NETL Research & Innovation Center’s Advanced Alloy Development Research

Jeffrey Hawk, Edward Argetsinger, Tianle Cheng, Casey Carney, Corinne Charlton, Christa Court, Martin Detrois, Omer Dogan, Michael Gao, Volker Heydemann, Gordon Holcomb*, Paul Jablonski, Tau Liu, Joseph Mendenhall, Paul Myles, Richard Oleksak, Christopher Powell, Kyle Rozman, Erik Shuster, Irene Spitsberg, Joseph Tylczak, Youhai Wen, Margaret Ziomek-Moroz, Marisa Arnold-Stuart, Travis Shultz, and David Alman

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*retired
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Advanced Energy Systems: Materials at Extremes

Structural Materials Development

**Materials Challenges:**

- Higher Temperatures, Higher Pressures, Corrosion & Oxidation → Extreme Environments
- Large Components → Manufacturability
- Long Service Life Span >100,000 hrs → Durability
- Penetration of Renewable → Cycling Operational Conditions

**Technology Enabler:** Affordable, Durable and Qualified Structural Materials for Harsh Service Life.
The Advanced Alloy Development (AAD) Field Work Proposal (FWP) supports the mission, goals, and objectives of the DOE-FE/NETL High Performance Materials Program by developing affordable, durable, cost-effective, heat-resistant alloys and tools necessary for improving the existing fleet of Fossil Energy (FE) power plants, and enabling advanced FE systems, such as advanced ultra-supercritical (A-USC) and supercritical carbon dioxide (sCO₂) power cycles.

**Scope**

Mission DOE-FE/NETL High Performance Materials Program: Characterize, produce, certify cost-effective alloys and high-performance materials suitable for extreme environments found in coal power generation to support existing and new plants.

**AAD-FWP Research**

- Identify supply chain issues and performance/cost benefits
- Develop alternative cast and wrought alloys for A-USC and sCO₂ application
- Increase temperature capabilities of steels, Ni alloys
- Improve melt processing of advanced alloys
- Assess, predict, and improve alloy cyclic & environmental performance
- Materials Performance under direct sCO₂ power cycles
- Enable manufacture of compact heat-exchangers for sCO₂ power cycles.
Techno-Economic & Market Assessments

Research Guidance and Direction (Systems Engineering & Analysis)

• High Performance Alloy Applications In Adjacent Markets
• Understanding the Supply Chain of Advanced Alloys
• Benefits of Advanced Materials for Boiler Tubes
• Export Potential for High-Performance Materials Study
• GADS Failures subsets analysis for boiler tubes, turbine, and BOP
Fe-9Cr Alloy Development

NETL CPJ-7 and NETL JMP Steels

**OPTIMIZE COMPOSITION**

- **Z-phase (CrNb)**
- **C$_2$Cr$_{23}$ Carbide**

DFT and CALPHAD used to optimize alloy composition. Simulations used to determine the effect of alloying elements on the formation and stability of unwanted (Z-phase) and desired strengthening phases (Carbides).

**OPTIMIZE PROCESSING**

NETL's R&D 100 award winning computational tool used to design heat-treating cycles to optimize the alloy’s microstructure and properties.

- **Creep Rupture: 648C**
- **COST-E vs. NETL-CPJ7**

- **Stress (ksi)**
- **Time to Failure (h)**

**Outcome:** New Fe-9Cr Alloy with an Increase Temperature Capability of ~50$^\circ$ F for this important class of power plant steel.

- **Cast and wrought forms**
- **70 kg (150 lb) ingots produced (VIM, ESR)**
  - Formulated ESR slag chemistry
- **Welding trials/studies**
  - Conventional NETL
  - Friction Stir Welding PNNL
- **Material available for evaluation**
  - EPRI (John Siefert, cast alloys, remnants of tested creep samples)

**Cast Version of Alloy 740H**

Alloy (and supply chain) options for thick wall castings

- **Conventional casting**
- **Non-Uniform Microstructure**

**Conventional castings (open circles) showed poor and inconsistent creep lives.**

**The NETL-process (FGH) to produce fine-grain casting o obtain a cast product matching the wrought alloy on the LMP plot.**

**Outcome:** Creep resistant cast version of Alloy 740H.

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Superalloy Development

Increase temperature capability and strength of superalloys.

