

**Microstructure, Processing, Performance  
Relationships for High Temperature Coatings**

**High Temperature Corrosion Behavior of  
HVOF, Fe<sub>3</sub>Al Coatings**

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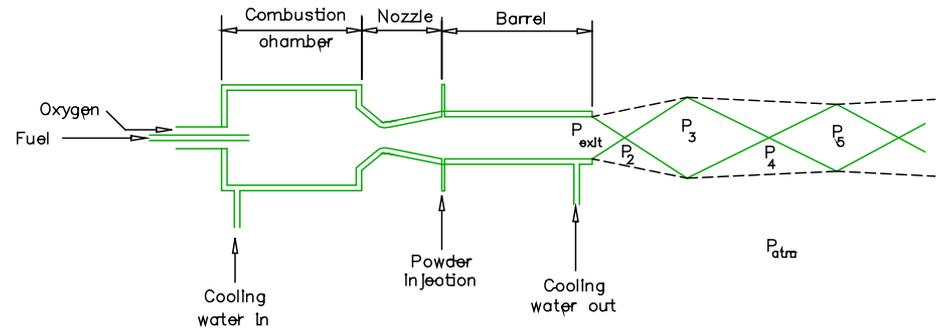
# Goals of the Program

Develop Fe<sub>3</sub>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<sub>3</sub>Al coatings

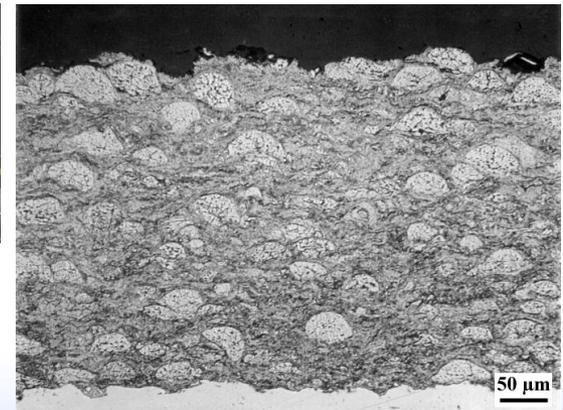
# Past Results

- 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
- Substrate surface preparation is critical in coating adherence
- Higher HVOF combustion chamber pressures result in better resistance to thermal cycling



## High-Velocity Oxy-Fuel (HVOF) thermal spray

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



$Fe_3Al$  Coating

# Current Project Focus

## *Goal:*

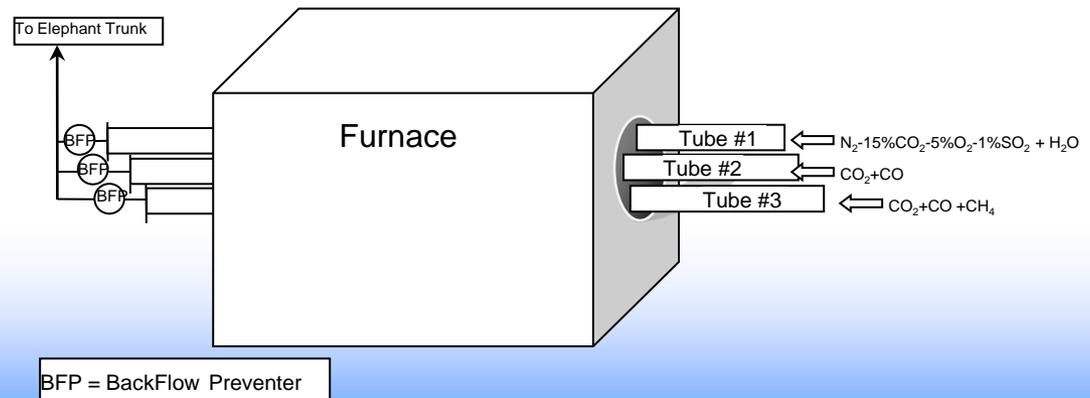
**Determine the corrosion/oxidation behavior of HVOF thermal spray coatings**

