

# HVOF Thermal Spray TiC/TiB<sub>2</sub> Coatings for AUSC Boiler/Turbine Components for Enhanced Corrosion Protection



US DOE Project Number: DE-FE0008864  
Project Officer: Richard Dunst



Principal Investigator: Kanchan Mondal  
Southern Illinois University Carbondale

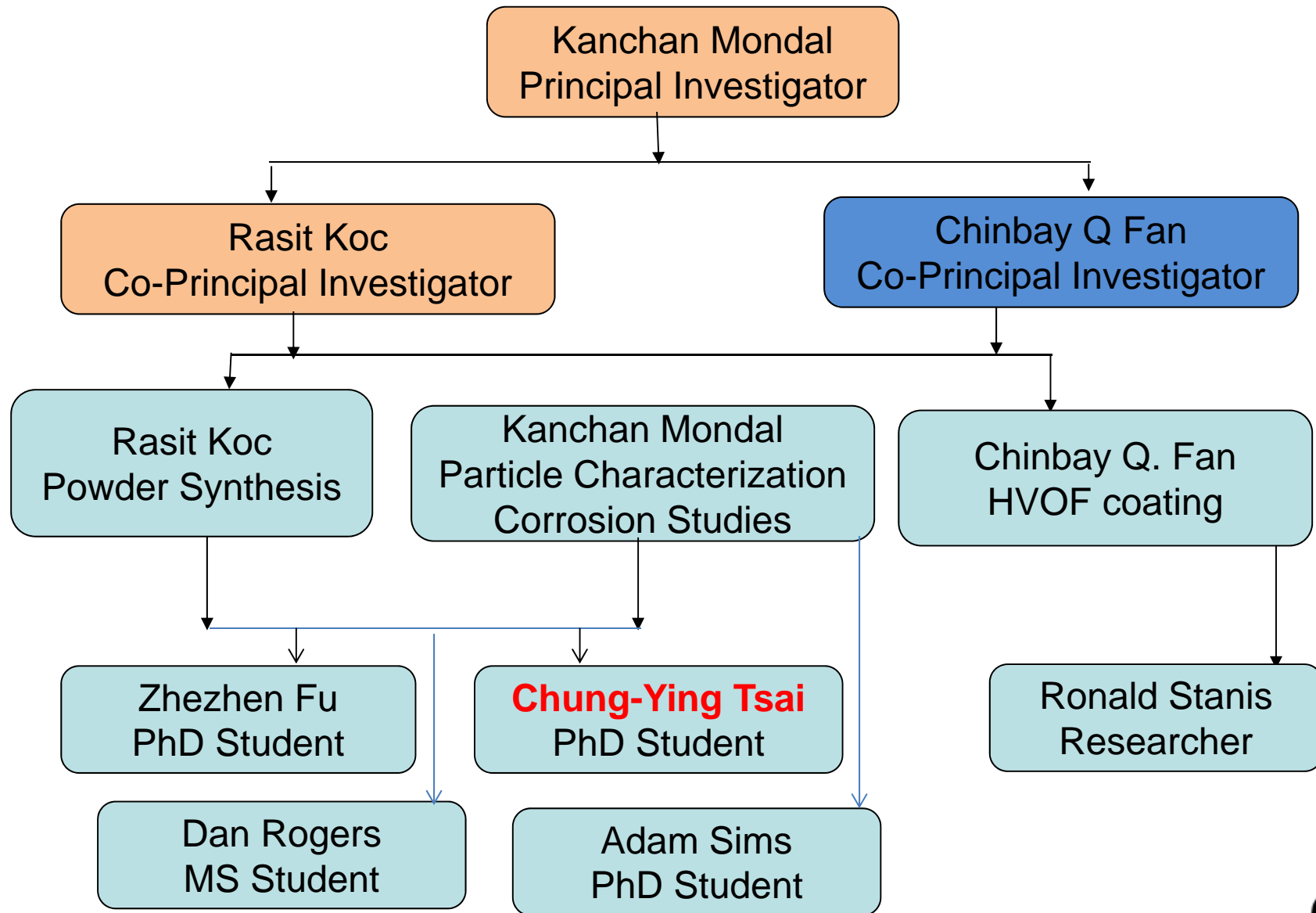
Co-Principal Investigator: Rasit Koc  
Southern Illinois University Carbondale

