

Degradation of HVOF, Fe₃Al Coatings in Simulated Coal Ash

PI: Thomas M. Lillo

Co-Investigators:

W. David Swank

D.C. Haggard

Arnold Erickson

2014 NETL Crosscutting Research Review Meeting
May 19-23, 2014, Pittsburgh, PA

Prepared for the U.S. Department of Energy, Office of Fossil Energy, under DOE Idaho
Operations Office, Contract DE-AC07-05ID14517

www.inl.gov



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**
 - Example – EPRI Technical Update, “*US Program on Materials Technology for Ultrasupercritical Coal Power Plants*”, March 2006:
 - 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

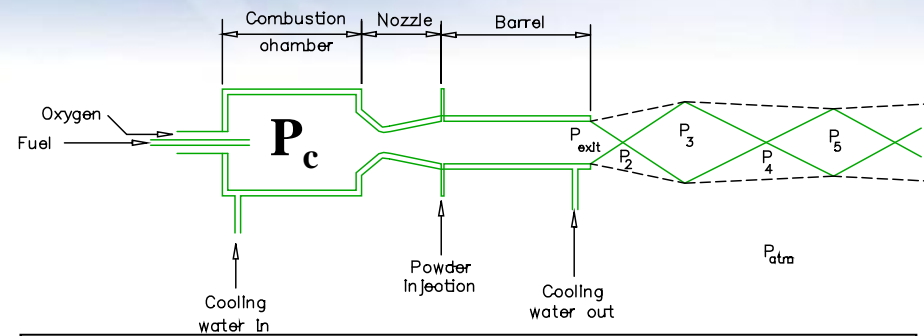
- **Chromia-formers - high-Cr weld overlays and laser cladding can provide corrosion resistance**
- **Silica-formers – (high silicon alloys, silicides)**
- **Alumina-formers – aluminides (iron or nickel)**

Aluminide Coatings

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

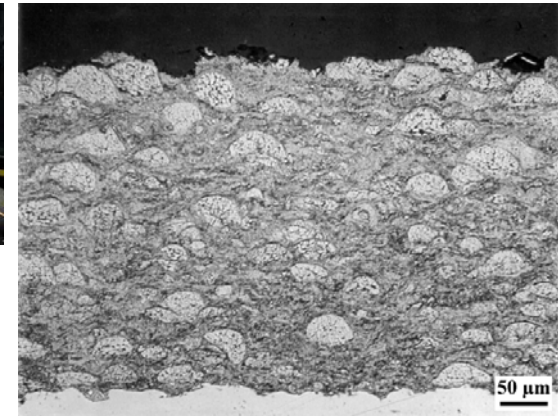
Past Results

- Thermal spray parameters can be used to generate highly dense coating with varying levels of residual stress:
 - P_c determines particle velocity
 - Φ determines particle temperature
- 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



High-Velocity Oxy-Fuel (HVOF) thermal spray

- Equivalence ratio (ϕ)-
$$\Phi = \frac{\text{Fuel} / \text{Oxygen}}{(\text{Fuel} / \text{Oxygen})_{\text{Stoich}}}$$
- Combustion chamber pressure
 P_c – Determined by total mass flow of O_2 and fuel



Fe₃Al Coating

Goals of the Program

Develop Fe₃Al 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
 - Low corrosion rates in N₂-15CO₂-5O₂-1SO₂ + 10-20% H₂O @ 800°C
 - Corrosion behavior in the presence of simulated ash

Current Project Focus

Goal:

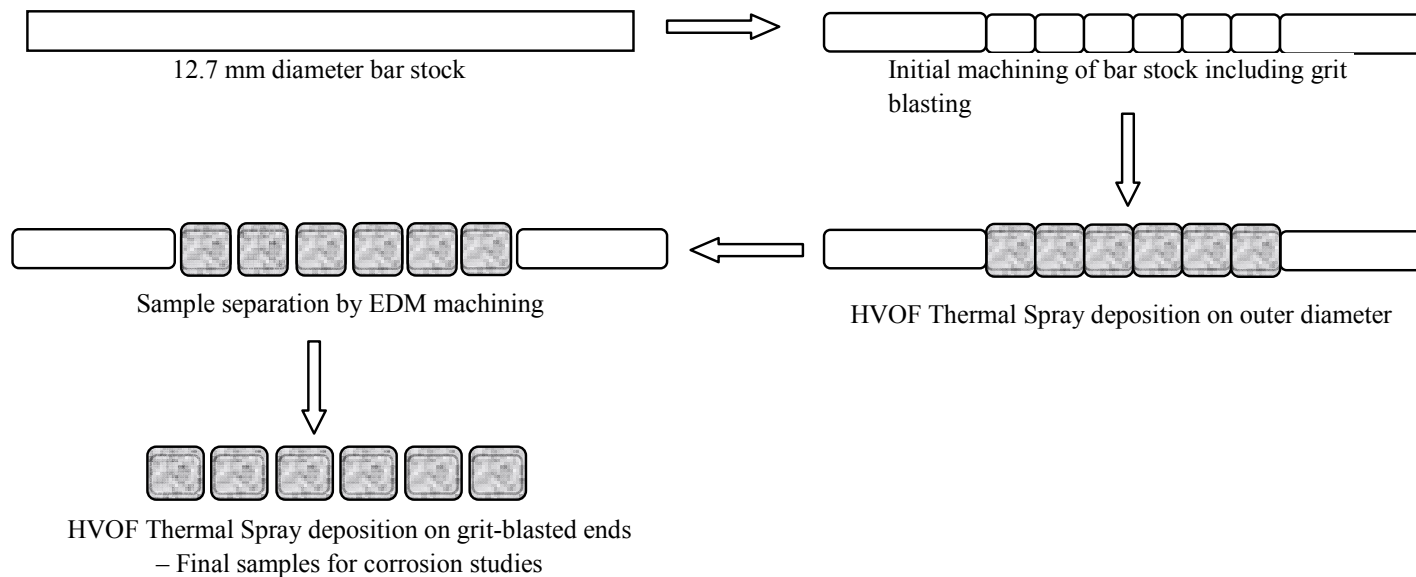
Determine the corrosion/oxidation behavior of HVOF thermal spray coatings in simulated fossil fuel combustion atmospheres with simulated coal ash:

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)
 - Simulated coal ash: 30% Al₂O₃, 30% SiO₂, 30% Fe₂O₃, 5% Na₂SO₄ and 5% K₂SO₄.
 - N₂-9%CO-4.5%CO₂-1.8%H₂O-0.12% H₂S-2% H₂O (low oxygen potential, high sulfur potential)
 - Simulated coal ash: TBD
- Comparison of HVOF, Fe₃Al coatings to conventional weld overlay coatings (C-22).

HVOF Coating Sample Fabrication

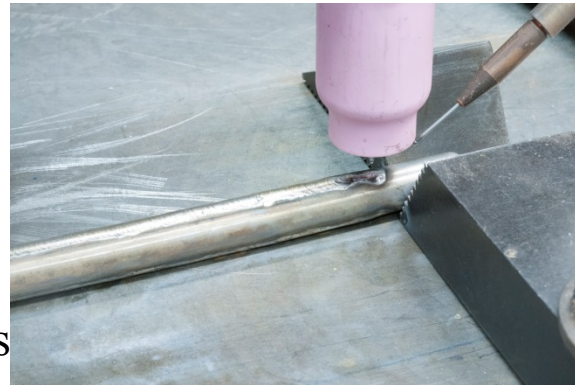
- Coatings that fully encapsulate samples to assess the effects of CTE differences (substrates: 316SS, 9Cr-1Mo steel, Alloy 600)
- Fabrication method cannot involve harsh machining of the coating
- Sample geometry must not have sharp corners



Coating Information

Weld Overlays

- Alloy 622 (21% Cr)
- Two passes
- Machined to ~1.0 mm thick
- 12.7 mm dia. rods



316 Stainless Steel



Inconel 600 (16% Cr)

HVOF Fe₃Al Coatings

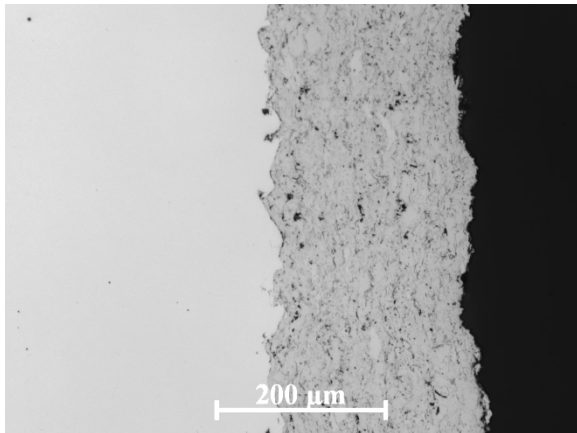
Supplier: AMETEK Product: FAS-C (-270)
Lot #: 037601

Element	Fe	Al	Cr	Zr	C
Wt. %	Bal.	15.7	2.4	0.2	0.02

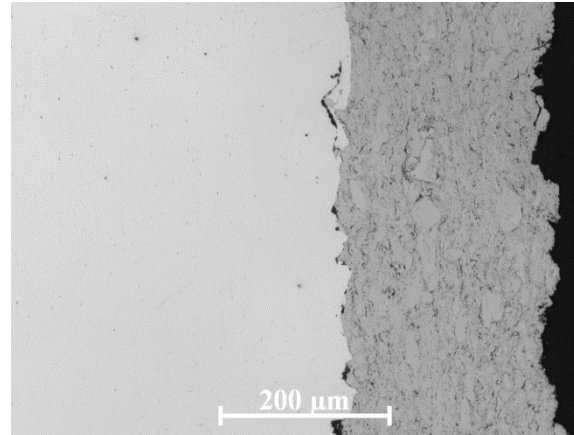
- Combustion Chamber Pressure, P_c :
 - 620 kPa
- 12.7 mm dia. rods
- Grit blasted (24 grit, Al_2O_3)
- Spray pattern - 10 mm/sec, 10 rpm
- EDM samples ~10 mm long

