High Temperature Corrosion Behavior of HVOF, Fe₃Al Coatings and Alloy 22 Weld Overlays

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Fireside Corrosion Mitigation in the A-USC Power Plant

Alloy Approach – Rely on corrosion resistance of structural alloy

- Alloys with the necessary high temperature mechanical properties usually do not possess the required corrosion resistance
    - Best mechanical properties for super heater applications are nickel-based alloys (Inconel 740, Inconel 617, Hastelloy 230, etc.)
    - Best fireside corrosion resistance exhibited by Fe-based or Ni-Fe-based alloys
  - Improved corrosion resistance obtained with increasing chromium levels

Coatings Approach – Rely on corrosion behavior of coating only

- Chromia-formers - high-Cr weld overlays and laser cladding can provide corrosion resistance
- Silica-formers – (high silicon alloys, silicides)
- Alumina-formers – aluminides (iron or nickel)
Aluminide Coatings

- High aluminum content (25-50 atomic % aluminum)
- Alumina corrosion product has better thermal stability than chromia at high temperatures
- Relatively inexpensive constituents
- Demonstrated applications methods:
  - Weld overlays
  - Thermal Spray (High Velocity Oxy-Fuel)
    - High deposition rates
    - Control residual stress state in the coating
Past Results

- Thermal spray parameters can be used to generate highly dense coating with varying levels of residual stress
- Residual stresses in coating arise from three sources - difference in CTE, solidification and peening
- Substrate surface preparation is critical in coating adherence
- Higher HVOF combustion chamber pressures result in higher coating density and better resistance to thermal cycling

[Diagram of High-Velocity Oxy-Fuel (HVOF) thermal spray]

- Equivalence ratio (phi): \[ \Phi = \frac{\text{Fuel} / \text{Oxygen}}{(\text{Fuel} / \text{Oxygen})_{\text{Stoick}}} \]
- Combustion chamber pressure \( P_C \) - Determined by total mass flow of \( O_2 \) and fuel

[Image of Fe3Al Coating]
Goals of the Program

Develop Fe$_3$Al coatings for high temperature service in fossil fuel environments

- Develop High Velocity Oxy-Fuel (HVOF) thermal spray techniques for applying the coating
- Understand factors and thermal spray parameters that affect the reliability of this coating
- Verify the corrosion resistance of the HVOF coatings in simulated, fossil fuel, combustion environments:
  - High temperature, gaseous corrosion behavior
  - Corrosion behavior in the presence of simulated ash
- Demonstrate repair of HVOF, Fe$_3$Al coatings
Current Project Focus

Goal:

Determine the corrosion/oxidation behavior of HVOF thermal spray coatings in simulated fossil fuel combustion atmospheres

Tasks:

• Corrosion behavior of Fe₃Al coatings on Fe- and Ni-base alloys in simulated fossil fuel combustion atmospheres
  – N₂-15CO₂-5O₂-1SO₂ + 10-20% H₂O (high oxygen potential)
  – N₂-9%CO-4.5%CO₂-1.8%H₂O-0.12% H₂S-2% H₂O (low oxygen potential, high sulfur potential)
  – FeS₂ as the aggressive species in coal ash

• Comparison of HVOF, Fe₃Al coatings to conventional weld overlay coatings.
Coating Information

**Weld Overlays**

- Alloy 622 (21% Cr)
- Single pass
- ~1.5 mm thick
- 12.7 mm dia.