Co-Principal Investigator: Chinbay Fan  
Gas Technology Institute, Des Plaines

**Presenter: Chung-Ying Tsai**  
Southern Illinois University Carbondale

**2015 NETL Crosscutting Research Review Meeting**  
**Apr 27-30, 2015**

# PROJECT TEAM





*the Energy to Lead*

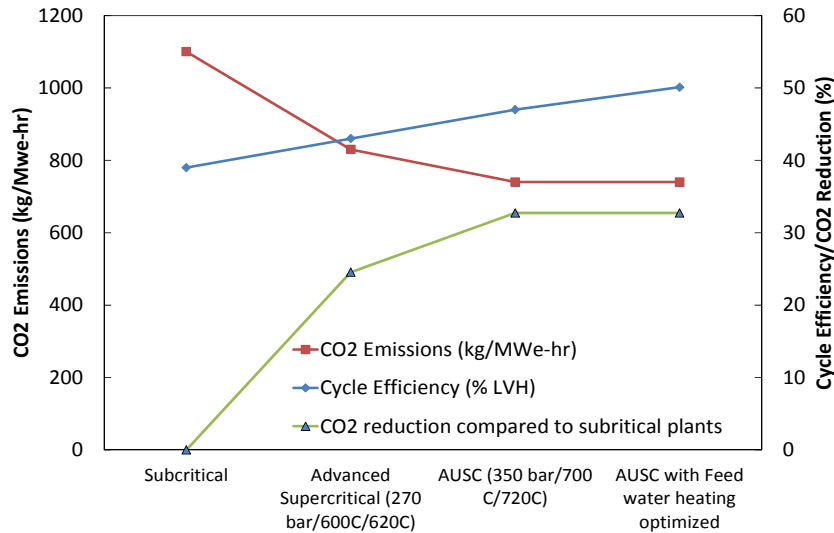
# HVOF, Flame Spray Coatings

---

GTI project number 21397

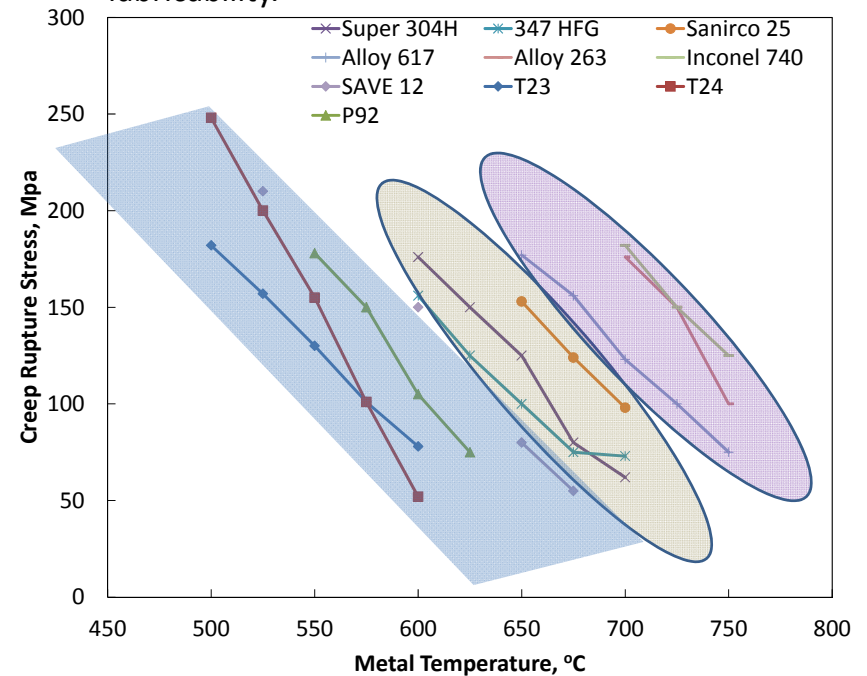
Chinbay Fan and Ronald Stanis

# Background

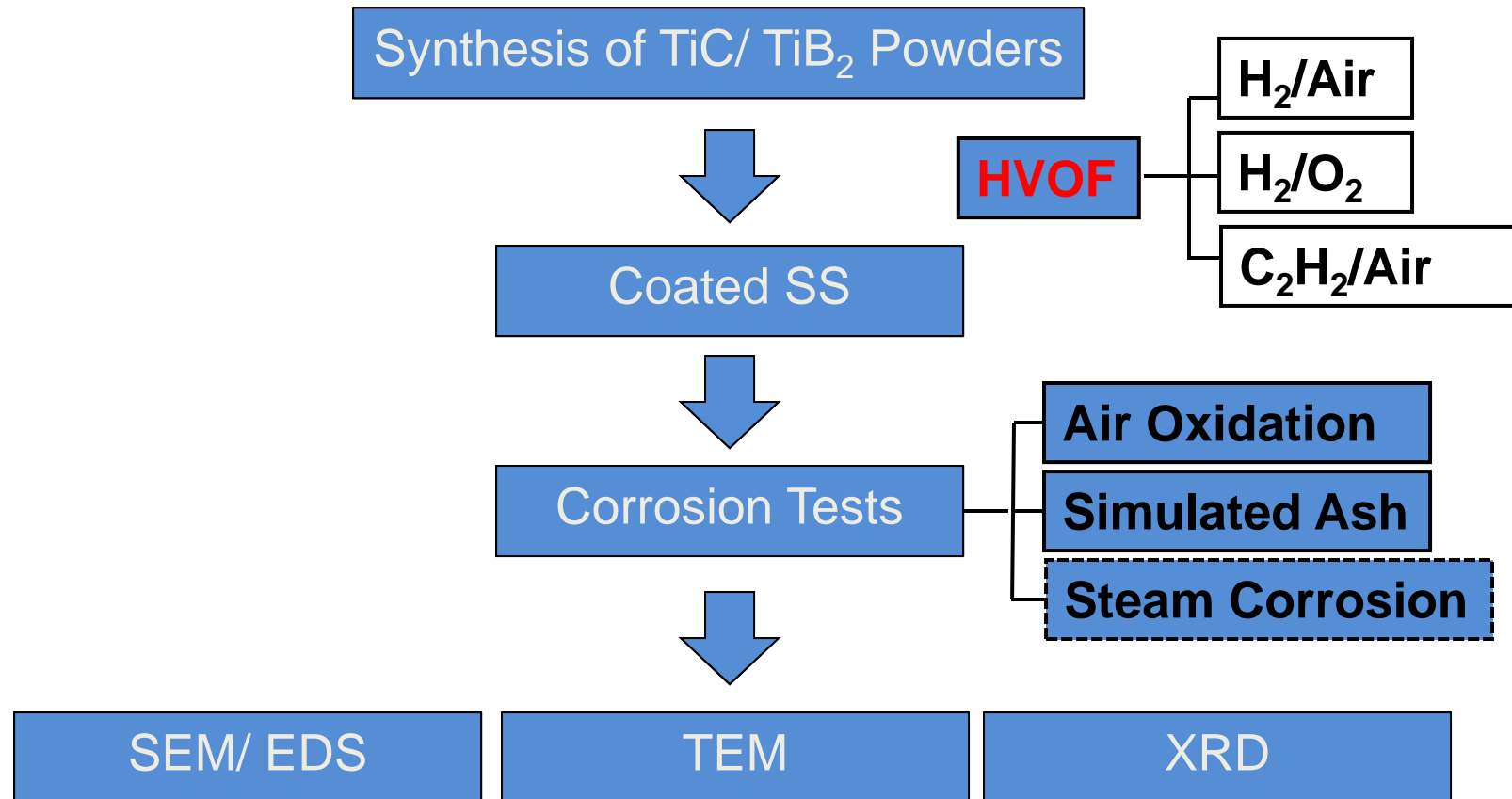


- Fire side corrosion
  - Due to molten Na/K/Fe trisulfates
  - Worst in the region of 600 – 750 °C
  - less than 600 – trisulfates are solid
  - above 750 – trisulfates vaporize
- Resistance increases with Cr content
  - 18-20 % Cr
  - Inconel 870H
  - Inconel 72
  - Inconel 671

- High Temperature, High Pressure, Supercritical water
- Mechanical Strength
  - Max Allowable Stress
  - Creep Rupture Stress
  - Fatigue Resistance
- Corrosion Resistance
  - Fireside Corrosion
  - Steamside Oxidation
- Thermal conductivity,
- Low coefficient of expansion, and
- Manufacturing process issues such as weldability and fabricability.



# Research Approach

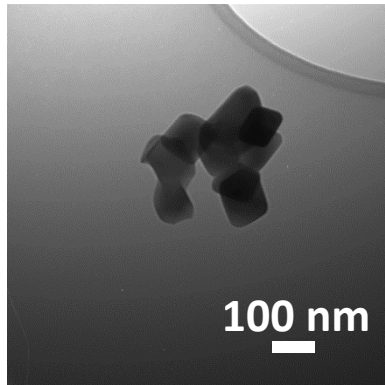


# Powder Physical Properties

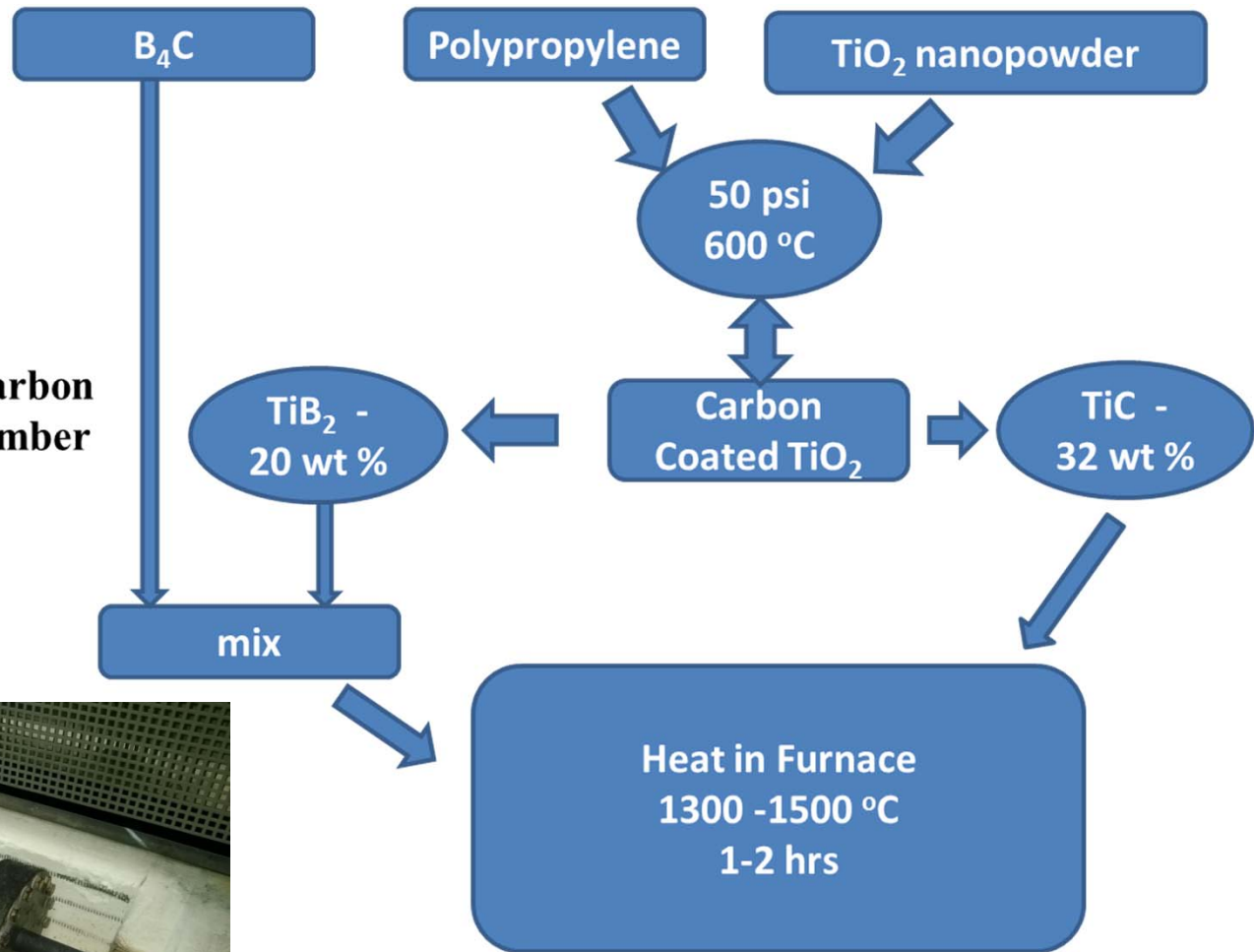
- High temperature strength retention
- Low thermal expansion coefficient
- High wear resistance
- High melting point
- Light weight

	Melting Temp	Density	Hardness	Young's
	°C	g/cm <sup>3</sup>	GPa	GPa
TiC	3070	4.65	28	456
TiB <sub>2</sub>	2900	4.5	34	570
B <sub>4</sub> C	2500	2.52	38	450

# Carbothermal Process for TiC and TiB<sub>2</sub> Powder Synthesis



Weight percent of carbon is determined by number of coating cycles



Different temperatures and reaction time were run to get fine particle size and distribution