As-Sprayed HVOF, Fe₃Al Coatings

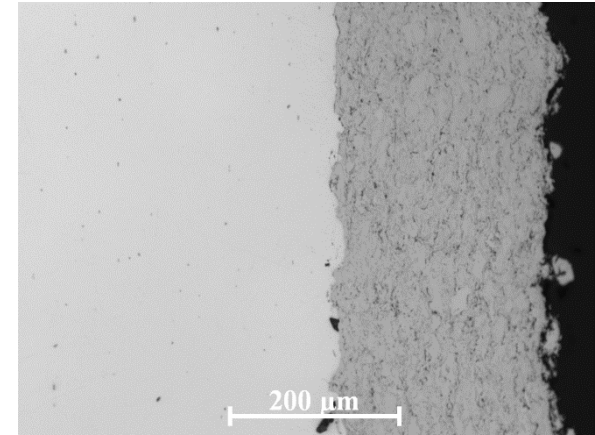
HVOF Combustion Pressure, $P_c=620$ kPa



9Cr-1Mo Steel substrate

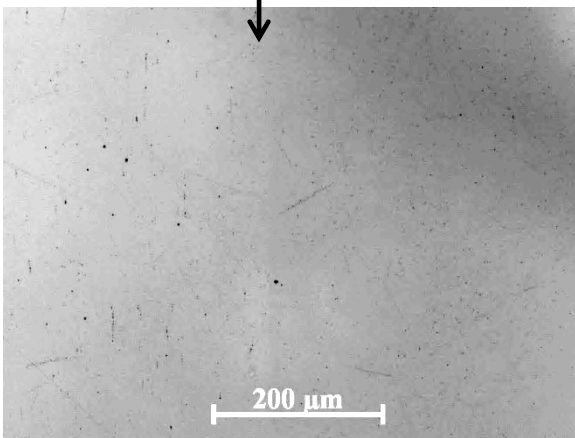
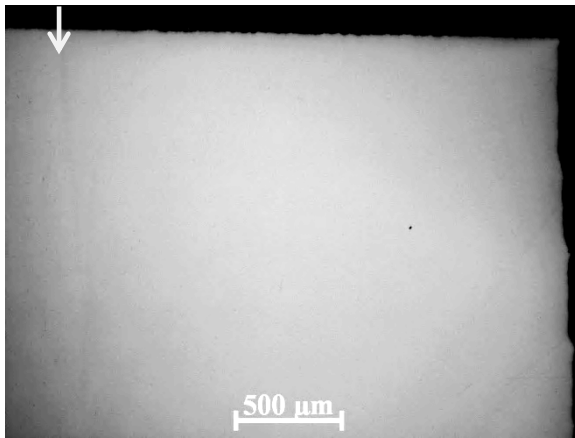


316 Stainless Steel substrate

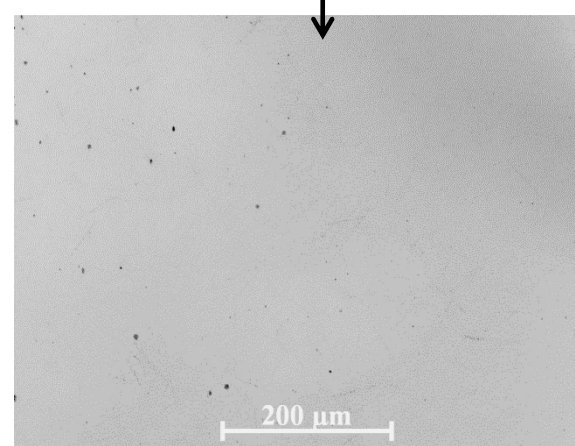
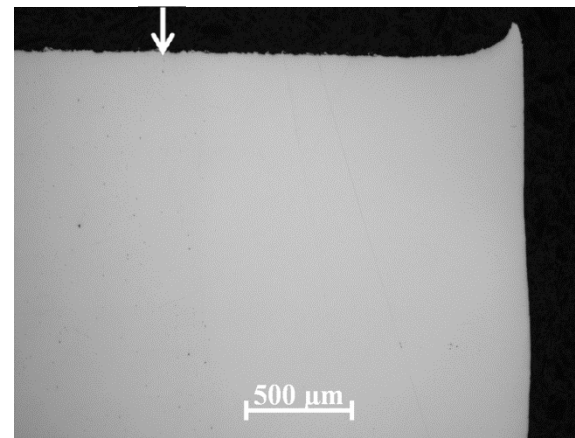


