Development of Cast, Higher Temperature Austenitic Alloys*

*Subtask 2B1 under the Powertrain Materials Core Program (PMCP)

Co-Lead PIs: Michael P. Brady, Yukinori (Yuki) Yamamoto

Contributors: Govindarajan Muralidharan, Sangkeun Lee, Jian Peng, Dongwon Shin, Michael Lance, Artem Trofimov, and Hsin Wang

Oak Ridge National Laboratory

June 3rd, 2020, Poster presentation, 2020 DOE Vehicle Technologies Office Annual Merit Review

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview: Subtask 2B1: Development of Cast, Higher Temperature Austenitic Alloys in PMCP

<table>
<thead>
<tr>
<th>Timeline</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Project Start: Oct. 2018</td>
</tr>
<tr>
<td>• Project End: Sept. 2021</td>
</tr>
<tr>
<td>• ~50% Complete</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Barriers and Technical Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Changing internal combustion engine regimes requiring higher-temperature capable materials</td>
</tr>
<tr>
<td>• Cost of high-performance materials</td>
</tr>
<tr>
<td>• Development time/cost of new materials</td>
</tr>
<tr>
<td>• Scaling new materials technologies to commercialization</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Budget</th>
</tr>
</thead>
<tbody>
<tr>
<td>• FY2019: $275k</td>
</tr>
<tr>
<td>• FY2020: $275k</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Partners</th>
</tr>
</thead>
<tbody>
<tr>
<td>• PNNL (advanced characterization under Thrust 4A): Bharat Gwalani, Libor Kovarik, and Arun Devaraj</td>
</tr>
<tr>
<td>• ORNL (advanced characterization under Thrust 4A)</td>
</tr>
<tr>
<td>• ORNL (data analytics under Thrust 4B)</td>
</tr>
<tr>
<td>• MetalTek International (materials supplier subcontractor)</td>
</tr>
</tbody>
</table>
Relevance: Increased Temperatures and Pressures to Enable Cleaner, More Efficient Engines

<table>
<thead>
<tr>
<th>Key Engine Metric</th>
<th>2013</th>
<th>2025</th>
<th>2050</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Cylinder Pressures</td>
<td>LD: ~ 50 bar</td>
<td>LD: &gt;103 bar</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HD: ~190 bar</td>
<td>HD: &gt;260 bar</td>
<td></td>
</tr>
<tr>
<td>Exhaust Temperatures</td>
<td>LD: 850°C</td>
<td>LD: 950°C</td>
<td>LD: 1000°C</td>
</tr>
<tr>
<td>(Exhaust Valve to Turbo Inlet)</td>
<td>HD: 700°C</td>
<td>HD: 800°C</td>
<td>HD: 900°C</td>
</tr>
</tbody>
</table>

(LD = light duty gasoline engine, HD = heavy duty diesel engine)

- Current exhaust component alloys*: lose oxidation resistance and strength ≥ ~800°C
- Ni-base alloys: meet these targets but are too costly (≥ 3 - 10x Fe-base)

Objective: Develop “Fe-base alloys” for “≥ 900-950°C”
- Improved oxidation resistance by utilizing protective Al₂O₃ scale formation (→ AFA alloy)
- Increased strength and creep resistance by nano-precipitation
- Low cost by use of Fe-base with Ni ≤ 25 wt.%

Benchmark exhaust component candidates*:
- Alloy 1.4826: 10Ni-22Cr base
- Alloy HK: 20Ni-25Cr base
- Alloy HP: 35Ni-25Cr base

Milestones listed in Technical Back Up section
**Approach: Cast AFA + ICME + Validation/Evaluation**

**Cast Alumina-Forming Austenitic Alloys (“AFA” alloy design for high-temperature)**
- Better protectiveness than chromia-scale
- Utilize empirical compositional guideline

**CALPHAD Databases**
(modification/optimization)
- Minimize the alloy selection iteration process

**Experimental Validation**
(lab-scale heats)
- ≤ 1 lb. arc-melt
- Drop cast → bar ingot
- Tensile, creep, oxidation, microstructure characterization

**Evaluation of Production Feasibility**
(trial industrial “scale-up” heats)
- > 50 lbs. induction melt
- Investment cast → bar ingots, keel blocks, and plates
- Tensile, creep, oxidation, microstructure characterization
**Technical Accomplishments: Proposed New Alloy Design to Maximize Strengthening Carbide ($M_{23}C_6$) Formation**

Ref.: Creep-ruptured cast AFA (Fe-25Ni-14Cr-4Al-Nb-C base, 750°C/100MPa/>10kh)

Design maximizes nanoprecipitates at service temperatures (Fe-25Ni-15Cr-4Al-Nb-C base, calculated by JMatPro v.9)

![Solidification and Equilibrium Diagram](image)