## Substrates of Interest

	Substrate Material	Class	Applicable Component
1	Super 304H	Austenitic	SH/RH tubes
2	347HFG	Austenitic	SH/RH tubes
3	Sarnico 25	Austenitic	SH/RH tubes
4	HR3C	Austenitic	SH/RH tubes
5	STD617/CCA 617	Nickel Alloy	Tubing, HP turbine-casing, piping, rotor - 700 °C
6	Haynes 230	Nickel Alloy	SH tubes, HP turbine rotor – 700°C
7	Inconel 740	Nickel Alloy	SH tubes, HP turbine - casing, piping, rotor- 760 °C
8	Haynes 263	Nickel Alloy	HP turbine casing – 700 °C
9	P91/P92	Ferritic	Low Temp SH/RH
10	T91/T92	Ferritic	Low Temp SH/RH, HP turbine piping – 620°C
11	430	Ferritic	Boiler Tubes
12	T23/T24	Ferritic	Furnace Tubes



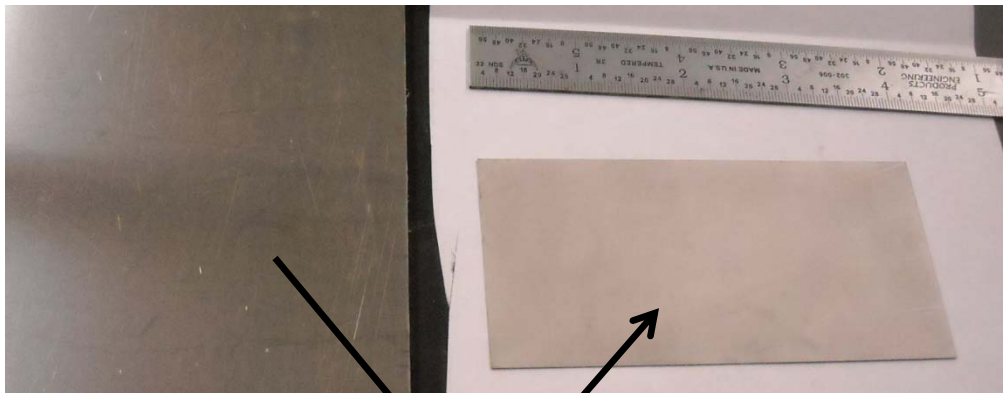
# GTI Flame Spray System

Fuel Flexible: Acetylene, H<sub>2</sub>, Kerosene...  
Oxidant Flexible: Air or O<sub>2</sub>



Stainless Steel As received

After surface roughening



Water honing

## Safety is first priority

Hearing protection

Eye protection (light)