Inconel 600 substrate

As-Deposited 622 Weld Overlays



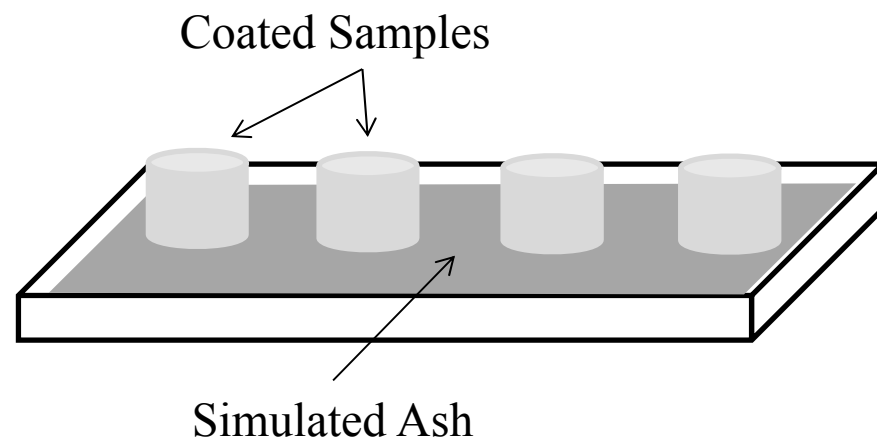
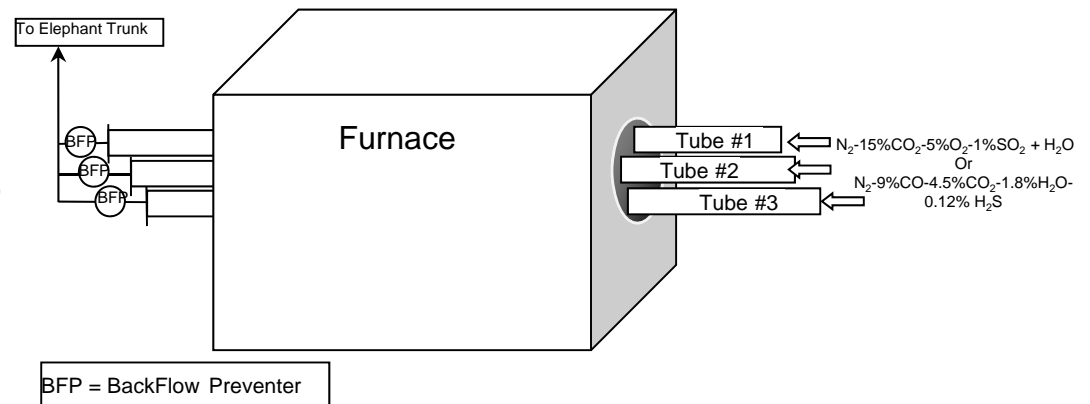
316 Stainless Steel substrate



Inconel 600 substrate

Coating Degradation Testing in Various Atmospheres

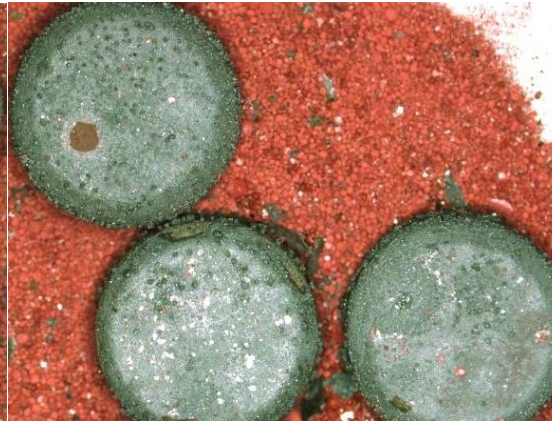
- Simulated fossil fuel, combustion atmospheres –
 - Dynamic/once-through gas flow (85 ml/min)
 - $N_2-15CO_2-5O_2-1SO_2 + 20\% H_2O$
 - 750°C (1000°C capable)
- Samples placed in low-walled alumina boat
- Ash: 30% Al_2O_3 , 30% SiO_2 , 30% Fe_2O_3 , 5% Na_2SO_4 and 5% K_2SO_4
- Sample geometry allowed investigation corrosion behavior at:
 - Coating/gas interface
 - Coating/ash interface
- 4 sets of samples



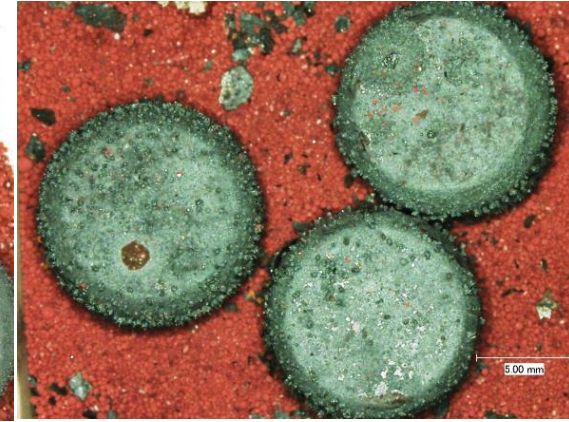
Degradation in Simulated Coal Ash - Macro



