation resistance of down-selected alloy at 950°C and submit final project report	On Track

Approach

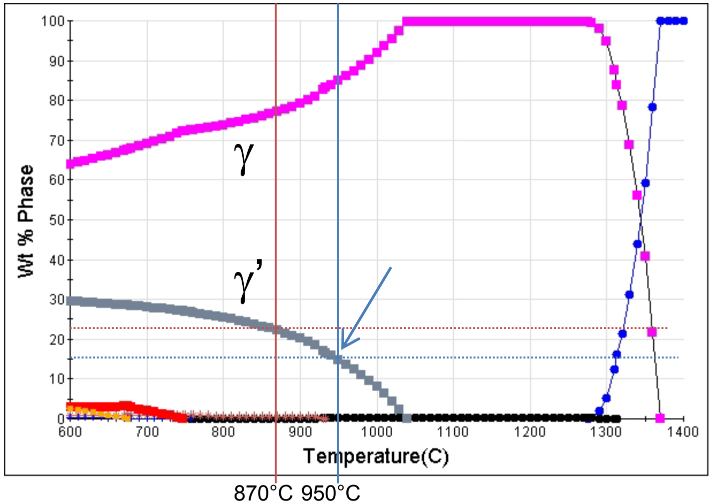
- Current baseline commercial valve alloy 751, a chromia-forming alloy is
  - Primarily strengthened by coherent, intermetallic precipitates- γ' ($Ni_3(Al,Ti,Nb)$)
  - Does not have significant strength above ~850°C due to dissolution of strengthening phase
- A previous project developed lower cost chromia-forming alloys for use at 870 °C
- Current project aims to develop lower cost alloys for 950 °C with low Ni+Co levels and WITHOUT expensive (Re, Ru etc.) alloying element additions
  - Challenge: Reducing Ni affects BOTH strength, and oxidation resistance
- Overall Approach:
  - Improve strength by increasing volume fraction and modifying other desirable characteristics (coherency etc.) of strengthening phases at 950 °C
  - Achieve a stable, chromia scale for good oxidation resistance

Approach: Computational Thermodynamics Predictions are Used to Guide Alloy Development

- Thermodynamic modeling used to identify alloy compositions with lower Ni levels but with high enough γ' content for required strength
  - Approach was successful in developing alloys for 870°C
- Models to predict oxidation behavior and lifetime are not well developed
  - Identify experimental strategies to achieve oxidation resistance comparable to high Ni-alloys with similar strength at 950°C