## *Tasks:*

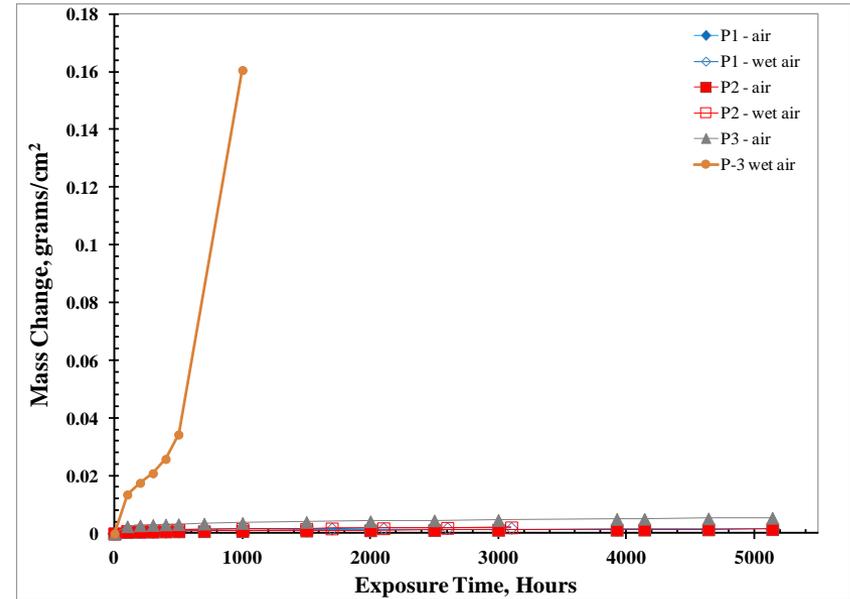
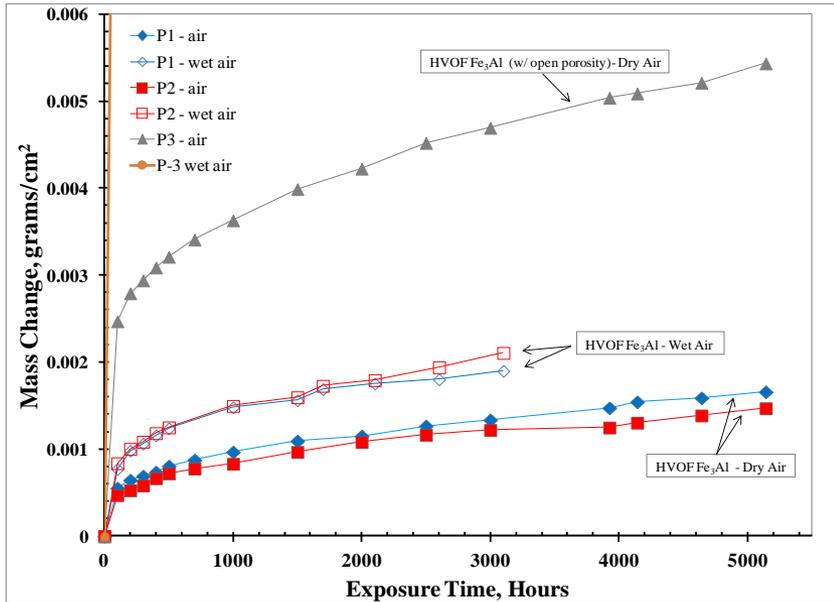
- Oxidation behavior of free standing HVOF coatings in dry and “wet” air
- Corrosion behavior of free standing coatings in simulated fossil fuel combustion atmospheres ( $\text{N}_2$ -15 $\text{CO}_2$ -5 $\text{O}_2$ -1 $\text{SO}_2$  + 10-20%  $\text{H}_2\text{O}$ )
- Degradation behavior in carbon-containing atmospheres –  $\text{CO}_2$ / $\text{CO}$  and  $\text{CO}_2$ / $\text{CO}$ / $\text{CH}_4$  mixtures
- Long term aging to assess interdiffusion potential and coating degradation
- Comparison of HVOF,  $\text{Fe}_3\text{Al}$  coatings to weld overlay coatings.