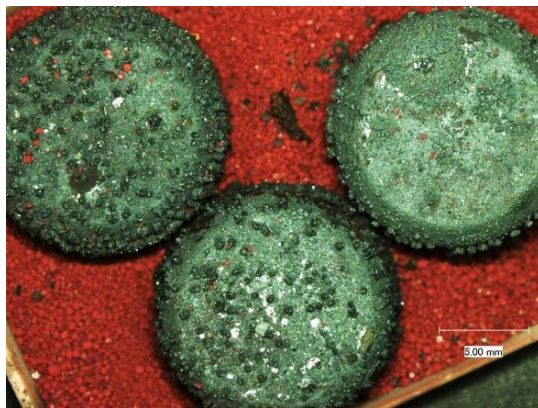
297 hrs, 750°C



610 hrs, 750°C



997 hrs, 750°C

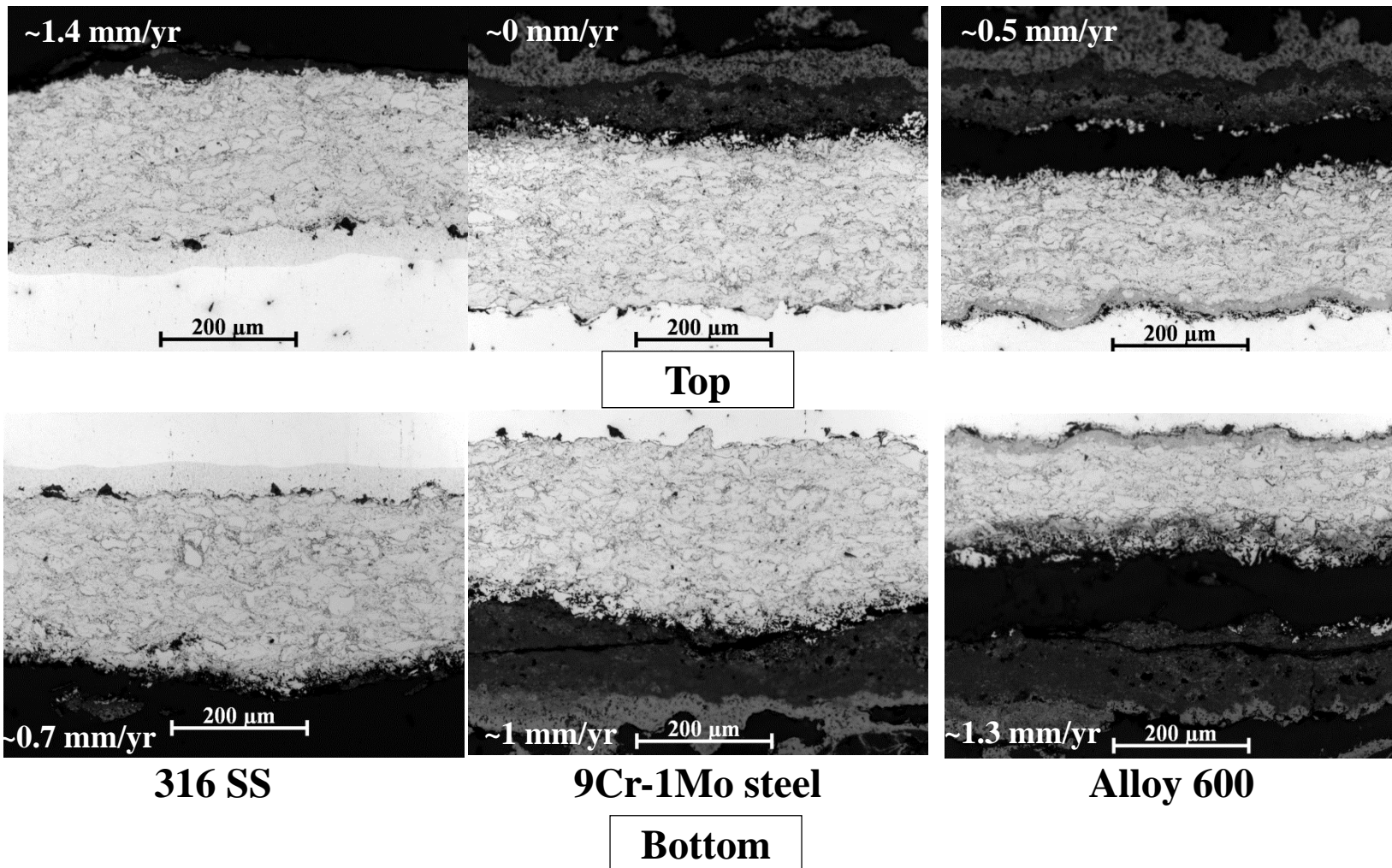


1500 hrs, 750°C

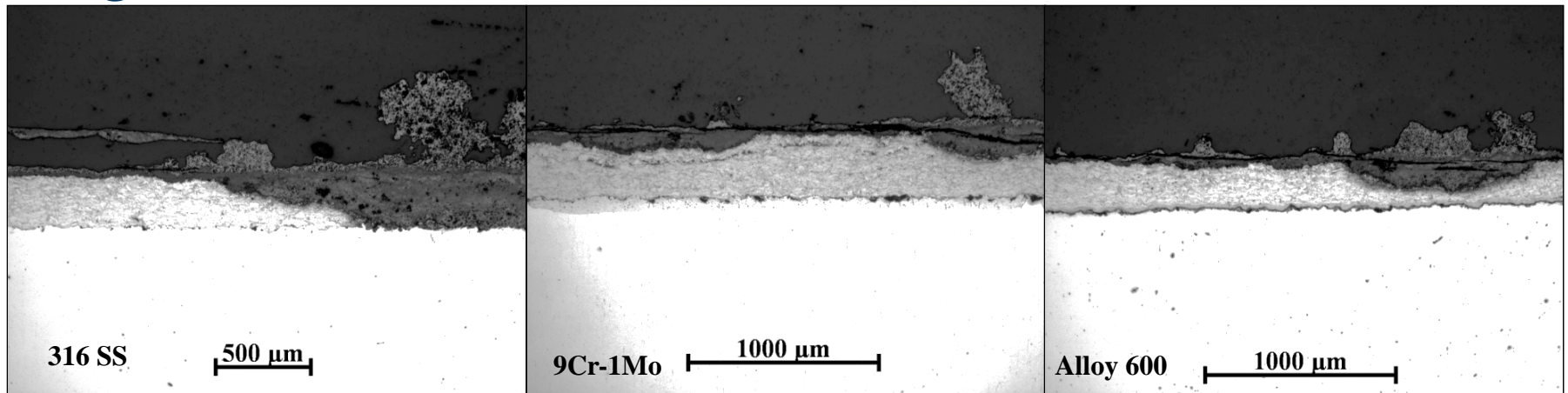


1984 hrs, 750°C

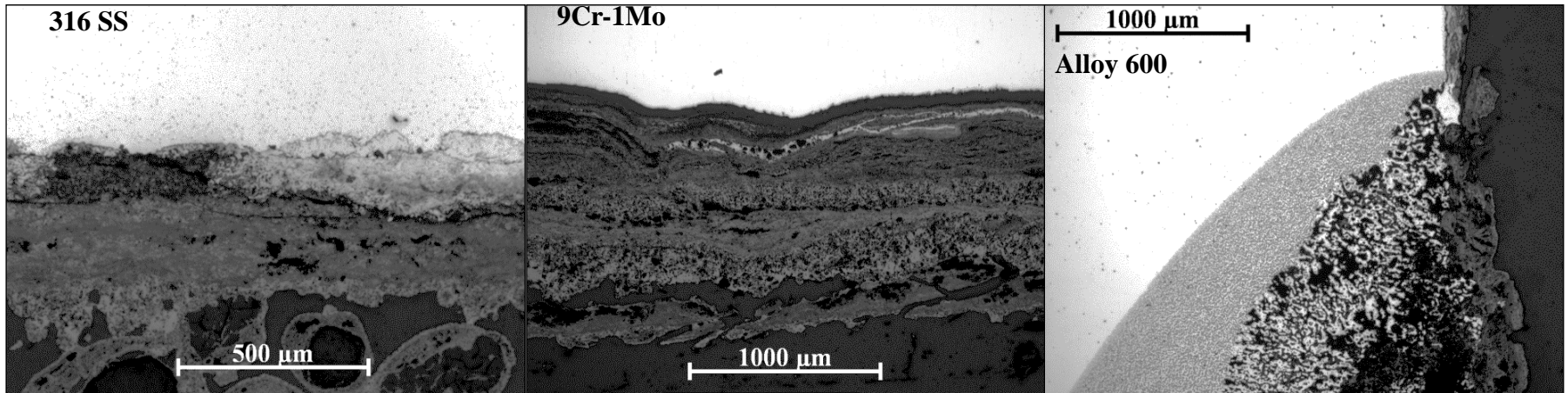
Degradation – 610 hrs, 750°C



Degradation – 1984 hrs, 750°C

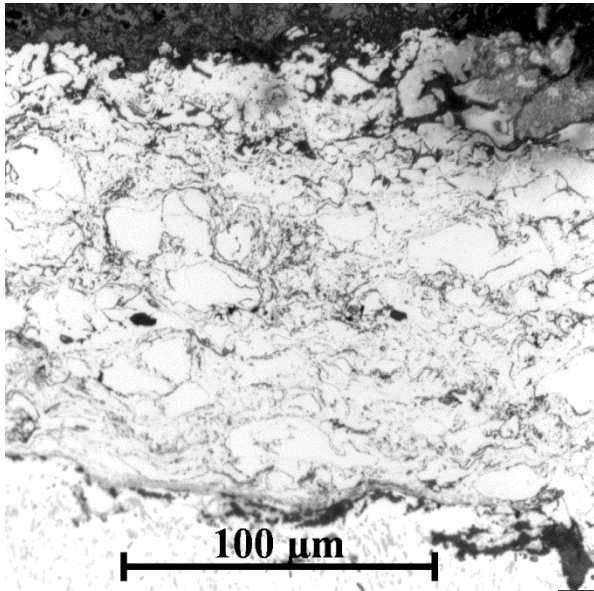


Top



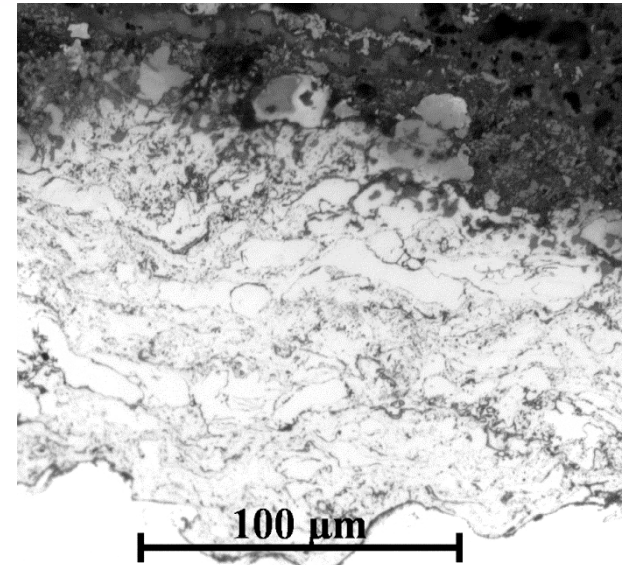