Alloy 751 Shows Complete Dissolution of Strengthening Phase at 950°C

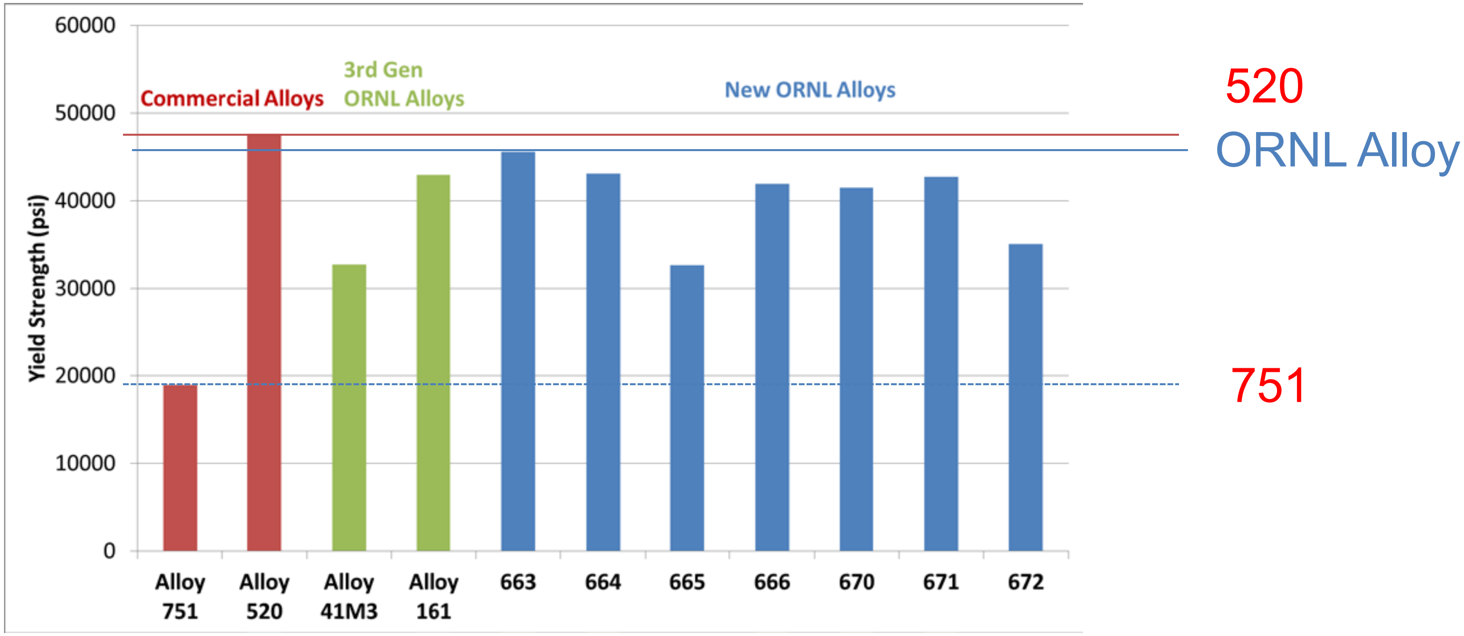


ORNL Alloy 161-9R Shows Presence of Strengthening Phase at 950°C

Approach: Strategies Used to Balance Cost, Strength, and Oxidation Resistance at 950°C

- Increase strength levels at temperatures up to 950°C using alloying element additions to achieve target of Alloy 520
  - Increase strengthening elements Al, Ti, Nb, ~~Ta~~
  - Increase Ni levels along with strengthening elements (changed APB, misfit etc.)
- Strategies for improving oxidation resistance in a chromia-former at 950°C (significant challenge at lower Ni levels)
  - Increasing Cr levels (need to balance with Ni+Co since Cr destabilizes F.C.C. structure)
  - Increase nickel +cobalt contents (limited by cost)
  - Trace additions of rare earths (Y, Hf, La) (typically less than 0.1% by weight) (limited by cost)
- Transition to an alumina-former (addressed by new FY 16 project)

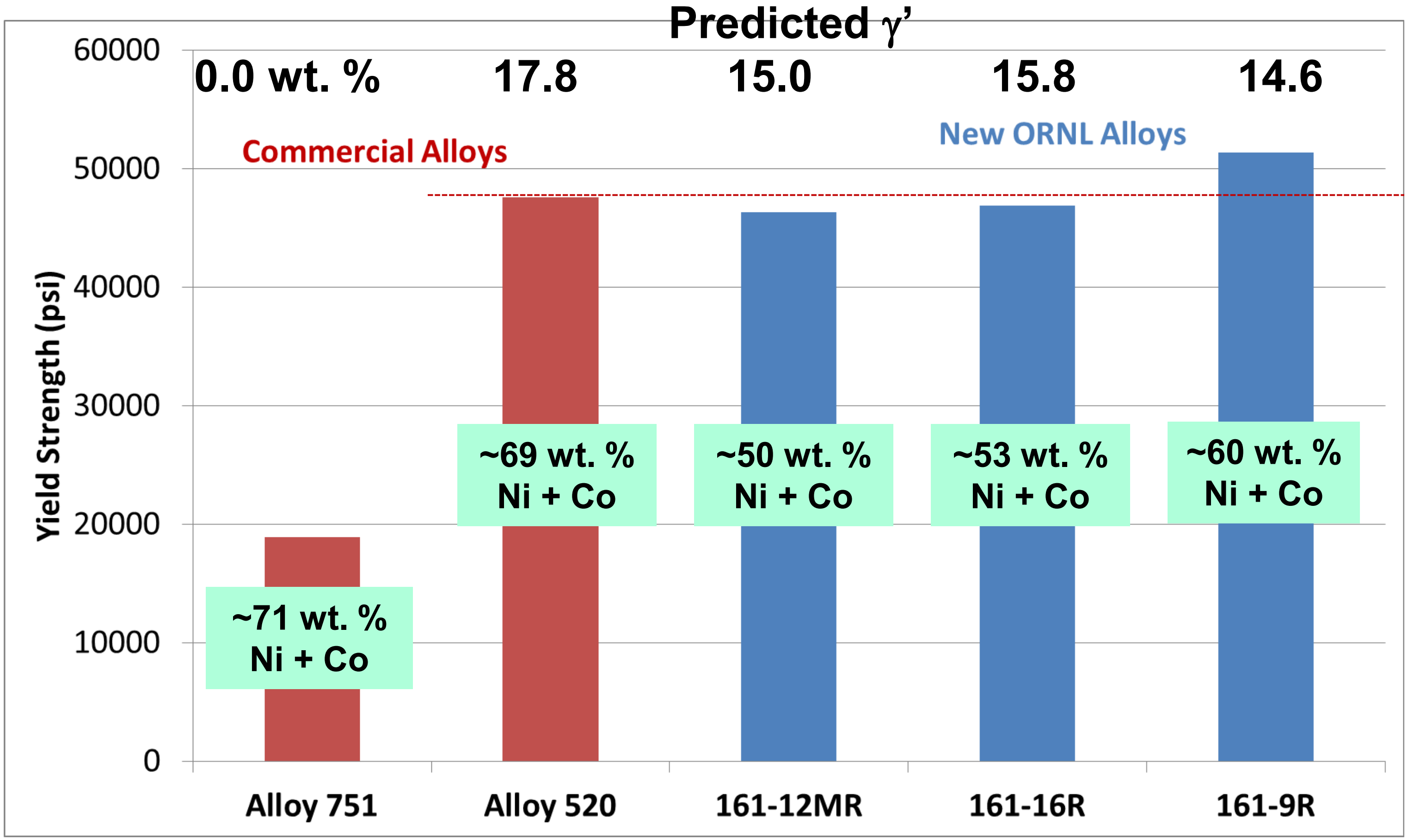
Previous Accomplishments and Progress: Lab-Scale Alloys With High Strengths at 950°C Have Been Developed