# Coating Degradation Testing in Various Atmospheres

- Air – dry and “wet”
- Simulated fossil fuel, combustion atmospheres –
  - Dynamic / once through gas flow
  - $\text{N}_2$ -15 $\text{CO}_2$ -5 $\text{O}_2$ -1 $\text{SO}_2$  + 10-20%  $\text{H}_2\text{O}$
- Oxidizing – control of  $p_{\text{O}_2}$  through the  $\text{CO}/\text{CO}_2$  ratio
- Carburizing -  $\text{CO}_2/\text{CO}/\text{CH}_4$  mixtures to control the carburization potential



# Oxidation of Free Standing HVOF, Fe<sub>3</sub>Al Coatings – 1000°C



- Dense HVOF coatings exhibit very low corrosion rates in both dry and “wet” air at 1000°C
- Oxidation rate in “wet” air is higher than in dry air.
- P-3 exhibited high oxidation rates and contained open porosity – P-1 and P-2 did not contain open porosity.

P-1:  $P_c=0.6$  MPa

P-2:  $P_c=0.7$  MPa

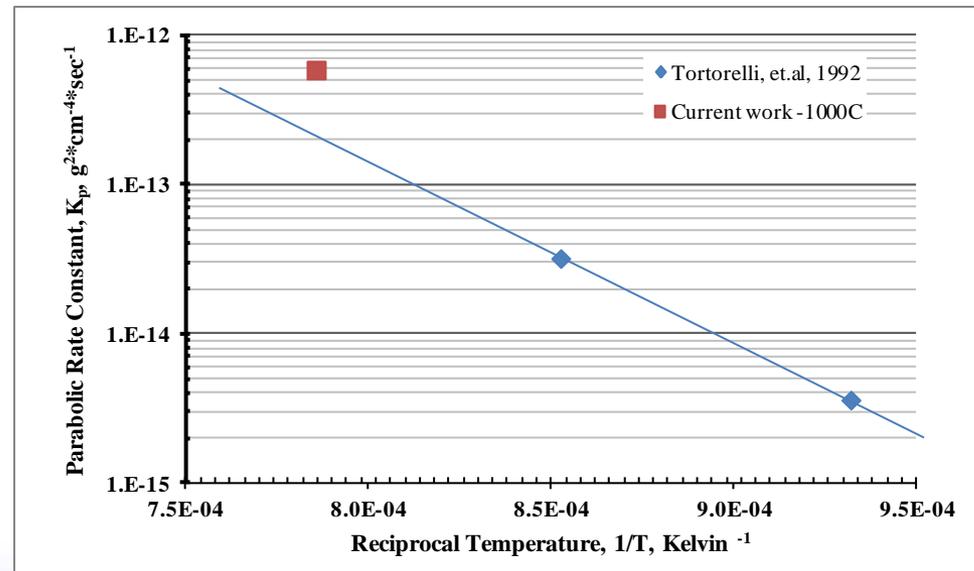
P-3:  $P_c=0.3$  MPa

# Parabolic Rate Constant for Oxidation

Temperature = 1000°C	Parabolic Rate Constant *, g <sup>2</sup> /cm <sup>4</sup> s			
Atmosphere	HVOF Fe <sub>3</sub> Al – P <sub>c</sub> =0.6 MPa	HVOF Fe <sub>3</sub> Al – P <sub>c</sub> =0.7 MPa	HVOF Fe <sub>3</sub> Al – P <sub>c</sub> =0.3 MPa	I-600 base metal
Dry air	1x10 <sup>-13</sup>	1x10 <sup>-13</sup>	1x10 <sup>-12</sup>	Not evaluated
Wet air	3x10 <sup>-13</sup>	3x10 <sup>-13</sup>	4x10 <sup>-10</sup>	2x10 <sup>-11</sup>

\*Parabolic rate constants determined from plots of mass (change/area)<sup>2</sup> versus time

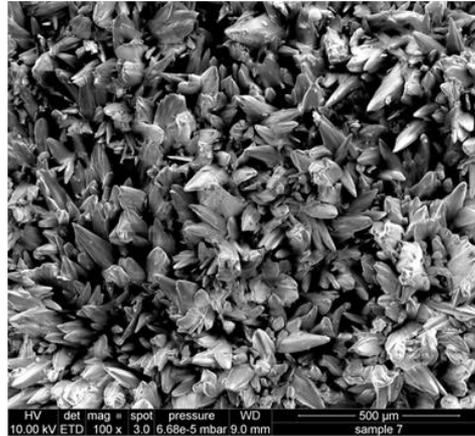
- Oxidation of HVOF, Fe<sub>3</sub>Al coatings in dry air are comparable to literature
- Activation energy for oxidation is close to that for alumina formation