Enable increased operational temperature (efficiency) and/or reduce amount of alloy needed for manufacturing component (reduce cost).
✓ Increasing γ' fraction/solvus in commercial Ni-based superalloys
✓ Grain boundary re-design for Ni-based superalloys (Alloy 725)
✓ High entropy matrix Ni-based superalloy

Re-design gamma matrix

High entropy matrix Ni-based superalloys

Outcome: More stable gamma matrix Increased strength compared to commercial superalloys.

Alloy 282: Increase the gamma prime fraction/solvus to enhance >800°C mechanical properties. Obtain a gamma prime fraction/solvus at 900°C equal to that of the commercial alloy at 800°C. Also looking at Alloy 263 and Nimonic 105.

Outcome: Higher strength version of H282 with ductility.


Superalloy Development

Grain boundary re-design of commercial alloys

**Alloy 725:**
The alloy is subjected to (1) **NETL computationally optimized homogenization cycle** and (2) **high temperature (HT) post-TMP aging heat treatment** combined with **targeted elemental additions** that enables the intentional precipitation of secondary phases (i.e., δ and/or η) at the grain boundaries to increase their resistance to deformation and damage and γ’ and/or γ'' precipitates in the grain interior to facilitate high room and high temperature yield stress and tensile strength.

<table>
<thead>
<tr>
<th>Standard alloy</th>
<th>E HT</th>
<th>F HT</th>
</tr>
</thead>
<tbody>
<tr>
<td>E 100h 800C</td>
<td>E1 100h 800C</td>
<td>F2 100h 800C</td>
</tr>
</tbody>
</table>

**Outcome:** Improvement in creep life of >256% with similar ductility from the standard alloy.
High Entropy Alloy (HEA) Development

Design of Co-Cr-Fe-Ni-Mo HEAs

Properties of NETL HEAs

Corrosion of Co-Cr-Fe-Ni-Mo (A36) HEA compared to Hastelloy C276 and Multimet

Oxidation at 850C of NETL HEAs compared to Alloy 2828. Similar behavior observed at 750C


Materials Issues for Supercritical CO₂ Power Cycles

HIGH-TEMPERATURE OXIDATION OF STEELS AND SUPERALLOYS

Effects of impurities and pressure

- No SO₂
- 0.1% SO₂

LOW-TEMPERATURE CORROSION

Identifying low-cost steels resistant to acidic condensates

OXIDATION AND PERFORMANCE OF JOINED STRUCTURES AND MANUFACTURE OF COMPACT HEAT-EXCHANGERS

SELECT RECENT PUBLICATIONS

Oxidation of Steels: Direct-Fired sCO₂ Environments

CO₂+4%H₂O+1%O₂+SO₂ Time: 2500 hrs
CO₂+4%H₂O+1%O₂ suggested by NETPower

Determining critical Cr content required for protective scale formation

Effect of SO₂ impurities (347H)

The role of surface finish (347H)

Pure CO₂ – repeating experiment under direct cycle environments
Oxidation of Ni Alloys: Direct-Fired sCO₂ Environments

The role of minor alloying elements in chromia-forming alloys

[Graphs showing mass change vs. content for various elements (Cr, Mn, Si, Al, Ti) under different conditions (no SO₂, 0.1% SO₂, fits omitting alloy 263).]

Effect of pressure

CO₂+4%H₂O+1%O₂+SO₂
750°C-2500 hrs (2500 hrs in progress)

Effect of SO₂ impurities

[Graphs showing mass change at different temperatures (600°C, 650°C, 700°C, 750°C, 800°C) with and without SO₂.]

CO₂+4%H₂O+1%O₂ suggested by NETPower
Impact of sCO\textsubscript{2} on Dissimilar Metal Welds

**Dissimilar Welds**
- P22-P91
- P91-347H
- P22-Alloy 263
- Alloy 625-Alloy 263
- 347H-Alloy 263

At Edison Welding Institute (EWI)
By Gas Tungsten Arc Welding (GTAW).
With Post Weld Heat Treatment.