**Strategies of cast AFA alloy design:**

- Optimized Ni/Cr/Al/Nb contents for alumina-scale formation + stable austenite matrix
- Maximized the amount of $M_{23}C_6$ formation at 900°C

![TEM-BF Image](image)
Tech. Accom.: Excellent Oxidation Resistance in Simulated Exhaust Gas Environments through $\text{Al}_2\text{O}_3$ Scale Formation

Oxidation kinetics
(1-h Cycles at 950°C in Air + 10% $\text{H}_2\text{O}$)

- $\text{Al}_2\text{O}_3$ grows > 10x slower than currently used $\text{Cr}_2\text{O}_3$
- $\text{Al}_2\text{O}_3$ far more resistant in $\text{H}_2\text{O}$ exhaust than $\text{Cr}_2\text{O}_3$
  - resists rapid Fe-oxide formation and spallation

Cross-section confirms protective $\text{Al}_2\text{O}_3$
on AFA5 after 1000 h test

STEM-DF
- Al-rich Transient
- $\text{Al}_2\text{O}_3$
- Alloy
- 500 nm

$\text{Al}_2\text{O}_3$ grows > 10x slower than currently used $\text{Cr}_2\text{O}_3$
$\text{Al}_2\text{O}_3$ far more resistant in $\text{H}_2\text{O}$ exhaust than $\text{Cr}_2\text{O}_3$
  - resists rapid Fe-oxide formation and spallation
Tech. Accom.: Improved Creep Performance Exceeding Competitive Industrial Cast Austenitic Steels (Milestones Met Q1-3)

Creep-rupture lives

**900°C, 50MPa**

**Graph Data**
- **Cast AFA alloys (lab-scale heats)**
  - AFA2 (25Ni)
  - AFA2L (20Ni)
  - AFA5 (22Ni)
  - AFA5L (18Ni)
  - CN12 Plus
  - CF8C Plus
  - HK30Nb
  - EN1.4826
  - HP

**Reference alloys (chromia former)**

**Base alloy compositions, wt.%:**
- CN12+: Fe-13Ni-25Cr-1.8Nb-0.4C
- CF8C+: Fe-13Ni-19Cr-0.8Nb-0.1C-4Mn-0.25N
- **HK30Nb**: Fe-21Ni-25Cr-1.3Nb-0.3C
- EN1.4826: Fe-11Ni-22Cr-0.4C (GX40CrNiSi22-10)

- Superior creep and oxidation of **AFA5** at estimated raw material cost within 5% of **HK30Nb**
- Further studied Ni level variation in AFA 2 and AFA5 to establish specification range

→ Almost no changes in creep, but negative impact on oxidation at < 20Ni
Tech. Accom.: Trial Scale Industrial Heats of AFA 5 Under Evaluation

- Delivered total 80 lbs. of cast ingots
- Property screening (creep, oxidation) is currently in progress
- Tolerance of alloy to typical microstructure and chemistry variations in industrial casting processes will be key

*Industrial heats are provided from MetalTek International per purchase subcontract

Keel blocks / round bars

Weld plates

(Size: 0.5” x 4” x 11.5”)

1 inch
Collaboration and Coordination with Other Institutions

- **Pacific Northwest National Lab (PNNL)**
  - Microstructure characterization (SEM, TEM, APT) under PMCP Thrust 4A to aid alloy understanding and optimization during alloy design and scale up efforts

- **MetalTek International**
  - Materials supplier subcontractor for trial industrial heats

- **ORNL Computational Sciences Under PMCP Thrust 4**
  - Explore novel AFA alloy design with machine learning (see project mat194)
  - Data correlation/visualization to leverage prior developed AFA wrought family alloy datasets to current development efforts
Proposed Future Research

• Industrial casting feasibility evaluation:
  – Compositional sensitivities (tolerance to secure the target properties)
  – Castability (defect formation, fluidity, etc.)
  – Additional property screening (toughness, fatigue, torsion, corrosion, thermophysical, etc.) to develop an alloy datasheet for potential end users
  – Trial production of high-temperature components

• Understand and guide alloy scale up w/ support from PMCP Thrusts 4A and 4B for advanced characterization and computational models
  – Multi-scale characterization to understand microstructure-property relationships in lab scale and industrial scale castings
  – Alloy design optimization aided by machine learning and data analytics

Any proposed future work is subject to change based on funding levels.
Summary: Promising New Cast Al₂O₃-Forming Austenitic Alloy Developed for 900-1000°C Exhaust Components

• Cast AFA alloy design successfully balanced oxidation resistance, creep strength, and low materials cost in lab scale arc-castings:
  – Down-selected alloy AFA5 exhibited superior oxidation and creep resistance with estimated raw materials costs within 5% of commercial Cr₂O₃-forming alloy HK30Nb