Alloy 751: 71 wt. %(Ni +Co), Alloy 520 : 69.3 wt. % (Ni+ Co), FY15 ORNL alloys: < ~50 wt.% Ni+Co , with varying levels of strengthening elements and Cr

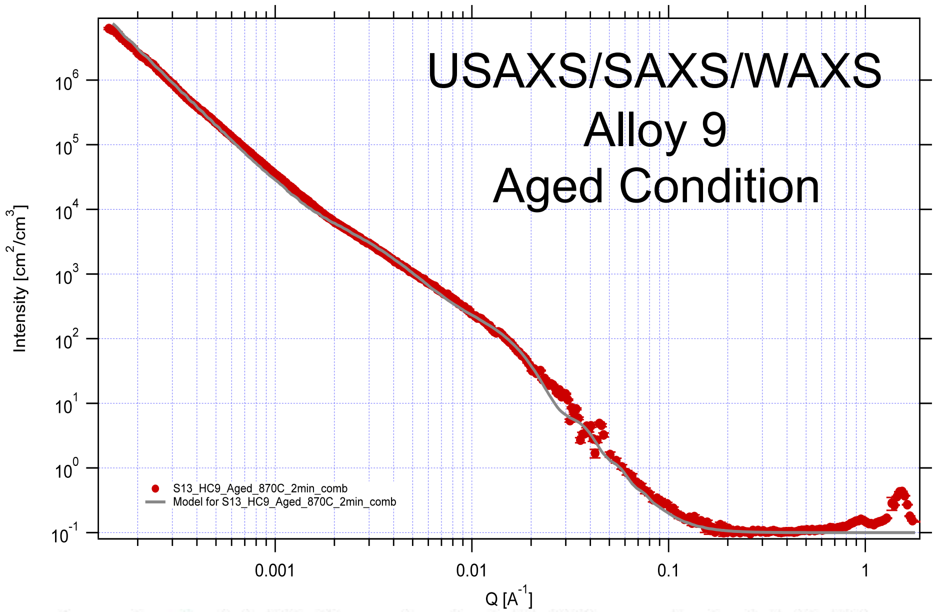
- **Strength close to that of Alloy 520 achieved**
  - **How can we improve?**
- **Improvement in oxidation resistance was also desirable**

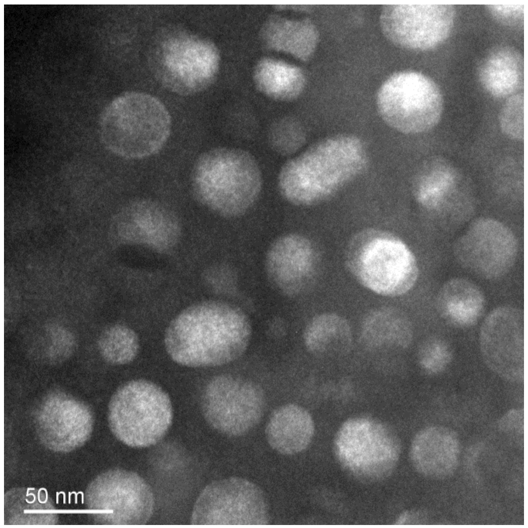
Accomplishments: New Alloys With Higher Strength at 950°C Have Been Developed