**Oxidation and Deformation Behavior of Dissimilar Metal Welds in Direct sCO\textsubscript{2} (CO\textsubscript{2}+4\%H\textsubscript{2}O+1\%O\textsubscript{2})**

P91-347H weld exposed to sCO\textsubscript{2}: 550 °C and 200 bar for 1000 h.

(a) P91 / HAZ Interface
(b) HAZ / Fusion Zone Interface
(c) P91
(d) HAZ
(e) Fusion Zone

Exposure to CO\textsubscript{2}+4\%H\textsubscript{2}O+1\%O\textsubscript{2} (DF4) for 1000h
Compact Heat-Exchangers for sCO$_2$ Power Cycles

Micro-channel HX Via Diffusion Bonding Ni-Superalloy Sheets

Transient-liquid-phase (TLP) bonding using Ni-P interlayers developed for Alloy 230.

Strength of the bonded stacks was greater than 85% of base alloy 230 yield stress. Bonded stacks possessed acceptable low-cycle fatigue and creep properties. However, plastic strain localization in the bond region caused low tensile and creep elongation.

Oxidation in sCO$_2$


**NETL Materials Performance Simulations**

**Gamma Prime Coarsening in H282**

**Oxide Scale Spallation**

Spallation due to:
- Temperature (Different thermal expansion)
- Oxide growth strain with geometric constraint
- Different creep rate between oxide and metal

**Creep modeling of polycrystalline with/without GBS**

**LCF modeling**

3. Fei Xue et al., “Stress analysis of the steam-side oxide of boiler tubes: contributions from thermal strain, interface roughness, creep, and oxide growth,” *Oxidation of Metals*, accepted for publication, 2020

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**Alloy**

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
<th>Ti/Al</th>
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<tbody>
<tr>
<td>Nominal</td>
<td>18.5-20.5</td>
<td>9.11</td>
<td>8.9</td>
<td>1.9-2.3</td>
<td>1.38-1.65</td>
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<tr>
<td>H282-B</td>
<td>19.22</td>
<td>9.86</td>
<td>8.49</td>
<td>2.22</td>
<td>1.27</td>
<td>1.75</td>
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<tr>
<td>H282-C</td>
<td>19.19</td>
<td>9.85</td>
<td>8.50</td>
<td>1.94</td>
<td>1.54</td>
<td>1.26</td>
<td></td>
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**After 5 years of operation**

- $\varepsilon_{\theta}$
- $\varepsilon_{z}$
- $\varepsilon_{r}$

**Evolution of stresses**

- $\sigma_{ox}$ (MPa)

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**U.S. DEPARTMENT OF ENERGY**
Alloy Fabrication Capabilities
For Mission Critical Applications. Scales Translate to Industrial Practice.

Melt Processing Capabilities
• Air Induction Melting: up to 300 lbs
• VIM: 10, 50 and 500 lbs
• Vacuum Arc Remelt/Electro-Slag Remelt
  VAR/ESR: 3 to 8 inch diameter crucibles

Thermo-Mechanical Processing Capabilities
• Heat-treatment furnaces: 1650°C, inert atmospheres and controlled cooling.
• Press Forge: 500 Ton
• Roll mills: 2 and 4 high configurations.
Materials Performance in Extreme Environments

**SECERF**
Severe Environment Corrosion/Erosion Research Facility

- **Corrosion & Oxidation Laboratories**
  - Ultra-super-critical (USC) Steam Autoclave: Dual rated: 310 bar at 760C and 345 bar at 746C. System to control steam chemistry (dissolved oxygen). Computer controlled for 24/7 unattended operations.
  - Supercritical CO₂ Autoclave: rated at 800C and 275bar
  - Autoclaves (5000psi-250°C), Flow Through Autoclaves (5000psi-500°C), Rocking Autoclave (7250psi-400°C). CO₂, O₂, SO₂, H₂S. Autoclave for performing electrochemical experiments under pressure and temperature.
  - Potentiostats, Galvanostats, Electrochemical Impedance Spectroscopy.
  - Static and cyclical oxidation furnaces for 24/7 exposures to O₂, H₂O vapor, CO₂
  - Rotary kiln furnace for evaluating refractory materials performance in flowing slag environments under thermal gradients in combustion atmospheres