Face Shield

Flame arrestors

Two person operation

One holding gun

One operating gas flows

Emergency Stop Button

# Spray Deposition

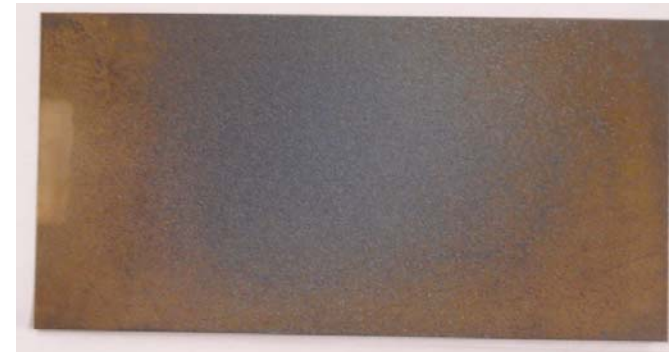
Just Flame



Partially Covered Samples



Flame with Powder

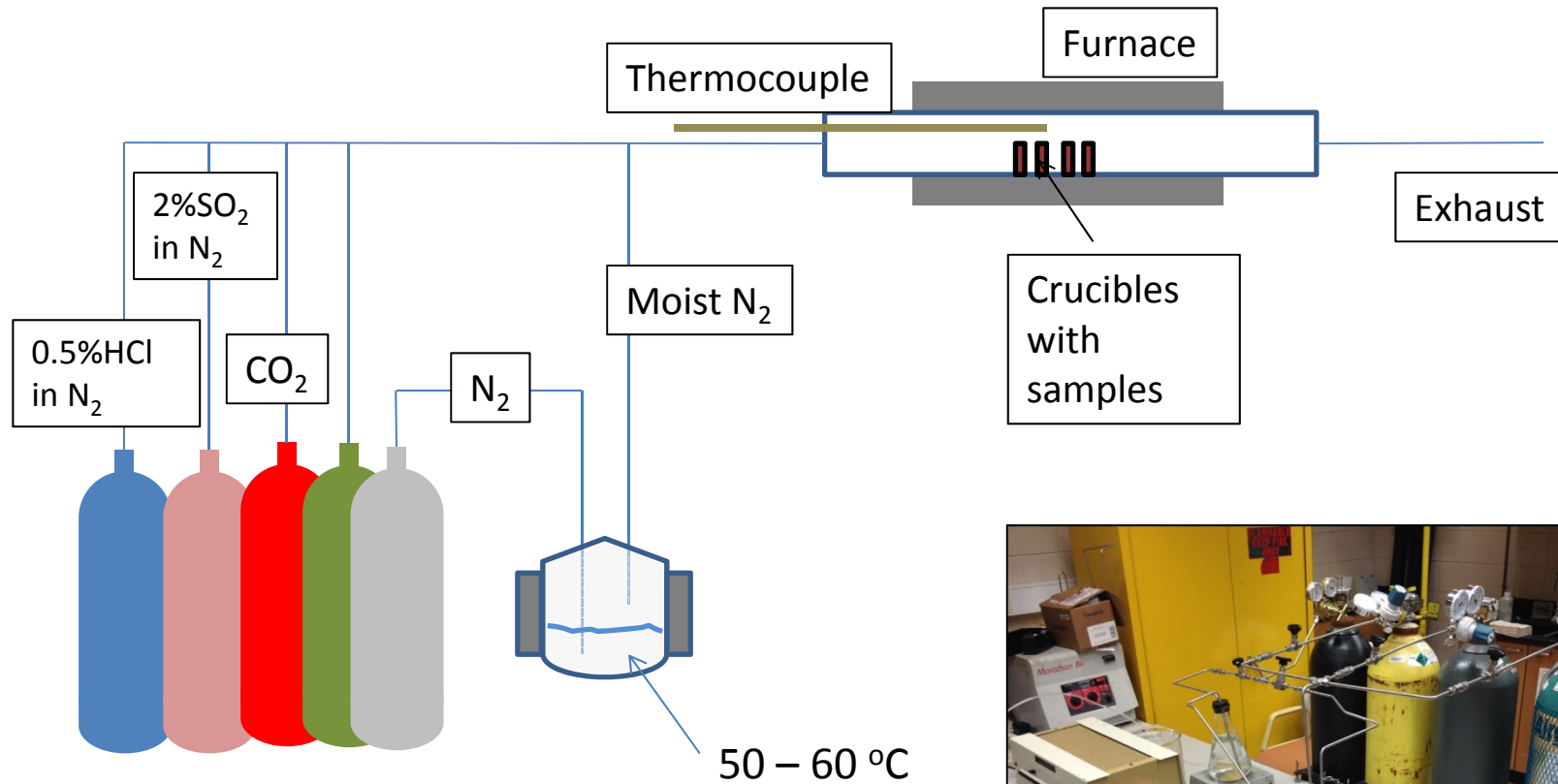


**SS 304H** C(0.04-0.1) Si(0.75) Mn (2) P (0.045) S (0.03) **Cr (18-20) Ni (8-10.5)**

**SS 430** C(0-0.12) Si (0-1) Mn (0-1) **Cr(16-18) Ni(0)**

**P91** C(0.08-0.12) Si(0.2-0.5) Mn (0.3-0.6) **Cr(8-9.5) Ni(0.4 max)**

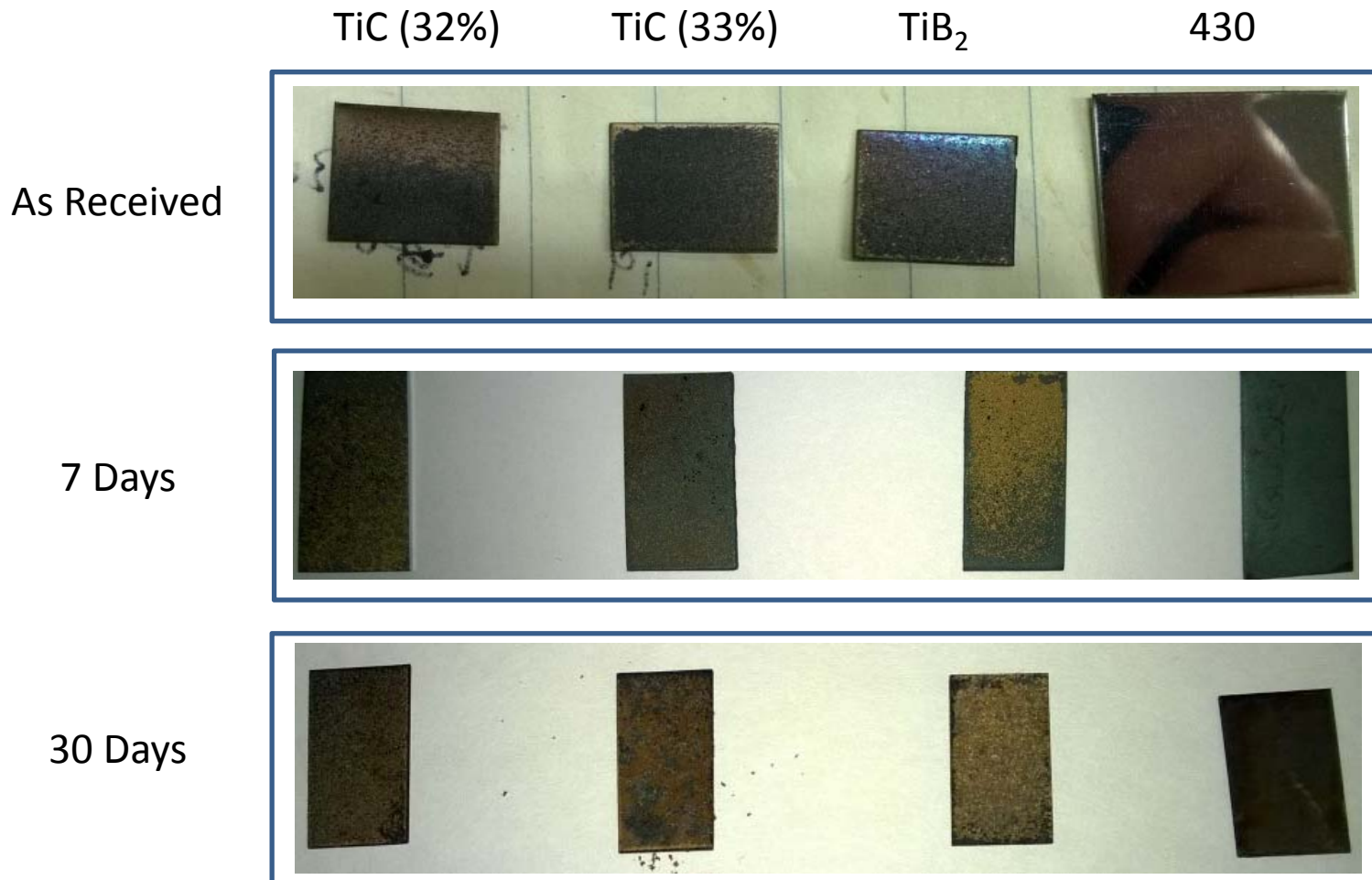
# Corrosion Test Setup



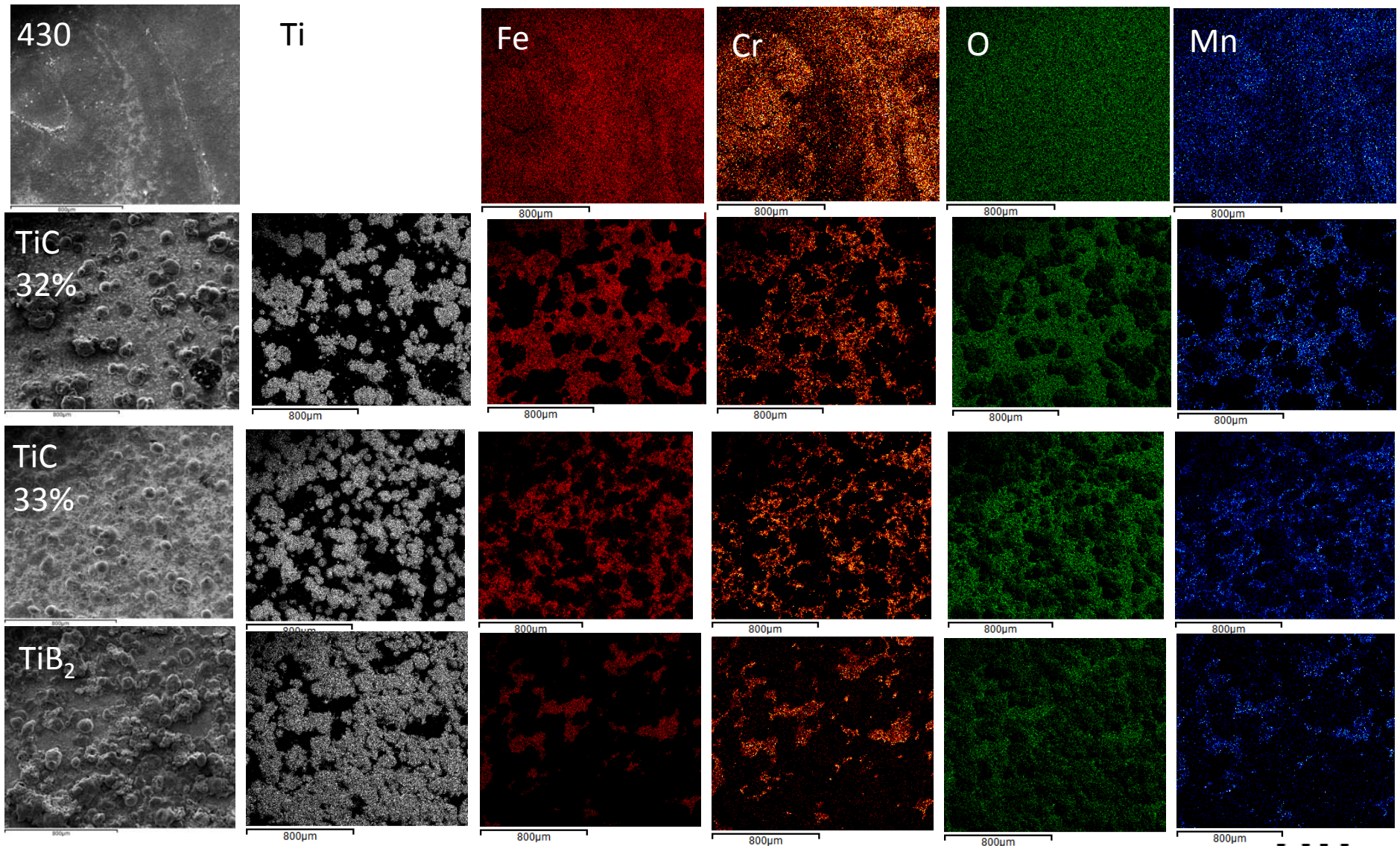
# Summary of Coated 304H Samples after Simulated Flue Gas Tests

	500°C	600°C	650°C	700°C
Titanium	No noticeable oxidation or sulfurization (coated)	S - Less (coated)	S, O – Less (coated)	O -Less (coated)
TiB <sub>2</sub>		S - <b>Significantly</b> less (coated) O -slightly less (coated)	S - <b>Significantly</b> less (coated) S, O – concentrated (around coated)	O -Less (coated)
TiC		S - <b>Significantly</b> less (coated) O- <b>Significantly</b> less (coated) S, O – concentrated (around coated)	S - <b>Significantly</b> less (coated) O -slightly less (coated)	S - <b>Significantly</b> less (coated) O -slightly less (coated)