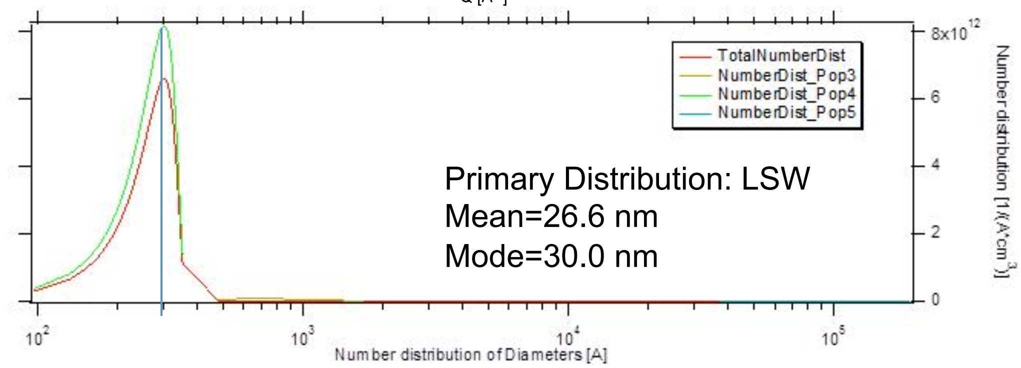


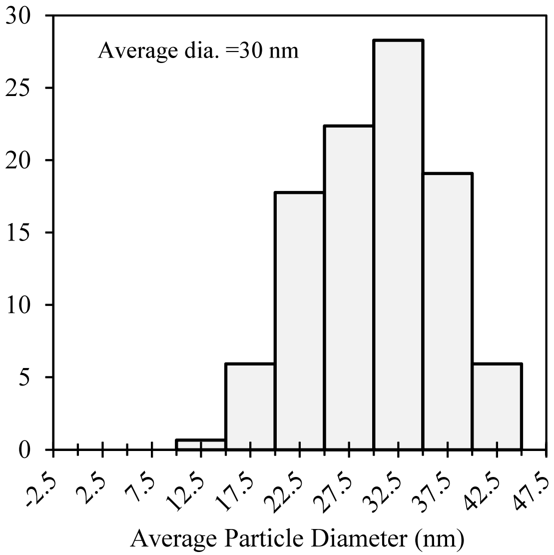
- ~60 wt. % Ni+Co level needed to surpass yield strength of Alloy 520 at 950°C

Accomplishments: Transmission Electron Microscopy and Small-Angle X-ray Scattering Was Initiated to Understand Precipitate Size Distribution (PSD)









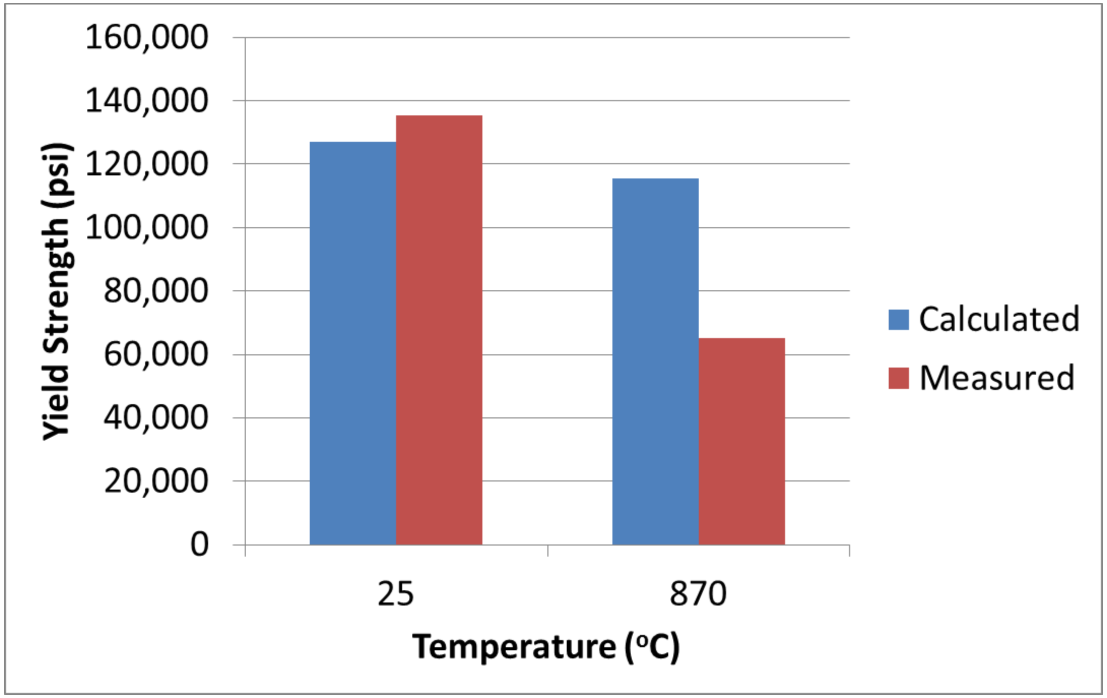
Precipitate size distribution influences alloy strength

***Collaboration with R. N. Andrews, and J. Ilavsky, Advanced Photon Source, Argonne National Lab**

***Collaboration with Dean Pierce, ORNL**

Accomplishments: Input from Microstructural Characterization was Used for ICME Predictions of Yield Strength

