Development of Corrosion- and Erosion-Resistant Coatings for Advanced Ultra-Supercritical Materials

Ying Zhang
Center for Manufacturing Research
Department of Mechanical Engineering
Tennessee Technological University

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Materials Issues for Advanced Ultra-Supercritical (A-USC) Steam Turbine Blades

- Under A-USC conditions, γ'-strengthened Ni-base alloys (e.g., Haynes 282) are being considered for various power plant components.
  - Internal oxides along alloy grain boundaries (due to Al & Ti additions)
  - Solid particle erosion (SPE) of high-pressure (HP) blades: impact of exfoliated solid particles from boiler tubes

- Of the four SPE-resistant coatings, only Tribaloy T-400C showed acceptable erosion rates at 760°C.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Nominal composition (wt.%)</th>
<th>Process</th>
<th>Substrate</th>
<th>Steam (1000h, 760°C)</th>
<th>Erosion (760°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stellite 6B</td>
<td>Co-30Cr-4.5W-2Si-1.5Mo-1.1C</td>
<td>Wrought form</td>
<td>N/A</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Tribaloy T-400C</td>
<td>Co-14Cr-27Mo-2.6Si</td>
<td>Alloy fusion</td>
<td>304 SS</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Metco 45</td>
<td>Co-10.5Ni-25.5Cr-7.5W-0.5C</td>
<td>HVOF</td>
<td>Hastelloy X</td>
<td>Fair</td>
<td>Poor</td>
</tr>
<tr>
<td>NiCr-Cr₃C₂</td>
<td>(Ni-20Cr)-75%Cr₃C₂ composite</td>
<td>HVOF</td>
<td>Hastelloy X</td>
<td>Fair</td>
<td>Poor</td>
</tr>
</tbody>
</table>


Project Objectives and Proposed Tasks

- Develop and evaluate the corrosion- and erosion-resistant coatings for A-USC HP blade materials using a cost-effective electrolytic codeposition process
- Enhance and balance the corrosion and erosion resistance without compromising mechanical integrity of coated alloys
- Based on the study by A-USC Materials Consortium, a composition similar to Tribaloy T400-C was selected as the baseline coating composition.

Task 1.0 Project Management, Planning, and Reporting (TTU)

Task 2.0 Material Selection and Procurement (TTU, Purdue, & Siemens)

Task 3.0 Electro-codeposition of Corrosion- and Erosion-Resistant Coatings
3.1. Computational guidance for coating composition selection (ORNL & TTU)
3.2. Optimization of electro-codeposition coating process and post-plating heat treatment (TTU & ORNL)
3.3. Coating development on AM Ni-base alloys (TTU & Purdue)

Task 4.0 Coating Property and Performance Evaluation
4.1. Coating characterization (TTU & Purdue)
4.2. Oxidation testing of coated alloys in steam at 760°C (ORNL)
4.3. High-temperature erosion testing (at High Temperature Gas Turbine Erosion Lab, University of Cincinnati)
4.4. Long-term coating stability evaluation (TTU)

Task 5.0 Evaluation of Technology Transfer
5.1. Scale-up demonstration (Eastern Plating & Siemens)
5.2. Techno-economic assessment (Eastern Plating, Siemens, & TTU)
Tribaloy-Based Alloys and Coatings

- Tribaloy alloys were originally developed for applications of extreme wear in combination with high temperatures and corrosive media.
- Tribaloy alloys can be Ni-based (e.g., Ni-32.2Mo-13.9Cr-2.5Si), Co-based (e.g., T-400C: Co-27Mo-14Cr-2.6Si), or Co/Ni-based (e.g., T-900: Co-16Ni-23Mo-18Cr-2.7Si).
- T-400C consists of a large volume of hard intermetallic Laves phases (1000-1200 HV) dispersed in a relatively soft solid solution matrix.
- Current Tribaloy coating processes such as high-velocity oxy fuel (HVOF) spray are line-of-sight and not ideal for coating complex-shaped HP steam turbine blades.
- Compositional optimization and new coating process development are needed.

Why Electrolytic Codeposition?