Bottom

Coatings Failures at 1984 hrs

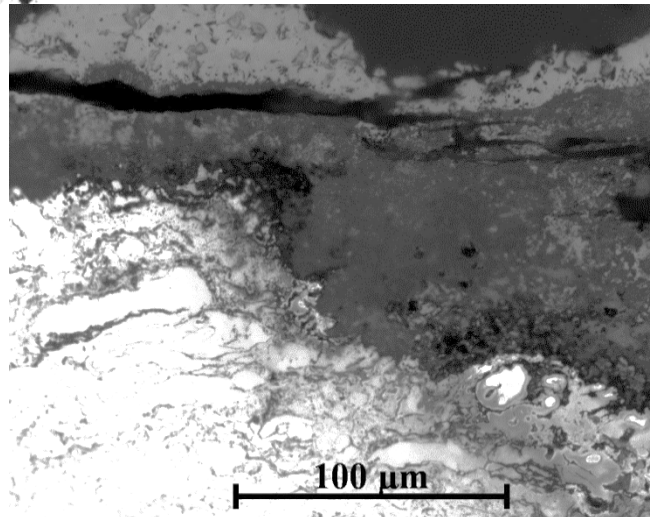


316 SS

Failure appears to occur by degradation along prior “splat” boundaries



9Cr-1Mo



Alloy 600

Corrective Actions for HVFO, Fe₃Al Coatings

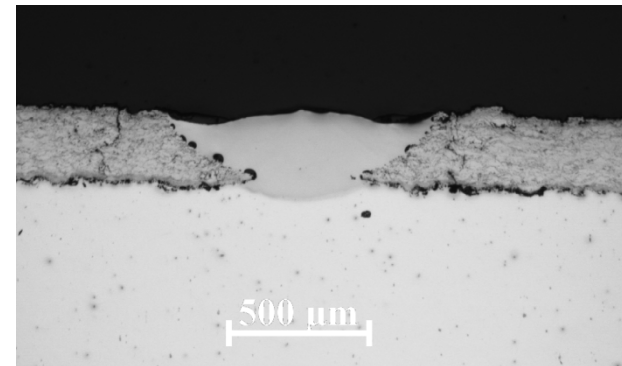
Need to improve splat-to-splat bonding

- **HVOF Parameters**

- Increase particle temperature
- Increase particle velocity (increase P_c)