• Project shifts to initial scale-up considerations and production feasibility evaluation of trial industrial castings:
  – Alloy tolerance for microstructure & chemistry variation in industrial production will be key
  – Property evaluation of trial AFA5 heats is currently in progress
  – Advanced characterization and data analytics will be used to guide alloy optimization
Technical Back-Up
Back-Up: Milestones

• Q1 VTO Milestone (Dec. 30, 2019):
  – Procure an industrial cast heat of down selected AFA5 suitable to provide samples for oxidation and creep testing. **Status: Completed** in Sept. 2019

• Q2 VTO Milestone (Mar 31., 2020):
  – Machine test samples and initiate 900°C/50MPa creep testing and 950°C/1 h cycle/air + 10% H₂O oxidation testing of the industrial AFA5 heat. **Status: Completed** in Feb. 2020

• Q3 VTO Milestone (June 30, 2020):
  – Complete at least 500, 1 h cycles at 950°C/1 h cycle/air + 10% H₂O oxidation testing of the industrial cast AFA5 heat. **Status: Completed** in Apr. 2020
  – Establish framework to Initiate Machine learning creep prediction and populate with 1 million hypothetical AFA alloys through Design of Experimental approach. **Status: Completed** in Apr. 2020

• Q4 VTO Milestone (Sep. 30, 2020):
  – Go/No go: Creep rupture life at 900°C, 50MPa of the down selected ORNL AFA alloy AFA5 trial industrial heat at least 50% greater than CF8Cplus, with protective alumina scale formation demonstrated by cross-section analysis after 900°C, 500, 1 h cycles, air + 10% H₂O. A Go decision finalizes the AFA5 composition for alloy property database development and initial scale up efforts. A No go decision results in further optimization of the base AFA5 composition to better tolerate industrial scale casting impurities and/or microstructures which may excessively degrade creep and oxidation behavior compared to high-purity, lab arc-cast material. **Status: Possible minor (< 1 quarter) delay due to slowed experimental work during pandemic. Preliminary testing suggests creep and oxidation targets will be met, but that the trial AFA5 heat may have degraded tensile elongation (investigation in progress)**
Back-Up: Five 2nd Generation Cast AFA Alloys Designed and Manufactured as Lab Scale Arc-Castings (FY19)

<table>
<thead>
<tr>
<th>Heat</th>
<th>Alloy composition wt.%</th>
<th>*$/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Ni</td>
</tr>
<tr>
<td>AFA1</td>
<td>50.69</td>
<td>25</td>
</tr>
<tr>
<td>AFA2</td>
<td>47.69</td>
<td>25</td>
</tr>
<tr>
<td>AFA3</td>
<td>49.19</td>
<td>25</td>
</tr>
<tr>
<td>AFA4</td>
<td>40.84</td>
<td>22</td>
</tr>
<tr>
<td>AFA5</td>
<td>51.69</td>
<td>22</td>
</tr>
<tr>
<td>HK30Nb</td>
<td>50.5</td>
<td>20.5</td>
</tr>
<tr>
<td>1.4826</td>
<td>64.52</td>
<td>11</td>
</tr>
</tbody>
</table>

*estimated raw material cost

- Computational thermodynamic alloy design
  - Optimize carbide formation, leverage past AFA related efforts (1st Gen. AFA, Propulsion Materials Program)
- Assess cyclic oxidation, tensile, and creep behaviors
- Promising early results, down selected AFA2 and AFA5 for trial industrial heats
**Back-Up: 22-25 Ni Gen. 2 Lab Cast AFA Stronger than 11Ni 1.4826 above 700°C**

Lab Cast Tensile Properties at RT, 700, and 900°C

- Lab cast AFA elongation at room-temperature lower than lab cast 1.4826 (still acceptable)
- Best balance, oxidation, tensile strength, and raw materials cost by 25Ni AFA2 (base + Mo, W) and 22Ni AFA5 (M$_{23}$C$_6$ optimized)
Back-Up: Promising Oxidation Resistance / Degraded Creep Resistance Due to High Cr in 1\textsuperscript{st} Comm. AFA5

- 1\textsuperscript{st} industrial AFA5 heat still exhibited acceptable creep resistance
  - 2\textsuperscript{nd} industrial heat procured with better Cr level control (high Cr impacts carbides)
- Also establishing Ni specification range with lower Ni AFA5 and AFA2 variations
• **Cr₂O₃**: most commercial heat-resistant alloys, volatilize in H₂O exhaust environments
• **SiO₂**: slower growth late, low CTE can cause oxide spallation, usually Cr + small Si
• **Al₂O₃**: > 10x slower growth, more stable than Cr₂O₃ in many environments (including H₂O)
  - Al weakens Fe, stabilizes BCC, interacts with N strengthening
  - strengthen with carbides (computational thermodynamic design)