- **Electrolytic codeposition ("composite electroplating"):** Fine particles dispersed in an electroplating solution are codeposited with the metal onto the cathode (substrate) to form a multiphase coating.
  - Non-line-of-sight
  - Low cost (capital investment, energy consumption, powder waste)
  - Dense and homogeneous composite coatings
  - A unique multi-phase coating achievable upon diffusion treatment

 NiCoCrAlY coating made via electro-codeposition

### Project Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Planned Completion Date</th>
<th>Actual Completion Date</th>
<th>Verification Method</th>
<th>Status/Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Submission of revised PMP</td>
<td>11/30/2019</td>
<td>8/29/2019</td>
<td>PMP file</td>
<td>Completed</td>
</tr>
<tr>
<td>2. Kickoff meeting</td>
<td>12/31/2019</td>
<td>12/20/2019</td>
<td>Presentation file</td>
<td>Completed</td>
</tr>
<tr>
<td>3. Material selection and procurement</td>
<td>01/31/2020</td>
<td>01/27/2020</td>
<td>All supplies &amp; materials for alloying, plating and AM experiments are acquired.</td>
<td>Completed</td>
</tr>
<tr>
<td>4. Optimization of electro-codeposited coatings</td>
<td>8/25/2020</td>
<td>08/20/2020</td>
<td>γ+Laves phase based coatings with the desired microstructures are synthesized.</td>
<td>Completed</td>
</tr>
<tr>
<td>5. Completion of 760 °C steam oxidation testing on coated samples</td>
<td>10/30/2020</td>
<td>12/8/2020</td>
<td>Mass change data for the coated samples are obtained for ≥ 1,000 h exposure in steam.</td>
<td>Completed</td>
</tr>
<tr>
<td>6. Completion of solid particle erosion testing for the coated samples</td>
<td>1/30/2021</td>
<td>5/3/2021</td>
<td>Erosion rate data for coated samples are obtained under a simulated turbine operating condition at 760°C.</td>
<td>Completed</td>
</tr>
<tr>
<td>7. Techno-economic analysis</td>
<td>3/31/2021</td>
<td>3/30/2021</td>
<td>Scale-up design and cost analysis of the coating process are completed.</td>
<td>Completed</td>
</tr>
</tbody>
</table>

- All seven milestones have been completed.
Task 3.0 – Electro-codeposition of Corrosion- and Erosion-Resistant Coatings

Subtask 3.1 Computational guidance for coating composition selection (ORNL & TTU)

- Dr. Pillai (ORNL) used Thermo-Calc to explore the $\gamma + \text{Laves}$ space.
- The two-phase region of Co (FCC) + C14 Laves phase lied within a large composition range.
- Increases in Cr and Mo contents could stabilize Laves phase.
- For 20% Cr, increasing Mo from 10 to 30% would not change the phase constitution, i.e., $\gamma$ (Co) + C14 Lave phase.
### Selected Model Alloys & Electrodeposited Coatings

<table>
<thead>
<tr>
<th>ID</th>
<th>Composition (wt.%)</th>
<th>Notes/Justification</th>
<th>Oxidation</th>
<th>Erosion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Air, 800°C</td>
<td>Steam, 760°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>200h</td>
<td>500h</td>
</tr>
<tr>
<td>H282</td>
<td>Ni-10Co-20Cr-8.5Mo-2.1Ti-1.5Al</td>
<td>Commercial Ni-base alloy</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>T-400C</td>
<td>Co-14Cr-27Mo-2.6Si</td>
<td>T-400C composition</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>T-900</td>
<td>Co-16Ni-18Cr-23Mo-2.7Si</td>
<td>T-900 composition</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#1</td>
<td>Co-20Cr-12.5Mo-2.6Si</td>
<td>Baseline low Mo</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#2</td>
<td>Co-20Cr-18Mo-2.6Si</td>
<td>Increased Mo to 18% in #1</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#3</td>
<td>Co-20Cr-22.5Mo-2.6Si</td>
<td>Increased Mo to 22.5% in #1</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#4</td>
<td>Co-20Cr-18Mo-2.6Si-0.4Y</td>
<td>Similar to #2, added 0.4Y</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#5</td>
<td>Co-20Cr-18Mo-2.6Si-0.7Y</td>
<td>Similar to #2, added 0.7Y</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#6</td>
<td>Ni-20Cr-18Mo-2.6Si-0.4Y</td>
<td>Similar to #4, replaced Co with Ni</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#7</td>
<td>Ni-41.3Co-20Cr-18Mo-2.6Si-0.4Y</td>
<td>Similar to #4, Ni/Co = 0.4</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#8</td>
<td>Ni-18Co-20Cr-18Mo-2.6Si-0.4Y</td>
<td>Similar to #4, Ni/Co = 2.3</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#9</td>
<td>Ni-16.5Co-20Cr-18Mo-2.6Si-0.6Y</td>
<td>Similar to #8, with 0.6 Y</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>#10</td>
<td>Ni-16.5Co-20Cr-14Mo-4X-2.6Si-0.6Y</td>
<td>Similar to #9, replaced some of Mo with X</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