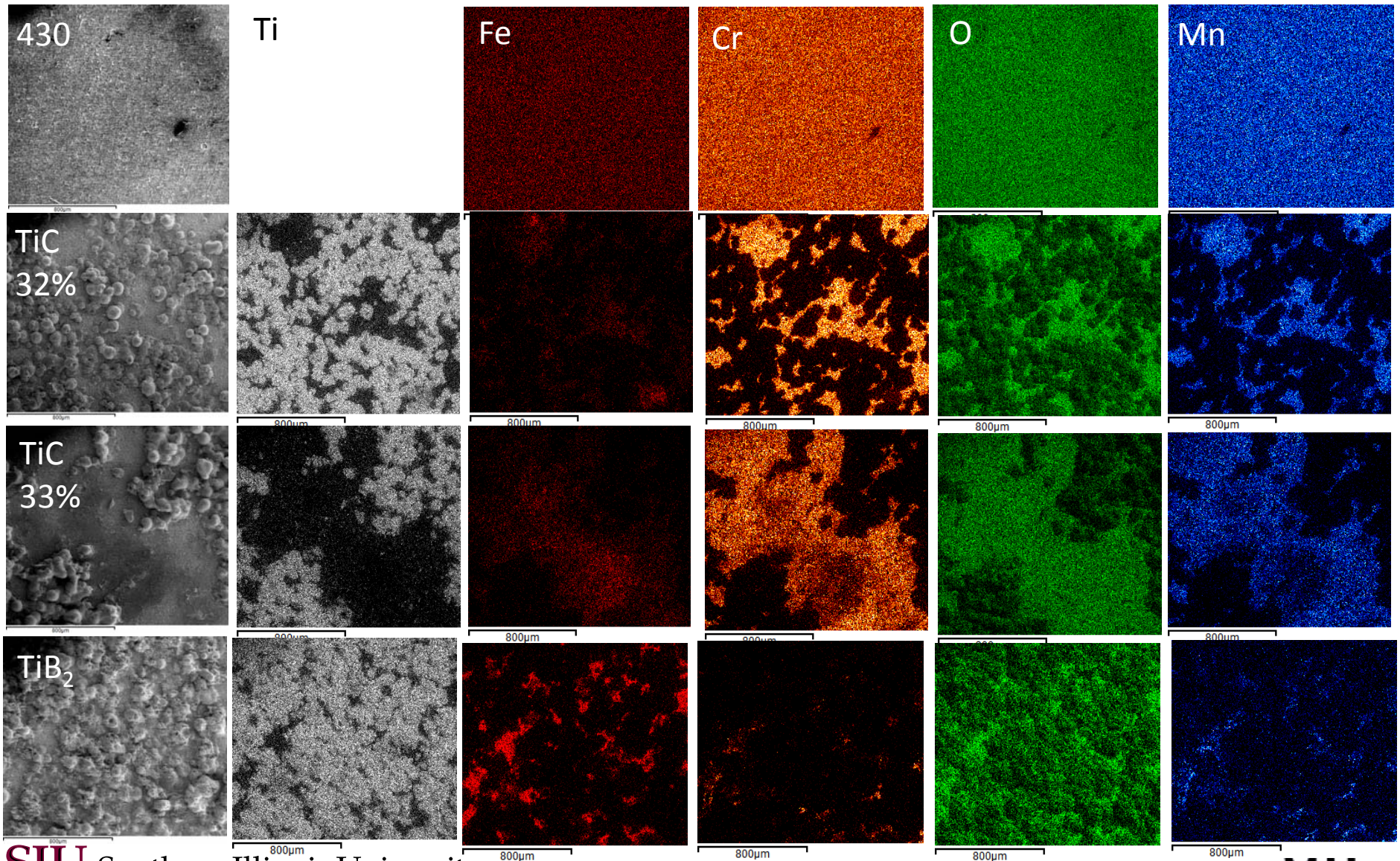
# Coated 430 Substrates: Simulated Flue Gas Test- 750 °C