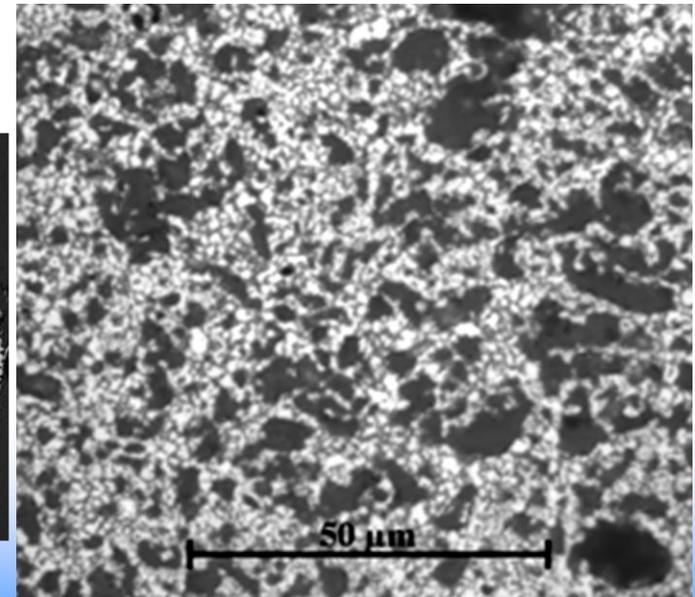
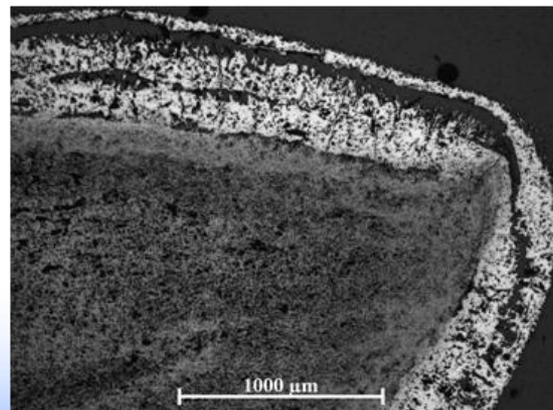
Calculated by the method of Tortorelli, et. al, 1992 at 200 hrs of exposure – dry air, bulk Fe<sub>3</sub>Al.