- **Additional processing**

- Laser processing of HVOF deposit
- Laser-assisted HVOF deposition (laser hybrid thermal spray)

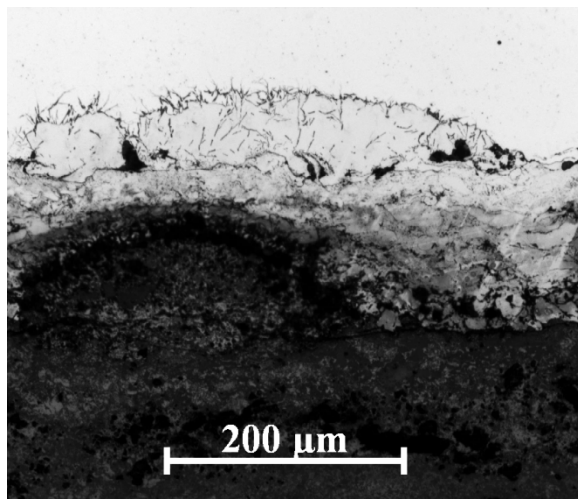


Laser Processing

Laser Power: 710 watts

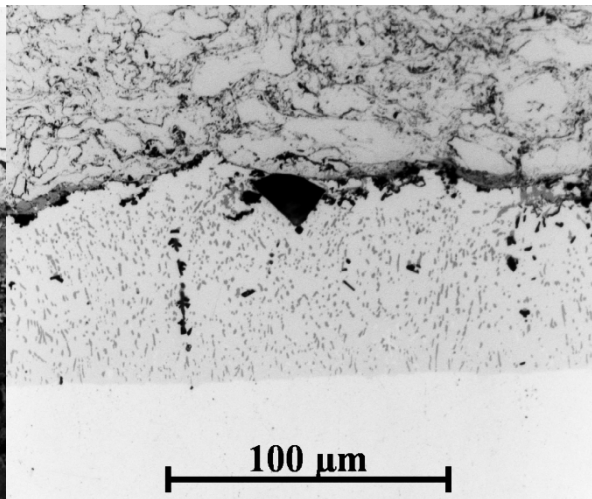
Traverse Speed: 40 mm/sec

Coating/Substrate Interactions – 1984 hrs



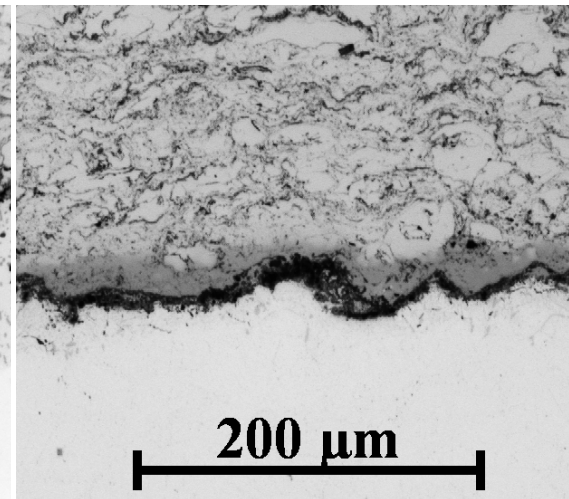
9Cr-1Mo

Interaction near a
pit ~70 μm.