### Gen-1 Coating
- Mo similar to and Cr slightly higher than that in T-400C/T-800
- Close to traditional Tribaloy alloy compositions

### Gen-2 Coating
- Higher Cr and lower Mo over Gen-1
- Higher Cr for improved oxidation resistance

### Gen-3-1
- Lower Mo over Gen-1, but with 0.4Y
- Y addition for improved oxidation resistance

### Gen-3-2
- Lower Mo over Gen-1, but with 0.7Y
- Higher Y addition for better oxidation resistance

### Gen-3-3
- Similar Mo & Cr to Gen-2, but with 0.7Y
- Y addition for improved oxidation resistance

**Note:** 35 alloy compositions and 3 generations of coatings were evaluated.
Tribaloy-based Model Alloys: Co-20Cr-xMo-2.6Si

- As the Mo content was increased, Laves volume fraction and alloy hardness increased almost linearly.

- Mo < 20%: adherent oxide scales
- Mo ≥ 20%: spallation, mainly at the $\text{Cr}_2\text{O}_3/\text{SiO}_2$ interface
Effect of Reactive Element Additions and Ni/Co Ratio on Oxidation Resistance of Tribaloy-based Alloys

- The optimal Y content in Co-based alloys was 0.6-0.7%.
- Coating costs could be reduced by reducing the Co content in the coating, which also lowered the mass gain after oxidation.
- With 0.7% Y, good oxidation resistance was obtained for alloys with a Ni/Co ratio of 2.6.
Subtask 3.2 Optimization of Electro-codeposition Coating Process and Post-plating Heat Treatment (TTU & ORNL)

- Electro-codeposition parameters were varied to optimize coating microstructure.
- Uniform and adherent coatings without blisters/cracks or other defects were achieved on the entire specimen.

- Type of electrolyte
- pH
- Current density
- Temperature
- Particle loading
- Particle composition/geometry/size
- Cathode position (configuration)
- Post heat treatment

Haynes 282 Substrate
Effect of Post-Deposition Heat Treatment

- Post-deposition heat treatment facilitates interdiffusion between CrMoSi particles and the (Co,Ni) matrix to form phases of $\gamma$, Laves, etc.

- Ideally, to combine the coating & substrate heat treatment H282: solution treatment (1121-1149°C) + two-step aging treatment (1010°C/2h/air cool + 788°C/8h/air cool)

<table>
<thead>
<tr>
<th>Element</th>
<th>$\gamma$-phase matrix (wt.%)</th>
<th>Laves phase (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>25.3</td>
<td>10.8</td>
</tr>
<tr>
<td>Mo</td>
<td>7.3</td>
<td>43.4</td>
</tr>
<tr>
<td>Si</td>
<td>0.9</td>
<td>5.3</td>
</tr>
<tr>
<td>Co</td>
<td>19.3</td>
<td>13.9</td>
</tr>
<tr>
<td>Ni</td>
<td>47.2</td>
<td>26.6</td>
</tr>
</tbody>
</table>

- Both 1080°C x 6h and 1149°C x 6h treatments resulted in the desired coating microstructure.
Subtask 3.3 Coating Development on AM Ni-Base alloys (TTU & Purdue)

• To demonstrate that electro-codeposition is a viable coating process for AM alloys

H282 deposited using Purdue’s powder bed fusion (PBF) system

AM H282
Coated AM H282

As-deposited side

As-ground side

Coated AM H282
(6h at 1080°C)
Task 4.0 – Coating Performance and Property Evaluation

• Subtask 4.1 Coating characterization (TTU & Purdue)
• Subtask 4.2 Oxidation testing in steam at 760°C (ORNL)

- Gen-1: high Mo (close to T-400C & T-800)
- Gen-2: lower Mo, higher Cr (close to T-900)
- Gen-3: 0.7% Y (to increase erosion resistance while maintaining good oxidation resistance)
Steam Oxidation Performance of Coated and Uncoated H282