# Breakaway Oxidation in P-3

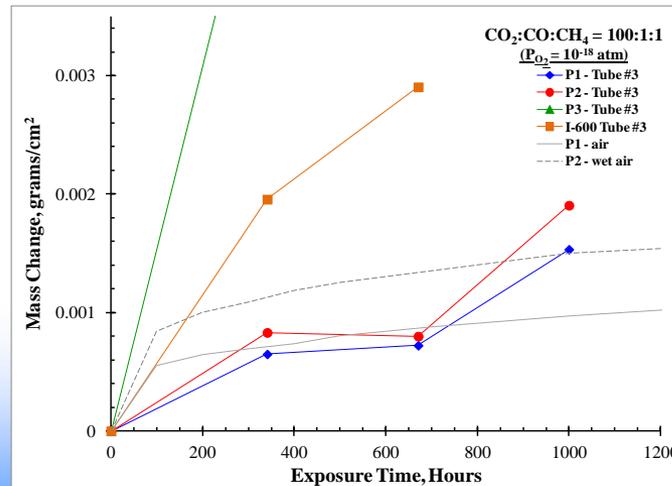
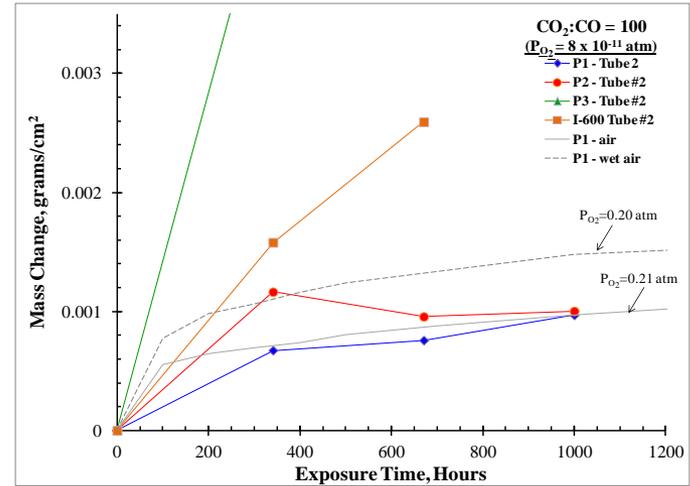
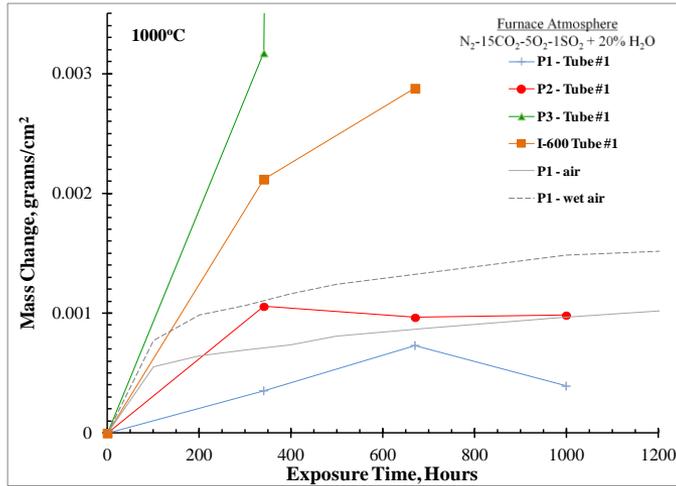
- Surface reaction product is iron oxide
- Coating interior is highly fractured
- Oxidation of open porosity resulted in volume change and fracturing of coating, resulting in further oxidation



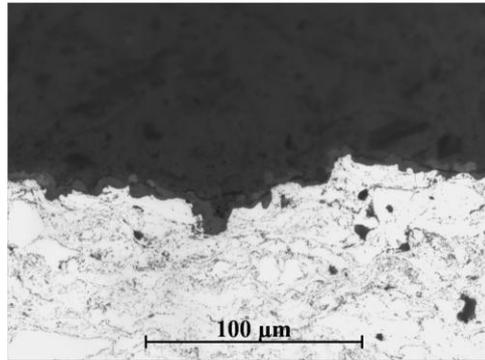
<i>Element</i>	<i>Wt %</i>	<i>At %</i>
<i>O K</i>	14.33	36.67
<i>AlK</i>	00.65	00.99
<i>CrK</i>	00.52	00.41
<i>FeK</i>	84.49	61.93



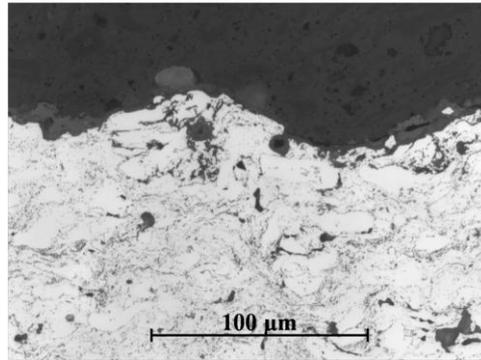
# Simulated Combustion, Oxidizing and Carburizing Atmospheres – 1000°C



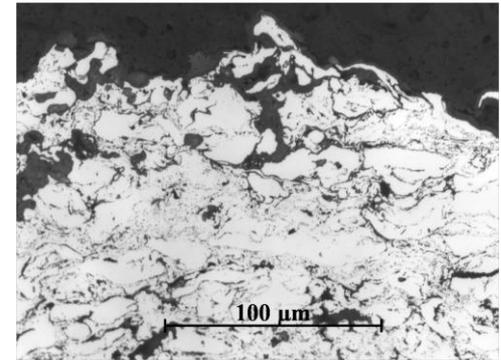
# Corrosion in Simulated Fossil Fuel Combustion Atmosphere - 1000°C, 341 hrs