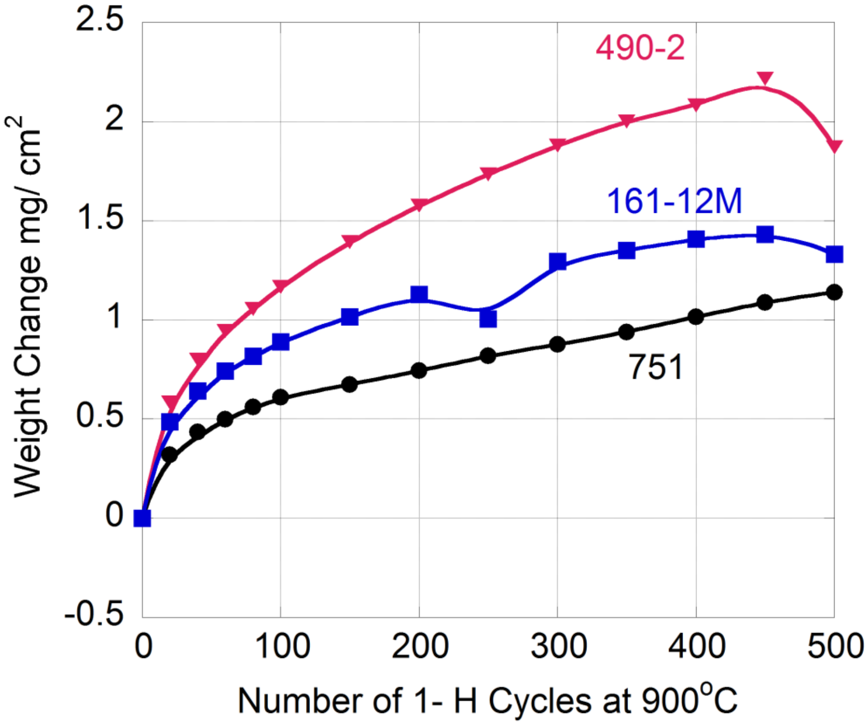
- Average particle size measurements from TEM/X-ray scattering were used to predict strength as a function of temperature using JMatPro v8 for Alloy 9
- Other parameters (volume fraction, APB energy etc.) were calculated internally
- A single particle size distribution was assumed



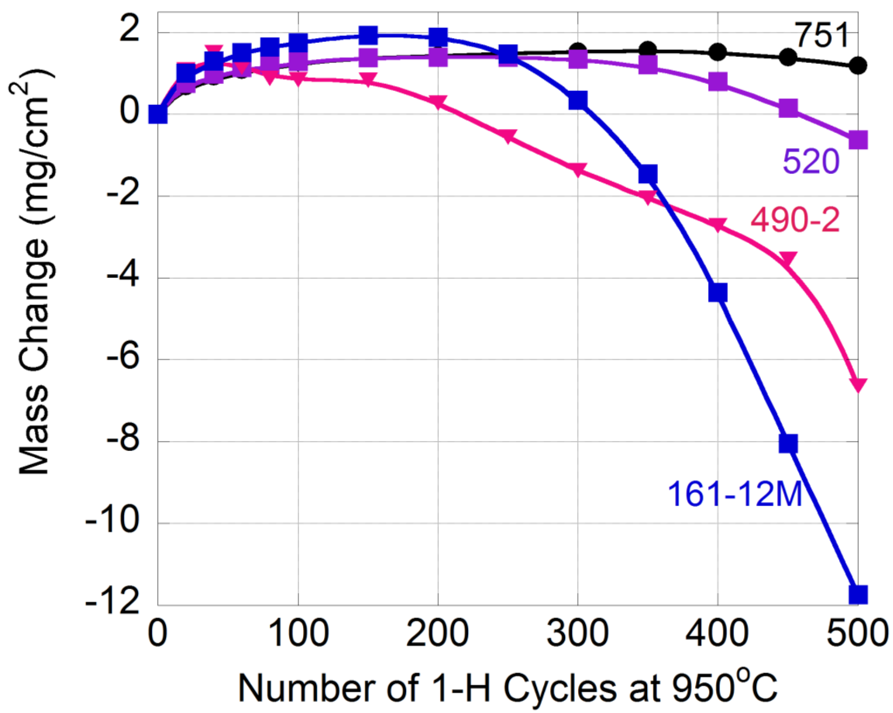
- Measured and calculated values for room temperature strength differ by ~6%
- Measured high temperature yield strength is lower than calculated value. Further characterization is on-going to understand reasons

Accomplishments: Increasing Temperature to 950° Shows Detrimental Effect on Oxidation*

900°C (FY 15 Results)