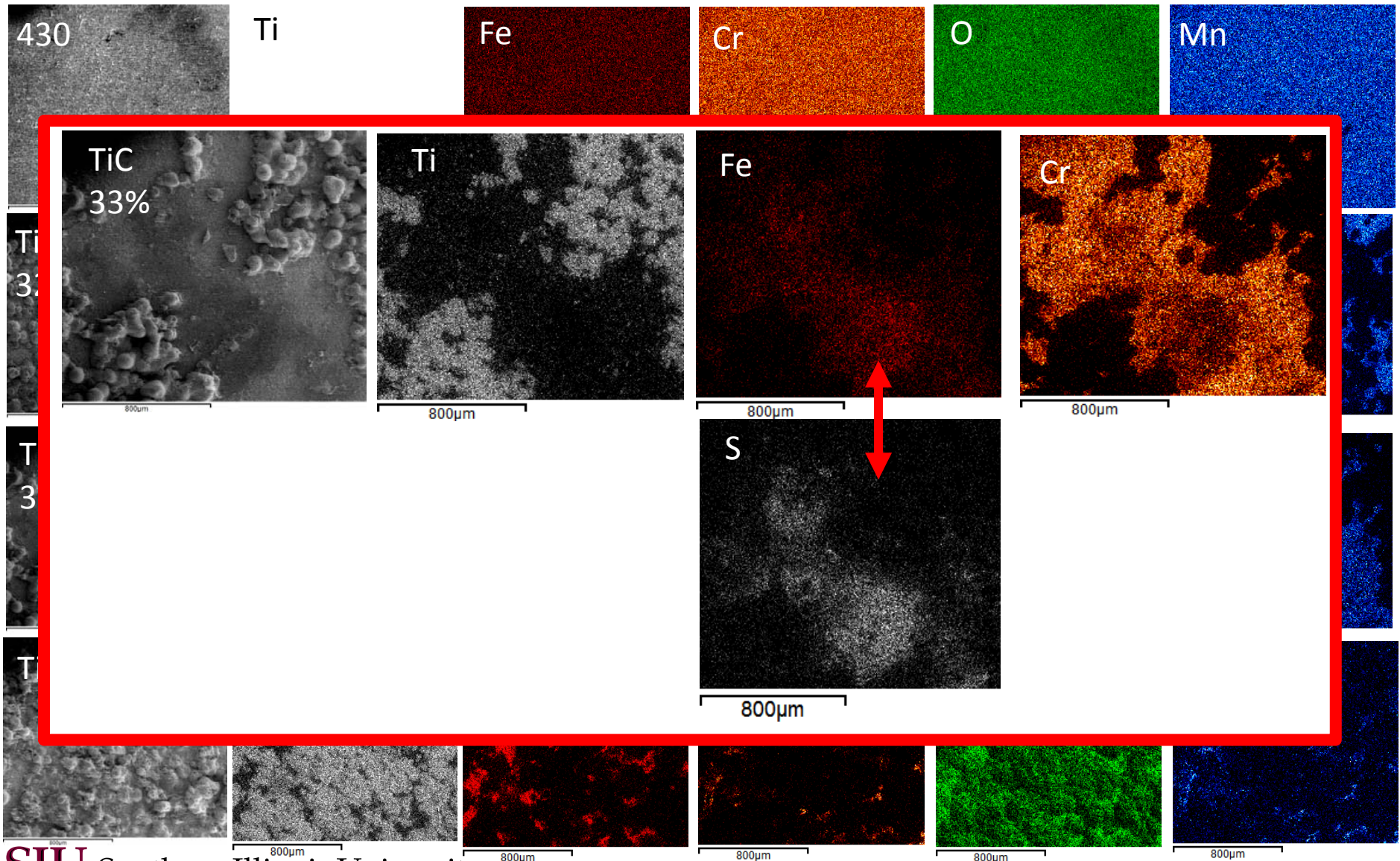
# Simulated Flue Gas Test: 7 Days



# Simulated Flue Gas Test: 30 Days



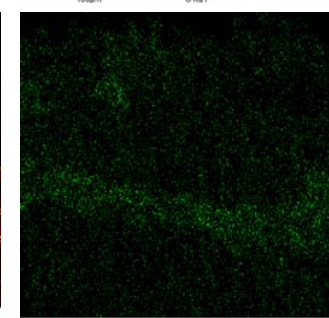
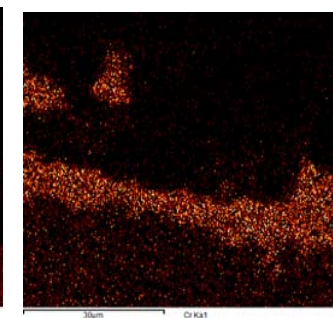
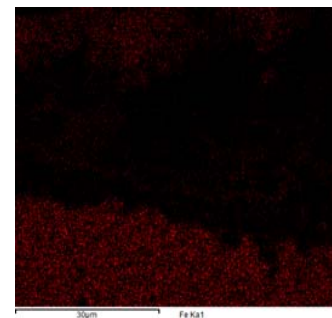
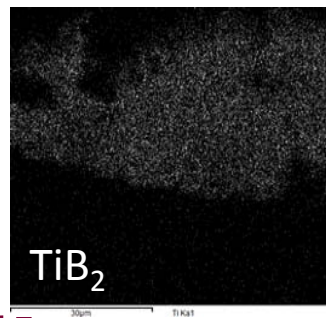
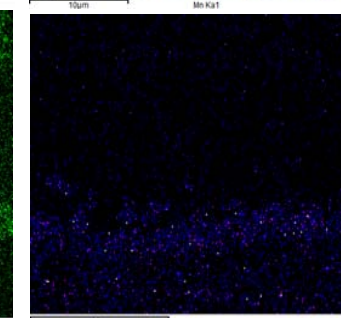
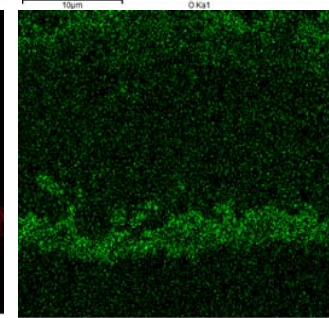
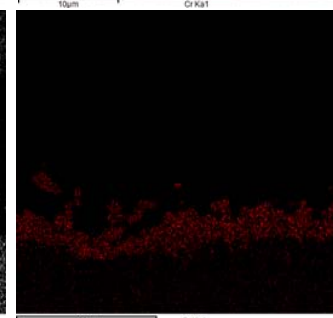
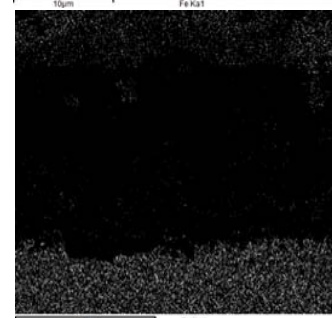
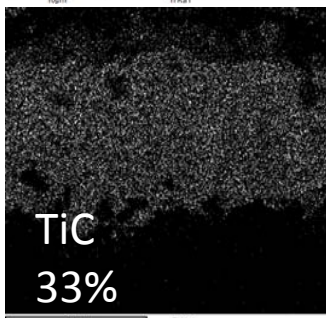
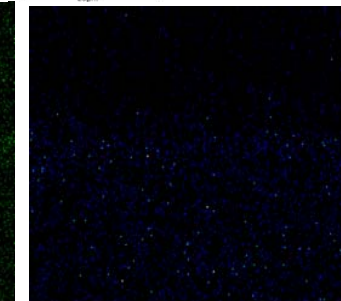
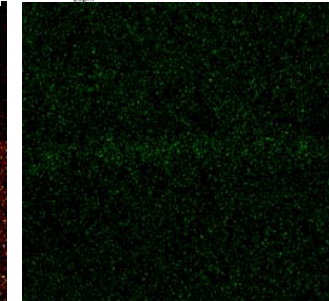
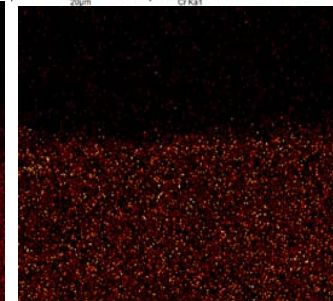
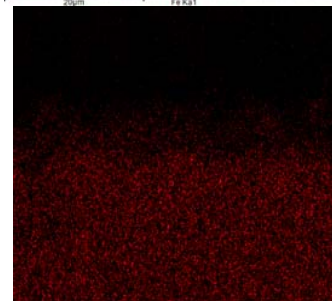
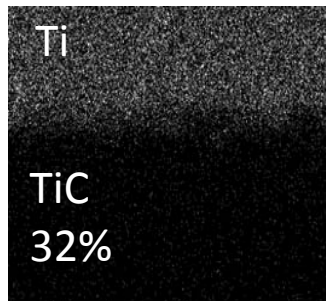
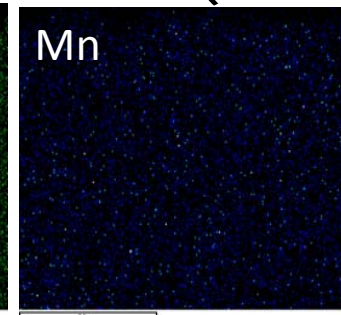
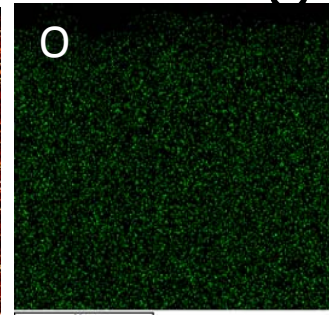
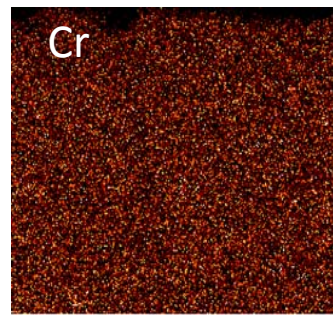
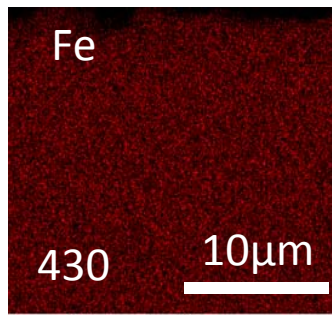
# Simulated Flue Gas Test: 30 Days