P-1



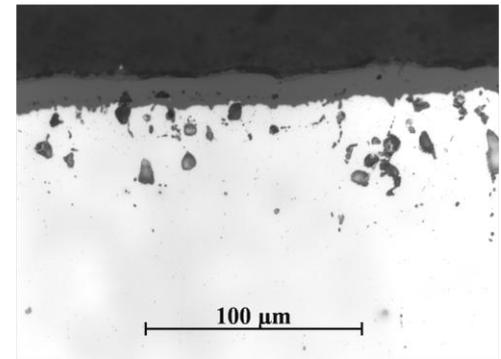
P-2



P-3

Furnace Atmosphere

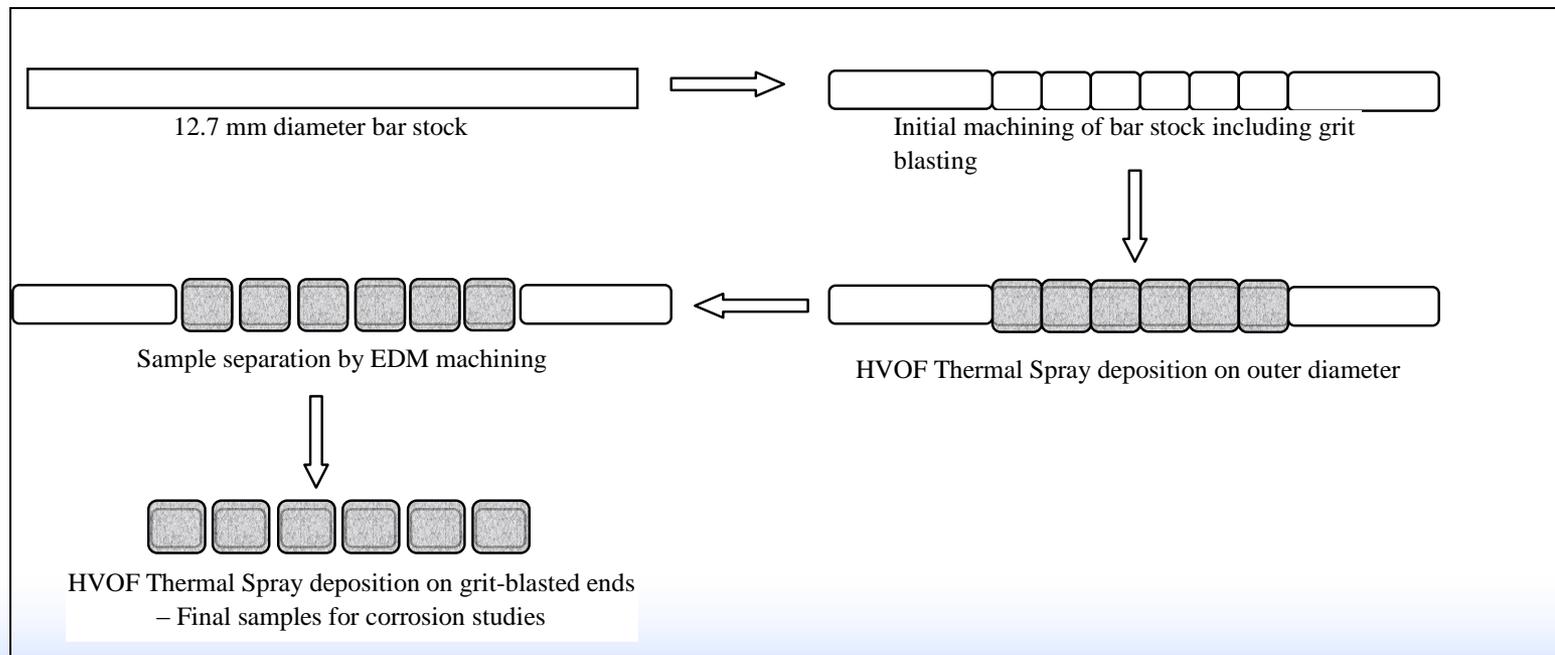
$N_2-15CO_2-5O_2-1SO_2 + 20\% H_2O$



Inconel Alloy 600

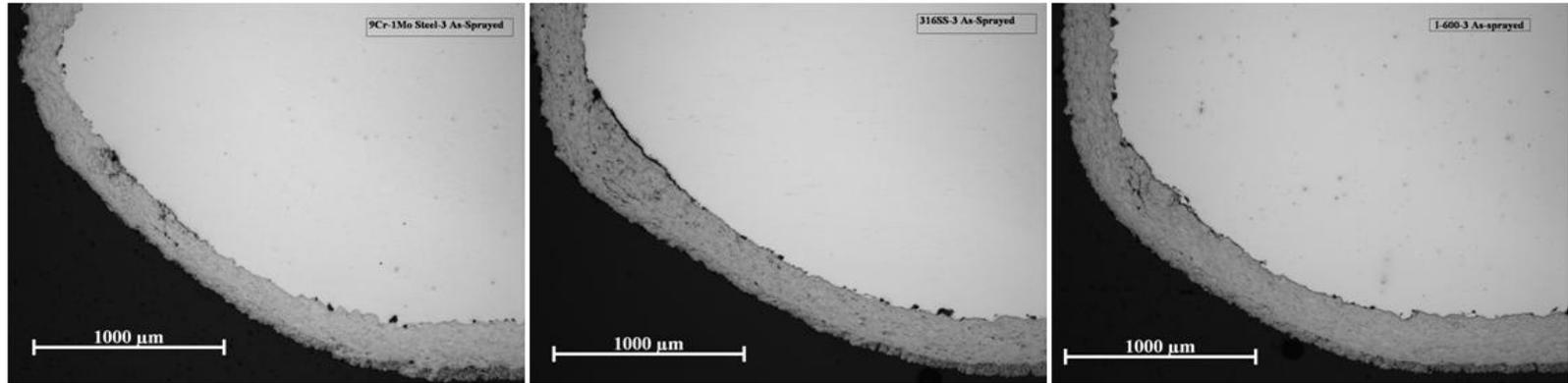
# Substrate Effects – Sample Fabrication

- Fully coating-encapsulated samples to assess the effects of CTE differences
- Fabrication method cannot involve harsh machining of the coating
- Sample geometry must not have sharp corners