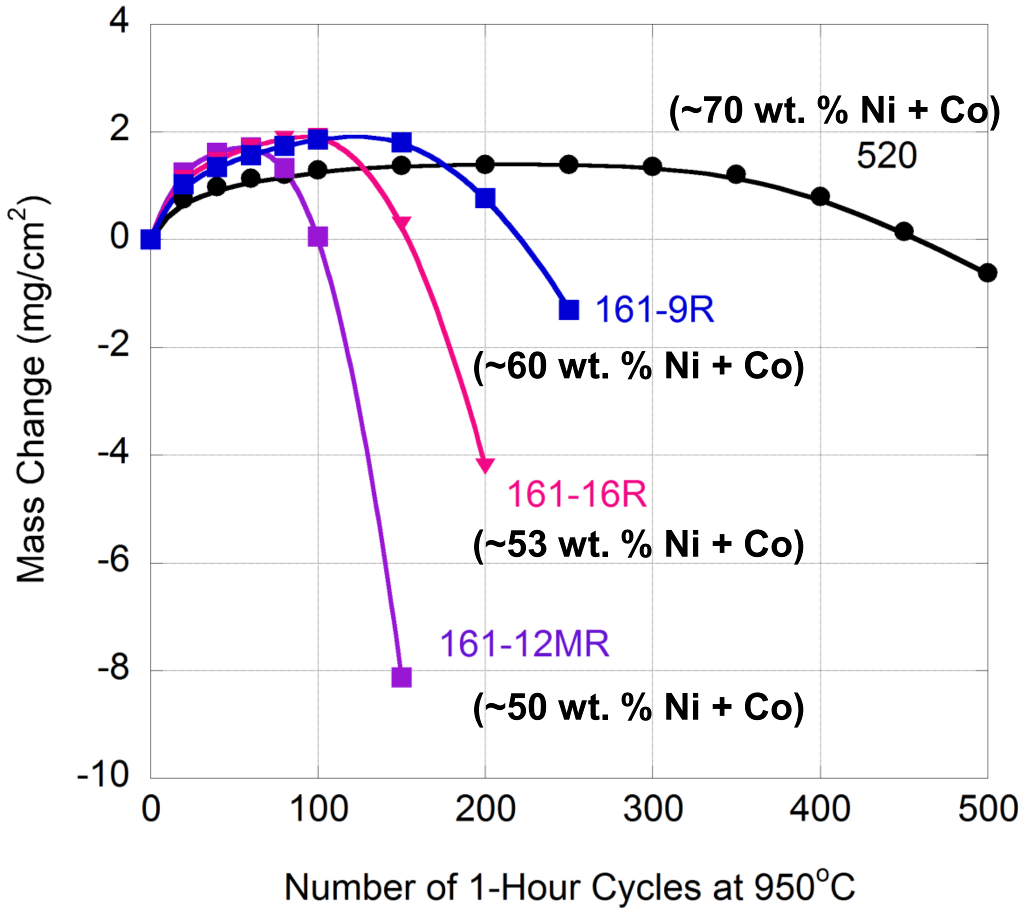
950°C



- **Higher temperatures result in earlier spallation**

*Collaboration with Bruce Pint, ORNL

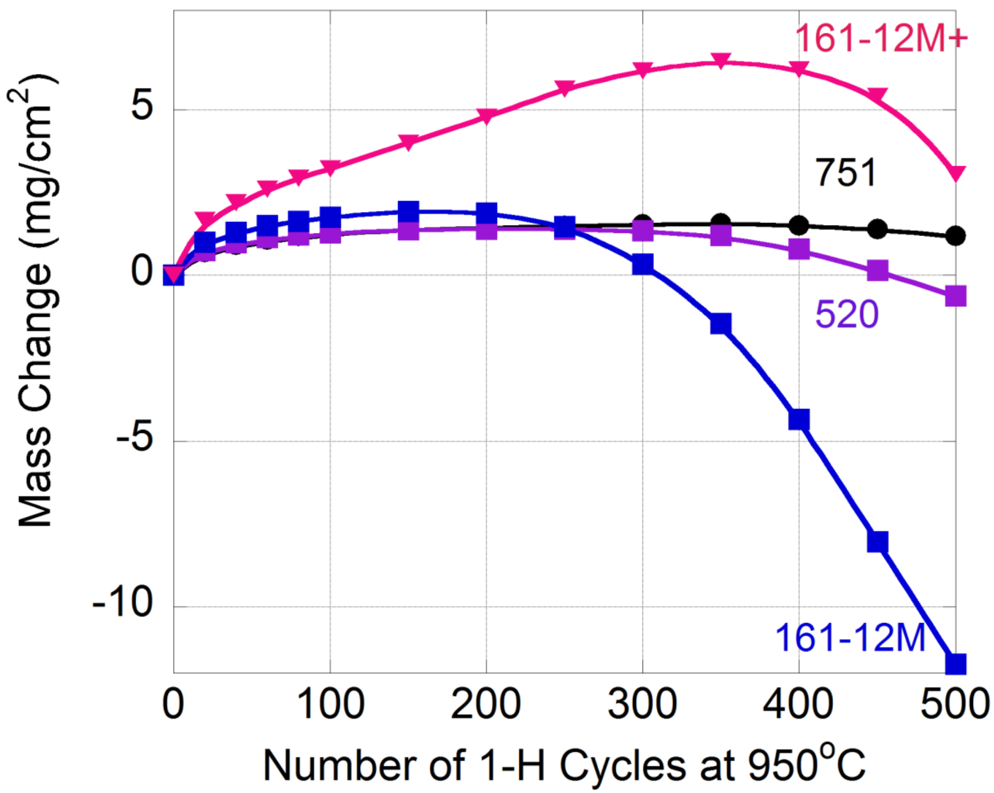
Accomplishments: Increased Nickel Additions Show Positive Effect on Oxidation Resistance at 950°C