After Oxidation in Steam at 760°C

Gen-1 Coating
500h

Gen-2 Coating
1000h

Bare H282
500h

Bare H282
1000h

Gen-2 coating after 1000h

Bare H282 after 500h
Comparison of New Tribaloy Coatings and Coatings Previously Evaluated by the A-USC Consortium

- Electro-codeposited Tribaloy coating (Gen-2)
  - Remained intact
  - Free of internal cracks

- Tribaloy coating previously evaluated by the A-USC Consortium

- After 1000h in Steam at 760°C
**Subtask 4.3 High-Temperature Erosion Testing**

- Factors affecting the SPE rate: temperature, environment, erodent, velocity, impact angle, etc.

<table>
<thead>
<tr>
<th>Test Facility</th>
<th>Erodent</th>
<th>Velocity (m/s)</th>
<th>Angle (°)</th>
<th>Erosion rate (mg/g)</th>
<th>Erosion rate ratio (Coating vs. H282)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H282</td>
<td>Univ. of Cincinnati (Viswanathan et al.)</td>
<td>Silica (149-850 µm)</td>
<td>274</td>
<td>2.42</td>
<td>7.94/3.3</td>
</tr>
<tr>
<td>T-400C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H282</td>
<td>DUCOM</td>
<td>Alumina (50 µm)</td>
<td>150</td>
<td>0.49</td>
<td>1.68/3.4</td>
</tr>
<tr>
<td>Coating-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coating-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coating-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H282</td>
<td>DUCOM</td>
<td>Magnetite (&lt;88 µm)</td>
<td>150</td>
<td>-0.008 (Net deposit)</td>
<td>-0.078 (Net deposit)</td>
</tr>
<tr>
<td>Coating-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coating-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coating-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- The erosion resistance of a coating is affected by **microstructure, hardness, and toughness**.
- Synergistic interactions between erosion and oxidation at high temperature
Task 5.0 – Evaluation of Technology Transfer

• Subtask 5.1 Scale-up demonstration (TTU, Eastern Plating & Siemens)
  – Design and construction of larger rotating barrels
  – HP steam turbine blades: 70-350 mm

<table>
<thead>
<tr>
<th>Element (wt.%)</th>
<th>Near Root</th>
<th>Mid-span</th>
<th>Near tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>3.4</td>
<td>4.3</td>
<td>3.9</td>
</tr>
<tr>
<td>Mo</td>
<td>24.1</td>
<td>32.0</td>
<td>28.3</td>
</tr>
<tr>
<td>Cr</td>
<td>21.9</td>
<td>30.2</td>
<td>25.8</td>
</tr>
<tr>
<td>Co</td>
<td>7.4</td>
<td>5.1</td>
<td>5.8</td>
</tr>
<tr>
<td>Ni</td>
<td>43.3</td>
<td>28.4</td>
<td>36.1</td>
</tr>
</tbody>
</table>
Subtask 5.2 Techno-Economic Assessment (TTU, Eastern Plating, & Siemens)

Electro-codeposition:
- Low capital investment
- Minimal powder waste (no overspray) and low energy consumption

- ~30% cost reduction could be achieved with the electro-codeposition coating process over the state-of-the-art HVOF spray.
Concluding Remarks

- It is feasible to develop Tribaloy-based coatings with enhanced corrosion and erosion resistance to protect Ni-base superalloy A-USC components (e.g., HP blades and valves).
  - The new electro-codeposited Tribaloy coatings showed excellent steam oxidation performance at 760°C.
  - Initial erosion testing indicates good erosion resistance at 760°C.
  - The electro-codeposition coating process could lead to ~30% cost reduction over the state-of-the-art HVOF spray.
  - Compared to other coating technologies, non-line-of-sight electro-codeposition is more advantageous, particularly for complex-shaped components

- New materials/coatings & manufacturing are the enabling technology for multiple advanced power generation technologies.
  - Transformational sCO₂ power cycles
  - Molten salt heat-transfer and thermal energy storage
  - Centrifugal particle receiver in concentrated solar power plants
Acknowledgments

• Brian Bates, Giovanni Mainardi, David Chesson, and Will Buida, TTU

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• Program Manager: Maria Reidpath, NETL

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