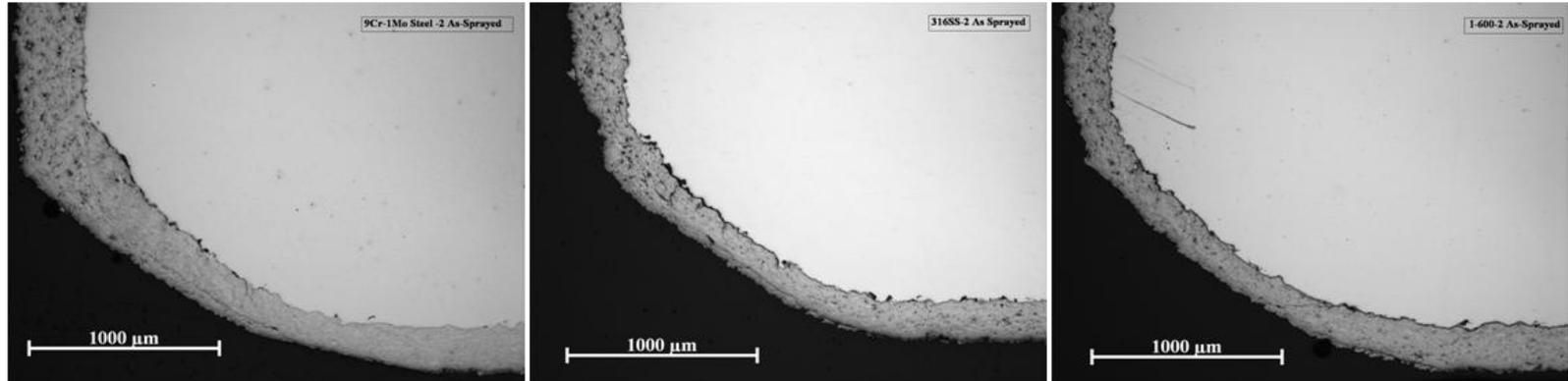


# HVOF, Fe<sub>3</sub>Al-Encapsulated Samples - Microstructure

$P_c=0.6$  MPa



$P_c=0.4$  MPa



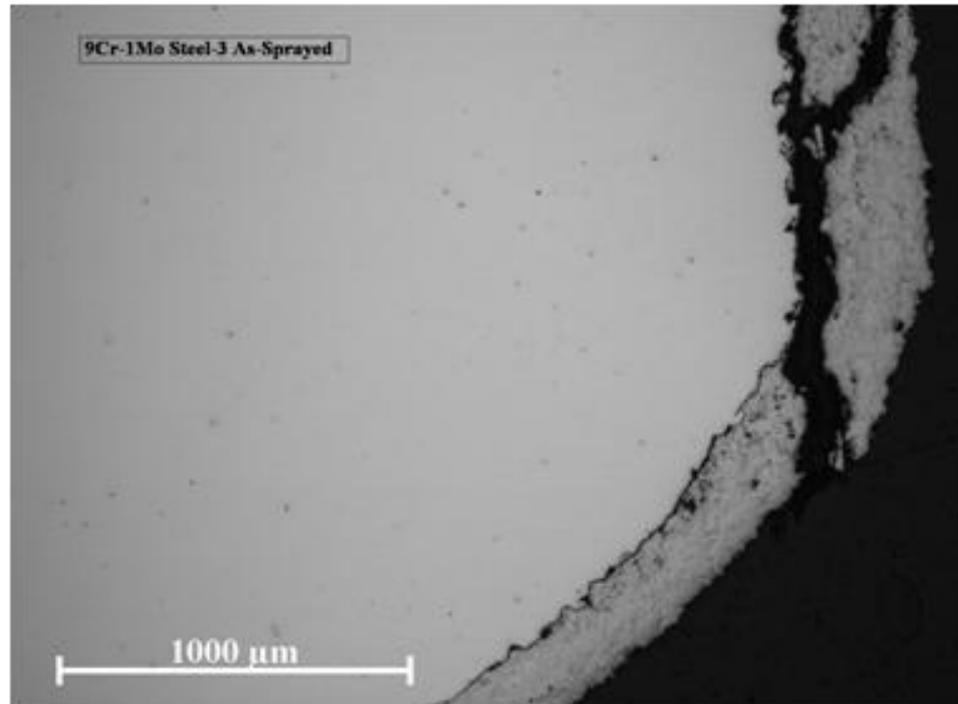
9Cr- 1Mo steel

316 SS

Inconel Alloy 600

# HVOF, Fe<sub>3</sub>Al-Encapsulated Samples – Potential Defects

- Delamination and cracking of the coating occurs occasionally on the parting surface
- Possible metallography artifact



# Exposure Tests for HVOF, Fe<sub>3</sub>Al-Encapsulated Samples

- **Started exposure tests using encapsulated samples, uncoated base metal samples and free standing coatings**
- **Long term aging tests (w/ periodic mass change data) in air to assess interdiffusion – 650°C for 9Cr-1Mo steel substrate and 800°C for 316 SS and Alloy 600 substrates – 5000 hrs tests**
- **Thermal cycling in air – 800°C, 4 hrs plus 500°C, 15 minutes – total time at 800°C to be 1000 hrs**

# Summary & Conclusions

- Oxidation of free standing HVOF Fe<sub>3</sub>Al coatings is similar to oxidation of bulk Fe<sub>3</sub>Al
- Open porosity in HVOF Fe<sub>3</sub>Al coatings results in breakaway oxidation
- Corrosion of HVOF Fe<sub>3</sub>Al coatings in simulated fossil fuel combustion atmospheres is similar to oxidation in air
- Corrosion/oxidation of HVOF Fe<sub>3</sub>Al coatings is lower than Inconel Alloy 600 in the environments studied
- Currently performing long term aging tests and thermal cycling tests in air on Fe<sub>3</sub>Al-encapsulated substrates to assess the effect of CTE mismatch on corrosion/oxidation behavior.