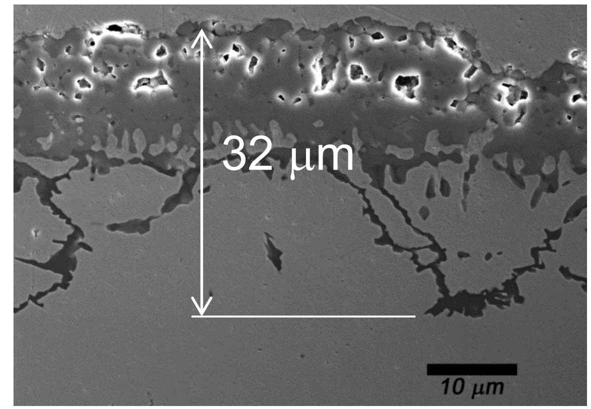
Actual valve duty cycles and hence required oxidation lifetime at 950°C not known

New alloys offer options that balance cost with performance

Accomplishments: Trace Amounts of Reactive Element Additions (< 0.1% of Hf/Y/La) Combined with Cr Provides Better Oxidation Resistance at 950°C



SEM image of scale after 200 hours



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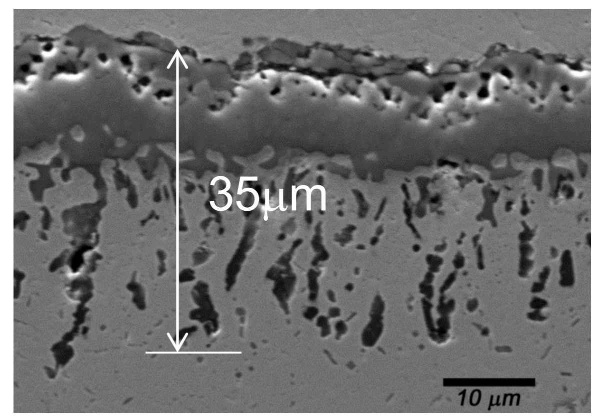


161-12M+

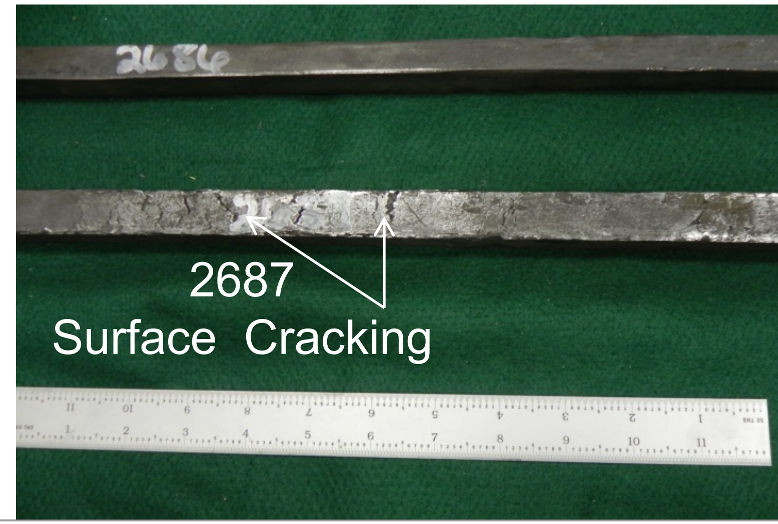
New alloy shows higher weight gain but resistance to spalling comparable to Alloy 520 at 950°C.

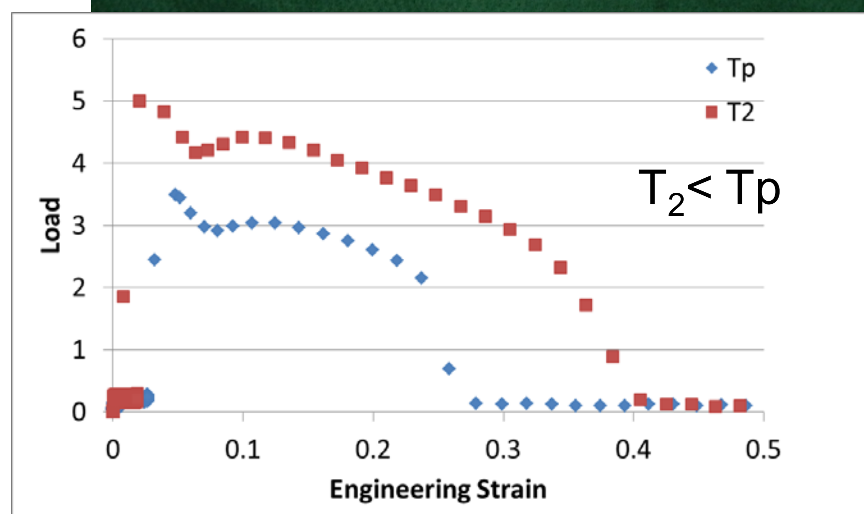
Accomplishments: Gleeble Testing Identifies Better Processing Window for ORNL Alloy