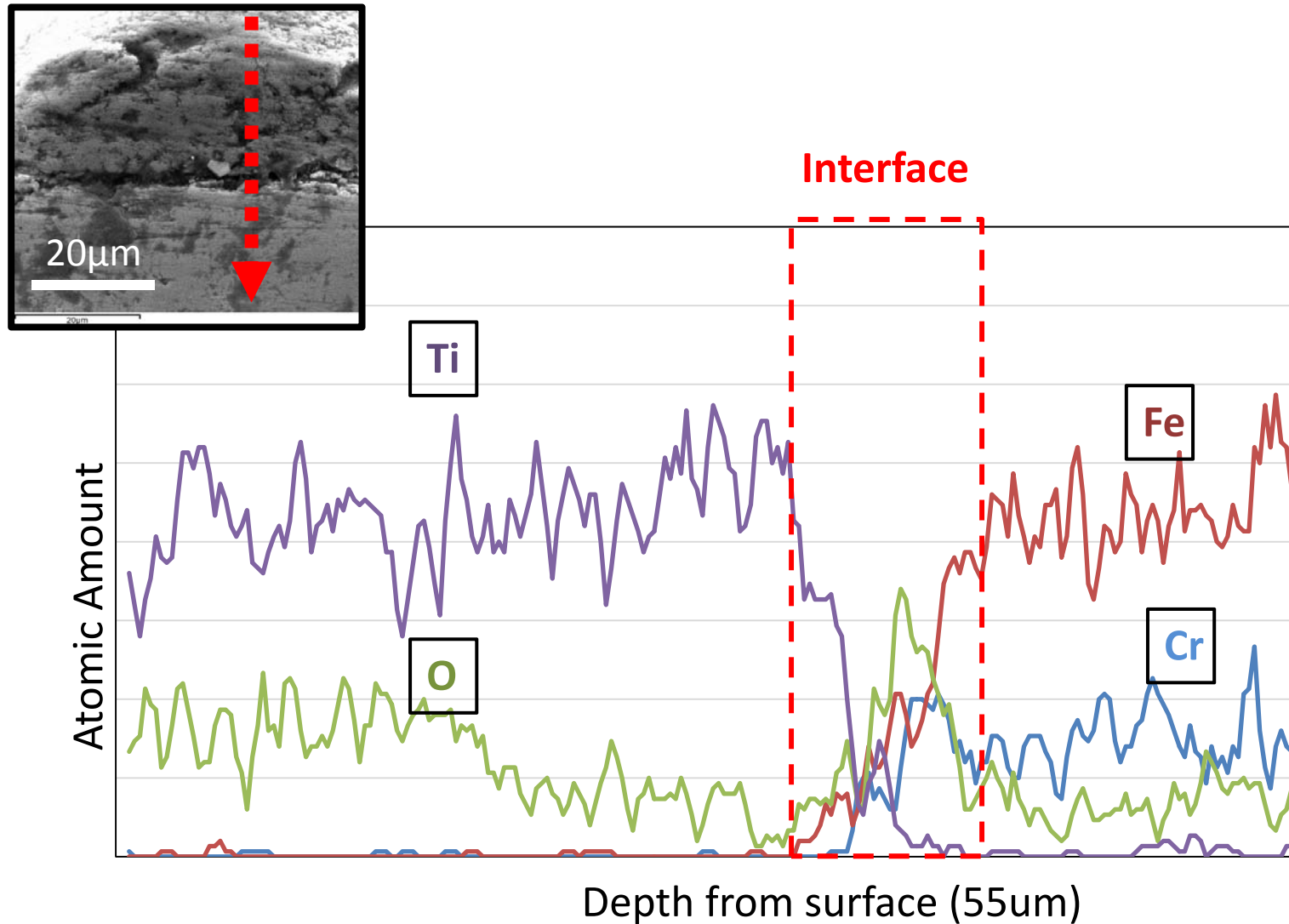


# Oxidation resistance from coating: TiC (32%)

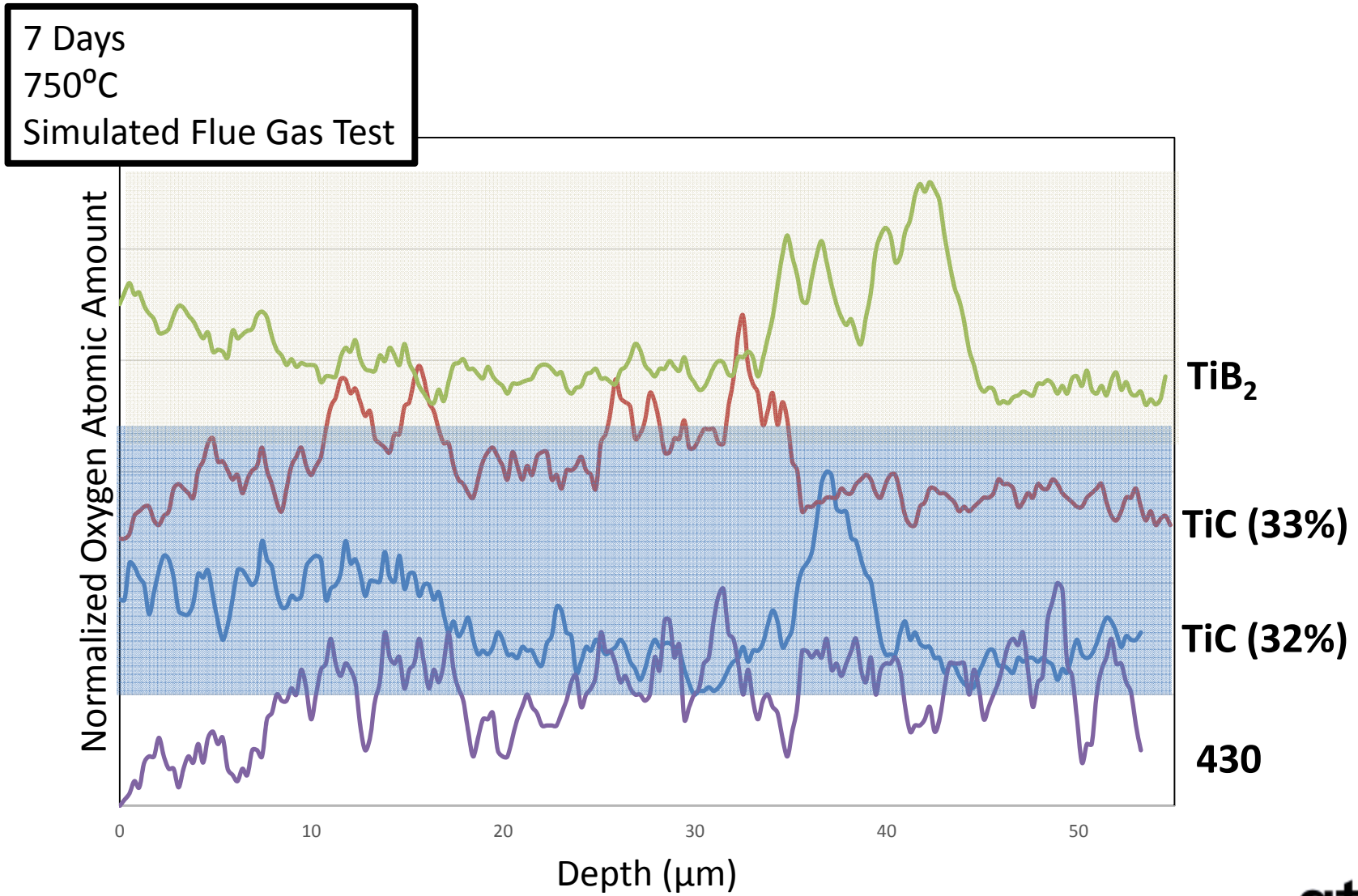
7 days



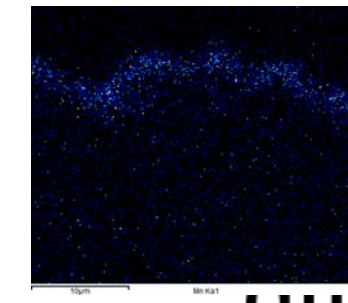
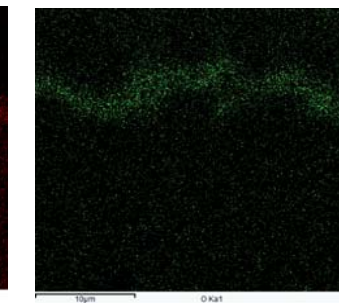
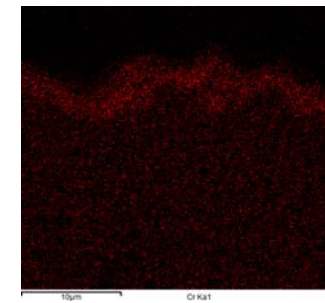
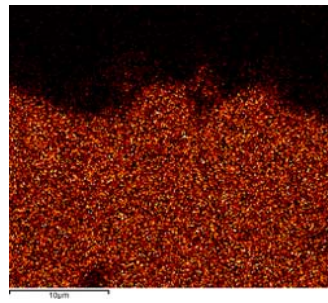
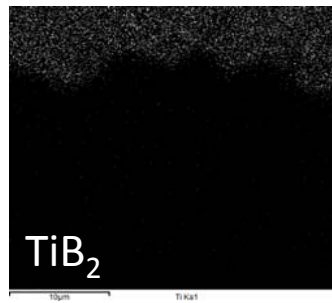
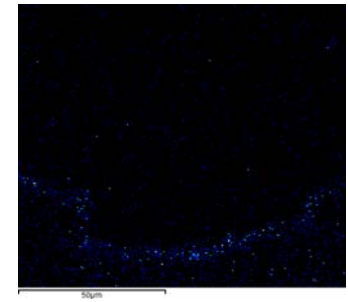
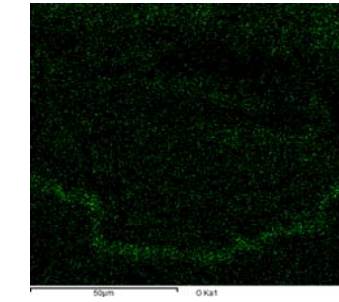
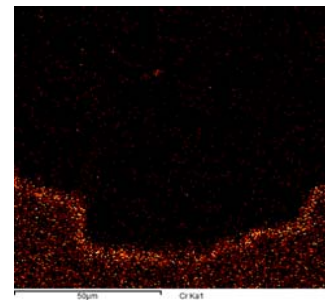
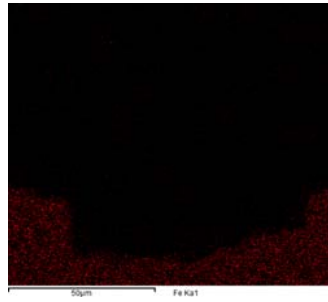
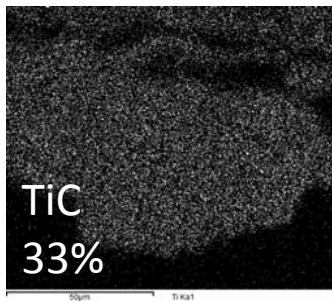
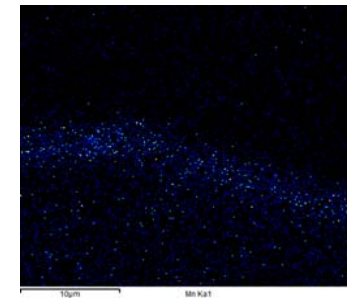
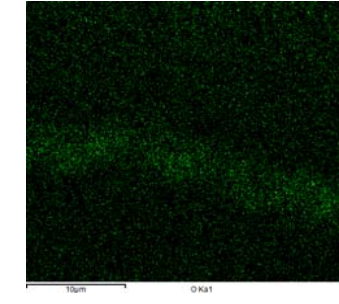
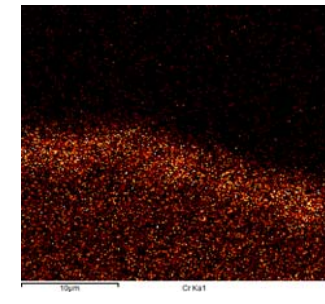
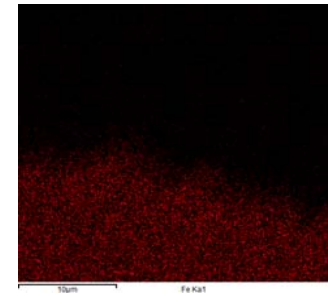
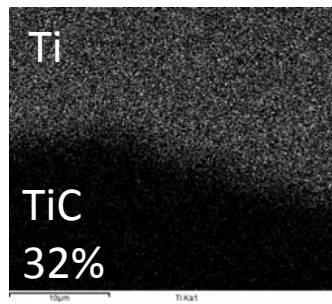
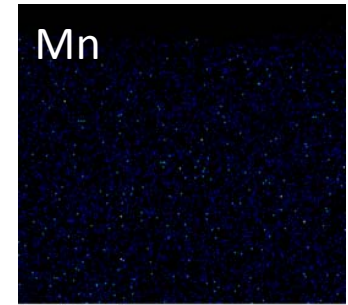
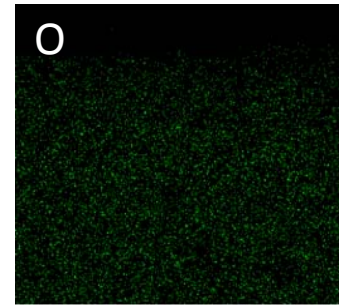
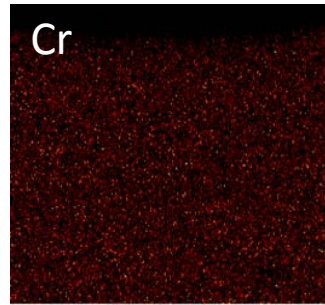
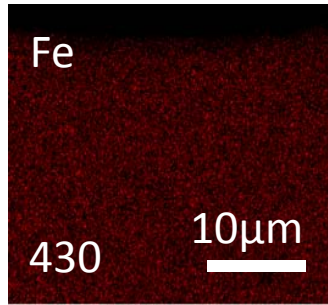
# Oxidation resistance from coating: TiC (32%)