316 SS

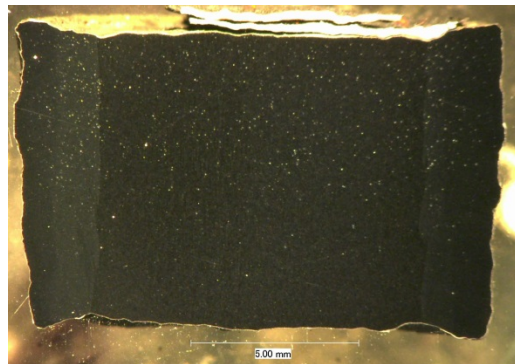
Inter-diffusion of coating
elements into substrate
~80 μm



Alloy 600

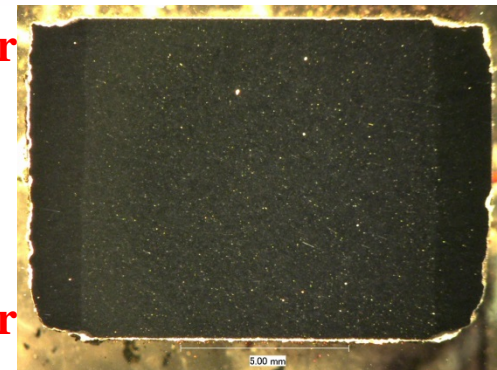
Inter-diffusion into
coating and into
substrate, ~20 μm and
~30 μm, respectively

Degradation of C-22 Weld Overlay Coatings



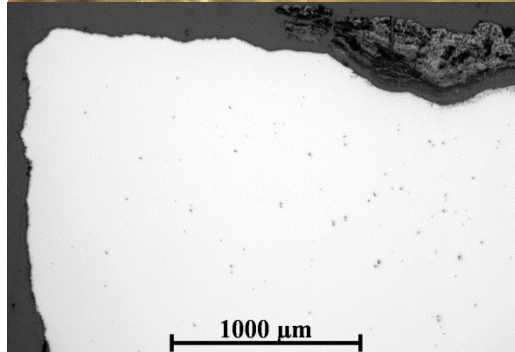
1.2 mm/yr

3.2 mm/yr

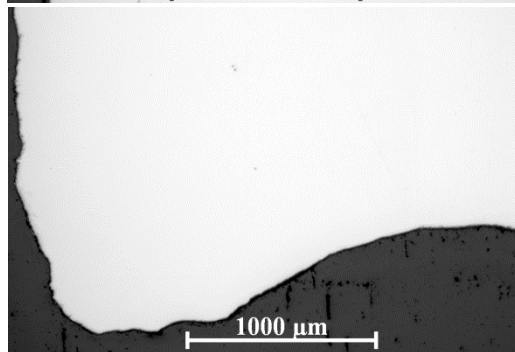
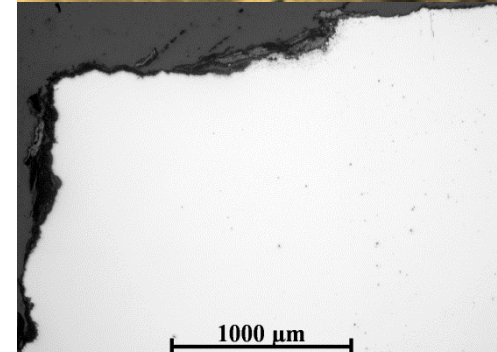


2.7 mm/yr

4.2 mm/yr

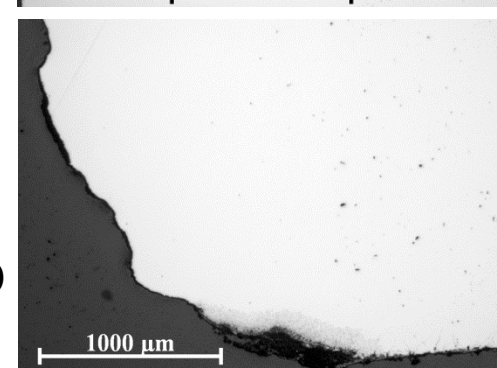


The weld overlays also exhibited significant degradation after 1984 hrs in contact with the simulated coal ash



316 SS

Alloy 600



Summary & Conclusions

- Corrosion rate is higher at ash/coating interface compared to coating/furnace atmosphere interface
- Degradation mechanism appears to attack prior splat boundaries
- Improved splat-to-splat bonding may be accomplished by increasing particle velocity and temperature during HVOF deposition or post-HVOF laser processing of the deposit
- Degradation of the HVOF, Fe₃Al coating in simulated coal ash is extensive and much faster than expected
- HVOF, Fe₃Al coatings do not appear to be suitable in the presence of coal ash
 - Degradation rate is in excess of 1 mm/yr
 - Exposure testing under these conditions will be terminated
- Previous results show HVOF, Fe₃Al coatings are very corrosion resistant in other fossil fuel combustion atmospheres and oxidizing environments.
- Weld overlays of C-22 also exhibited significant degradation in simulated coal ash (1-4 mm/yr)

Remaining Tasks

- Exposure of HVOF thermal spray coatings and C-22 weld overlay coatings in a reducing simulated fossil fuel combustion atmospheres (H_2S) and simulated coal ash at 475°C
- SEM/EDS characterization of reaction zone – determine the change of aluminum concentration in HVOF, Fe_3Al coatings
- Final Report