- Surface cracking observed in high strength alloy Heat # 2687 (47Ni-18Cr- Al-Ti)
  - Process modifications have been suggested by Carpenter

- Gleeble testing shows that processing temperature Tp was not optimized for ductility

2686
No cracking





Response to Reviewer's Comments

Comment: Fading away how, the reviewer asked. By spallation, the reviewer presumed, requesting that information be provided to clarify the evaluation and results.

Response: In oxidation tests, the specimens are suspended in test atmosphere. *Ex-situ* specimen weight measurements are repeated at predetermined cycle intervals. The evaluation of mass change in oxidation resistance is standard practice followed by the oxidation community and is a good screening tool. Increase in mass/unit area represents growth of oxide scale, while mass loss represents loss of oxide scale. Thick oxide can spall off the surface due to thermal expansion mismatch related stresses and poor adhesion. Cyclic growth and spallation resulting in ultimate depletion of protective elements from the alloy.

Comment: The path to achieving the oxidation resistance goals couple with tensile strength is vague. "No ICME feedback was highlighted.."

Response: Method to balance oxidation resistance with strength for a chromia-former at these Ni levels is NOT known. Several potential experimental approaches were outlined in FY15 and the results of these approaches have been presented this year. ICME models are not available to predict oxidation behavior. Development of ICME models is beyond scope of this project due to limited resources.

Collaborations and Coordination with Other Institutions

- Collaborations are on-going with Carpenter Technologies
  - Gleeble tests on C2687 are being conducted under guidance from Carpenter to identify the appropriate temperature for processing high strength alloy
  - Discussing avenues for commercialization
- Collaborations with Argonne National Laboratory have been initiated in X-ray based characterization on the following beamlines
  - Extended range Ultra Small-angle, Small-angle, and Wide-angle X-ray scattering facility
  - Powder diffraction facility

Remaining Challenges and Barriers

- Need to understand the effect of individual and combined reactive element additions on modifying oxide (chromia) growth characteristics

- Define alloy processing window that minimizes processing defects

Future Work

FY16

- Continue to explore reactive element additions to identify most effective combinations
- Fabricate one down-selected alloy, test oxidation resistance and high temperature strength at 950°C
- Complete characterization of selected additional alloys to understand precipitate size distributions
- Prepare final report (Sept. 2016)

Summary

- **Relevance:**
  - Temperatures are expected to increase from $870^{o}C$ to $950^{o}C$ in 2025 and to $1000^{o}C$ by 2050* in light-duty vehicles and from $700^{o}C$ to $900^{o}C$ by 2050 in heavy duty vehicles. Current valve alloy cannot meet strength requirements and new cost-effect materials are needed for use at these temperatures
- **Approach/Strategy:**
  - A computationally guided approach has been used to develop new lower Ni-alloys with high strength at temperatures up to $950^{o}C$. Similar approach has been used previously to develop new cost-effective alloys for use at temperatures up to $870^{o}C$. Several experimental strategies to improve oxidation resistance in these alloys were proposed and evaluated.
- **Accomplishments:**
  - New alloys with yield strength at 950 ° C better than that of alloy 520 have been designed but with lower Ni levels. Oxidation resistance was shown to improve with the additions of trace amounts of reactive elements. Transmission electron microscopy and x-ray scattering work is on-going to understand the effect of precipitation on strengthening and to help minimize the levels of strengthening additions that could adversely affect oxidation resistance. Gleeble tests show that changes in processing temperature will favorably affect the ductility of alloy during industrial processing.
- **Collaborations:**
  - Collaborations are on-going with Carpenter Technologies and Argonne National Laboratory
- **Proposed Future Work:**
  - Identify one best alloy for 950°C performance, project ends Sept. 2016

Technical Back-up Slides

Response to Reviewer's Comments

Comment: "What other factors than the Nickel-Chromium levels and what elements other than iron and titanium, which were being mentioned are being added to the low-cost alloy. Refractory alloys or rare earths, the reviewer pointed out, are generally apt to make Ni seem cheap by comparison."

Response: **No refractory or rare earths are added to achieve strength. Cost is a CRITICAL factor for market acceptance. Cost guidance was provided by Carpenter, a major supplier of valve alloys to the industry. Also processing costs are not considered in this comparison. Alloys such as 520 are difficult to process thus increasing costs significantly. Lower cost, iron-containing feedstock (instead of pure elements) is another avenue for cost reduction in these alloys compared to higher Ni alloys.**