**9Cr-1Mo Steel**

**316 Stainless Steel**

**Inconel 600 (16% Cr)**

**HVOF Fe₃Al Coatings**

Supplier: AMETEK       Product: FAS-C (-270)
Lot #: 037601

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Al</th>
<th>Cr</th>
<th>Zr</th>
<th>C</th>
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</thead>
<tbody>
<tr>
<td>Wt. %</td>
<td>Bal.</td>
<td>15.7</td>
<td>2.4</td>
<td>0.2</td>
<td>0.02</td>
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</table>

- Two sets of samples – differing Pₚ:
  - 480 kPa
  - 620 kPa
- 12.7 mm dia. rods
- Grit blasted (24 grit, Al₂O₃)
- Spray pattern - 10 mm/sec, 10 rpm
- EDM samples ~10 mm long
As-Sprayed HVOF, $\text{Fe}_3\text{Al}$ Coatings

- $\dot{p}_c = 620$ kPa
- $\dot{p}_c = 480$ kPa

$9\text{Cr}-1\text{Mo}$ Steel substrate | 316 Stainless Steel substrate | Inconel 600 substrate
As-Deposited 622 Weld Overlays

9Cr-1Mo Steel substrate 316 Stainless Steel substrate Inconel 600 substrate
Coating Degradation Testing in Various Atmospheres

• Simulated fossil fuel, combustion atmospheres –
  – Dynamic/once-through gas flow (50 ml/min)
  – N₂-15CO₂-5O₂-1SO₂ + 20% H₂O
  – N₂-9%CO-4.5%CO₂-1.8%H₂O-0.12% H₂S
  – 800°C (1000°C capable)

• Samples placed in low-walled alumina boat

• Sample geometry allowed investigation corrosion behavior at:
  – Coating/gas interface
  – Coating/ash interface
  – Substrate/gas interface
  – Substrate/ash interface

BFP = BackFlow Preventer

FeS₂
$N_2-15CO_2-5O_2-1SO_2 + 20\% H_2O$ (high oxygen potential)
– HVOF, Fe$_3$Al coatings

9Cr-1Mo Steel substrate  316 Stainless Steel substrate  Inconel 600 substrate
$N_2-15CO_2-5O_2-1SO_2 + 20\% H_2O$ (high oxygen potential)
– Weld Overlays

9Cr-1Mo Steel substrate
316 Stainless Steel substrate
Inconel 600 substrate
**Summary of Corrosion Behavior – High Oxygen Potential**

<table>
<thead>
<tr>
<th>Substrate Material</th>
<th>Coating Material</th>
<th>Initial Coating Thickness, µm</th>
<th>Post-exposure Coating Thickness, µm</th>
<th>Δ Thickness, µm</th>
<th>Substrate Recession, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>9Cr-1Mo Steel</td>
<td>HVOF, Fe$_3$Al P$_c$=620 kPa</td>
<td>237</td>
<td>228</td>
<td>10</td>
<td>324</td>
</tr>
<tr>
<td>316 Stainless Steel</td>
<td>HVOF, Fe$_3$Al P$_c$=620 kPa</td>
<td>245</td>
<td>232</td>
<td>13</td>
<td>93</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>HVOF, Fe$_3$Al P$_c$=620 kPa</td>
<td>257</td>
<td>264</td>
<td>-7</td>
<td>0</td>
</tr>
<tr>
<td>9Cr-1Mo Steel</td>
<td>Weld Overlay, 622</td>
<td>1054</td>
<td>1037</td>
<td>17</td>
<td>329</td>
</tr>
<tr>
<td>316 Stainless Steel</td>
<td>Weld Overlay, 622</td>
<td>2300</td>
<td>1837</td>
<td>464</td>
<td>69</td>
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<tr>
<td>Inconel 600</td>
<td>Weld Overlay, 622</td>
<td>1482</td>
<td>1480</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: Significant variation existed in the initial weld overlay thickness in all samples - little corrosion of the weld overlay was observed.