- **Fracture Mechanics and Creep Laboratories**
  - Screw driven & servo-hydraulic frames for strength and fatigue (max. load 1000 kn, 1600C, air). Constant stress & strain load frames for creep testing (1000C, air, CO₂)

• Safety Integrated System to allow for safe 24/7 unattended operations.
• Gas environment tailored by mixing with programmable mass flow controllers.
• Available gases: CO, CO₂, CH₄, H₂, H₂S, SO₂, HCl, O₂, N₂, He, air, H₂O vapor.
• Gas flow rates: 5-1600 ml/min (depending on gas).
• Maximum temperature: furnaces: 1600C; erosion rig: 750C
**Center for Computational Science and Engineering**

**JOULE 2.0**

- At **3.6 petaflops** JOULE is the **10th fastest** supercomputer within DOE National Laboratories.
- This provides NETL and partners with high-performance computational power to solve challenges in energy.

**Center for Artificial Intelligence and Machine Learning**

**WATT**

- Links **104 GPUs** with **16 petabytes** of storage to provide unparalleled opportunities for the use of AI/ML to enable scientific discovery and R&D acceleration.
Computational Materials Capabilities

Multiscale Modelling

- Gaussian, Molpro, Turbomole, Q-Chem, Dmol
- VASP, Wien03, Dmol3, Siesta, PWSCF, CP2K
- NAMD, GULP, LAMMPS, Compass, ReaxFF, MD/MC

- Microkinetics, Phase-Field, Micress, COMSOL, CALPHAD, ThermoCalc, CompuTherm, JMatPro, FactSage, DICTRA, FactSage, Ansys

Data Visualization, Analysis & Processing

- DFT Calculations for Systems with 1D/2D/3D PBC
- Classical MD & Equilibrium and Kinetic Monte Carlo Simulations in Various Statistical Ensembles

Data Archiving and Security

- Quantum Mechanics Based Simulation Capability
- Classical Mechanics Based Simulation Capability
- Meso-Scale Based Simulation Capability
- Ab Initio Molecular Orbital Calculations
- Management
**NETL’s Computational Tool to Specify Alloy Homogenization**


Specified heat-treatments:
- **Special Metals:** ESR/VAR 10,000 lb superalloy ingot.
- **GE:** ½ actual size cast valve body for an A-USC turbine 18,500 lb superalloy casting.

**NETL Developed Refractory Brick**

- Licensed to Harbison-Walker
- Commercially produced as Aurex 95P.
- Used in nearly every slagging gasifier world-wide.
- NETL technology doubled refractory service life.

**Materials Recovery & Recycling**

- **Carbothermal Reduction of Gasification Slags to Recover Nickel and Vanadium,** US Patent: 10,323,298 B2

**Advanced Membrane-Based Electrochemical Sensors**

- Increase in pipeline efficiency & safety.
- Real time simultaneous monitoring of natural gas environment and pipeline corrosion.

**Materials Performance Assessment for Reliability**

- Off-Shore
QUESTIONS?

CONTACTS

Jeffrey Hawk
Technical Portfolio Lead - Advanced Alloy Development FWP
Structural Materials Team
Office: (541) 918-4404
Email: Jeffrey.Hawk@netl.doe.gov

Marisa Arnold-Stuart
Supervisor
Structural Materials Team
Office: (541) 967-5809
Mobile: (541) 979-1421
Email: Marisa.Arnold@netl.doe.gov

Travis Shultz
Supervisor
Energy Process Analysis Team
Office: (304) 285-1370
Mobile: (412) 302-5874
Email: Travis.Shultz@netl.doe.gov

David Alman
Associate Director,
Materials Engineering & Manufacturing
Office: (541) 967-5885
Mobile: (541) 979-7007
Email: David.Alman@netl.doe.gov