**Conclusion – Alloy 622 weld overlays and HVOF, Fe$_3$Al coatings provide equivalent protection during short exposure tests.**
$N_2-9\%CO-4.5\%CO_2-1.8\%H_2O-0.12\%H_2S-2\%H_2O$ (low oxygen potential, high sulfur potential) - HVOF, $Fe_3Al$ coatings

9Cr-1Mo Steel substrate  
316 Stainless Steel substrate  
Inconel 600 substrate
$N_2 - 9\%CO - 4.5\%CO_2 - 1.8\%H_2O - 0.12\%H_2S - 2\%H_2O$ (low oxygen potential, high sulfur potential) – Weld Overlays

- 9Cr-1Mo Steel substrate (500 hrs)
- 316 Stainless Steel substrate (300 hours)
- Inconel 600 substrate (200 hours)
Summary of Corrosion Behavior – High Sulfur Potential

<table>
<thead>
<tr>
<th>Substrate Material</th>
<th>Coating Material</th>
<th>Initial Coating Thickness, µm</th>
<th>Post-exposure Coating Thickness, µm</th>
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<th>Substrate Recession, µm</th>
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<tr>
<td>9Cr-1Mo Steel</td>
<td>HVOF, Fe₃Al Pc=480 kPa</td>
<td>244</td>
<td>225</td>
<td>19</td>
<td>485</td>
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<tr>
<td>316 Stainless Steel</td>
<td>HVOF, Fe₃Al Pc=480 kPa</td>
<td>230</td>
<td>217</td>
<td>12</td>
<td>206</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>HVOF, Fe₃Al Pc=480 kPa</td>
<td>236</td>
<td></td>
<td></td>
<td>Severe Degradation</td>
</tr>
<tr>
<td>9Cr-1Mo Steel</td>
<td>HVOF, Fe₃Al Pc=620 kPa</td>
<td>237</td>
<td>218</td>
<td>19</td>
<td>334</td>
</tr>
<tr>
<td>316 Stainless Steel</td>
<td>HVOF, Fe₃Al Pc=620 kPa</td>
<td>245</td>
<td>194</td>
<td>51</td>
<td>178</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>HVOF, Fe₃Al Pc=620 kPa</td>
<td>257</td>
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<td>Severe Degradation</td>
</tr>
</tbody>
</table>

Conclusion – HVOF, Fe₃Al coatings provide adequate corrosion resistance during short exposure tests while ni-based alloys suffer severe corrosion.
Additional Observations - Fe₃Al on 316SS, High Oxygen Potential

- Exposed coating/substrate interface is not a preferential corrosion path
- Development of significant reaction zone (90-100 µm) after 500 hrs
Additional Observations – Alloy 622 on 9Cr-1Mo Steel, High Oxygen Potential

Alloy 622 Weld Overlay on 9Cr-1Mo steel – As-deposited

Alloy 622 Weld Overlay on 9Cr-1Mo steel – 800°C, 500 hrs
Additional Observations - Fe₃Al on Inconel 600, High Oxygen Potential

- Exposed coating/substrate interface is not a preferential corrosion path
- Development of significant reaction zone (50-60 µm) after 500 hrs
Additional Observations - Fe$_3$Al on 316SS, High Sulfur Potential
Remaining Tasks

- Longer exposure tests –
  - Look for breakaway corrosion
  - Characterization the rate of diffusion
- SEM/EDS characterization of reaction zone – determine the change of aluminum concentration in HVOF, Fe$_3$Al coatings
- SEM/EDS characterization of reaction zone in weld overlays
- SEM/EDS of reaction products
- Estimate time to breakaway corrosion
Summary & Conclusions

• HVOF, Fe₃Al coatings provide suitable corrosion resistance in high sulfur potential, low oxygen potential high temperature environments.

• Nickel-base alloys and weld overlays are not suitable in high sulfur potential, low oxygen potential, high temperature environments.

• HVOF, Fe₃Al coatings, nickel-base alloys and weld overlays provide suitable corrosion resistance in high oxygen potential, high temperature atmospheres.

• HVOF, Fe₃Al coatings on iron and nickel-base structural alloys exhibit inter-diffusion after relatively short exposure tests – the extent of inter-diffusion remains to be characterized.

• Exposed substrate/HVOF, Fe₃Al coating interfaces in iron-based substrates do not exhibit preferential corrosion.