# Oxidation Resistance: Oxygen Penetration

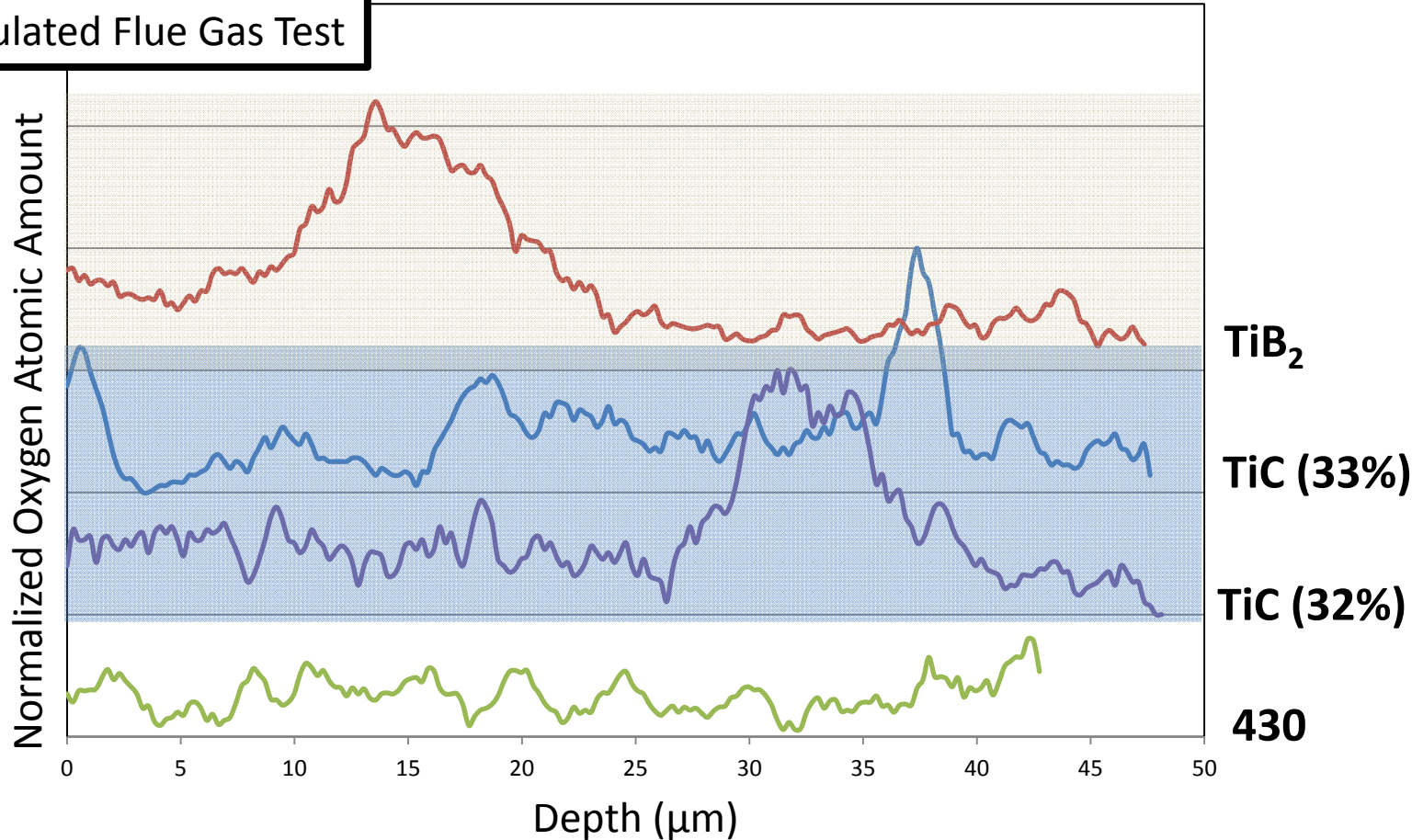


30  
days

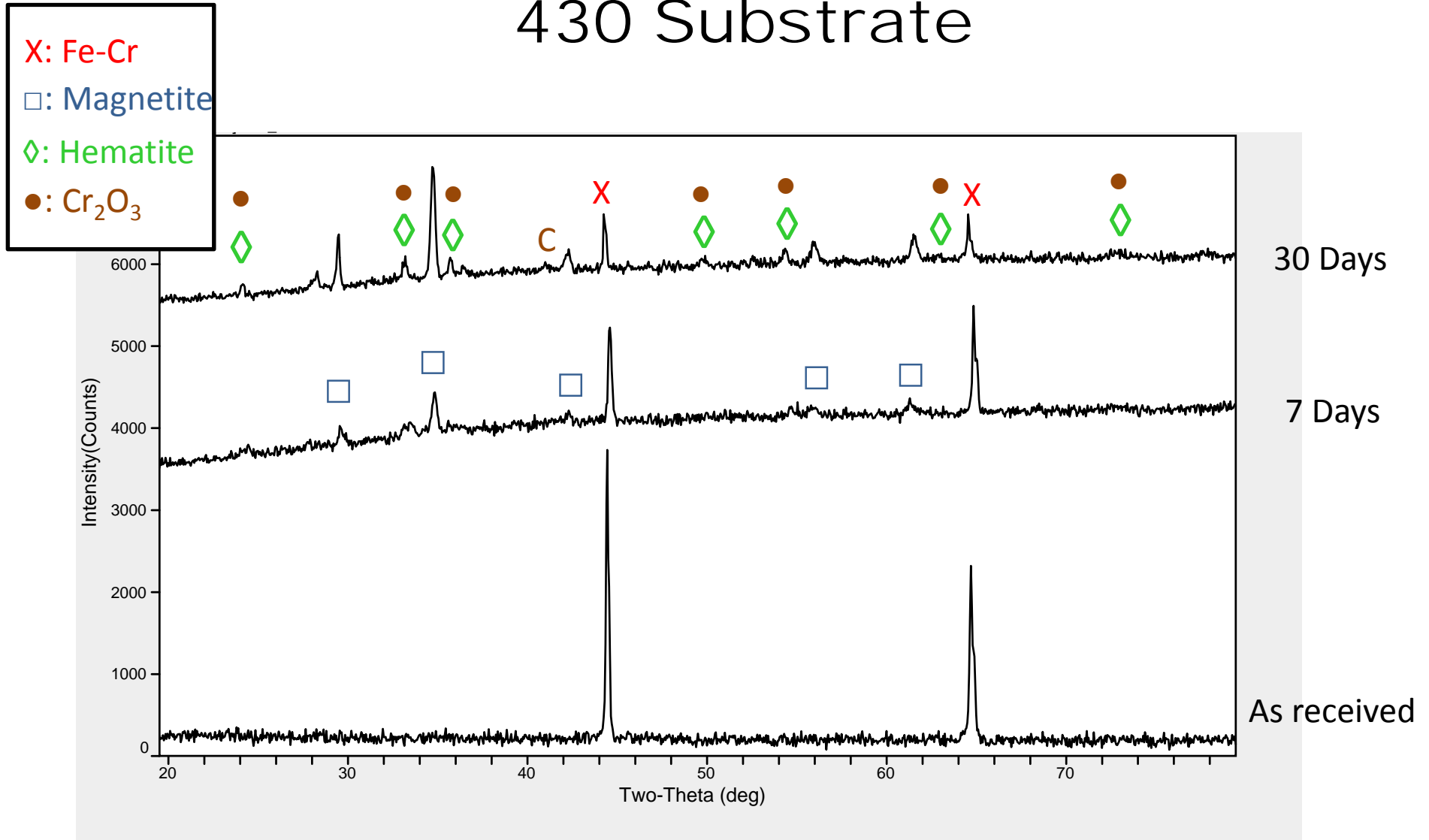


# Oxidation Resistance: Oxygen Penetration

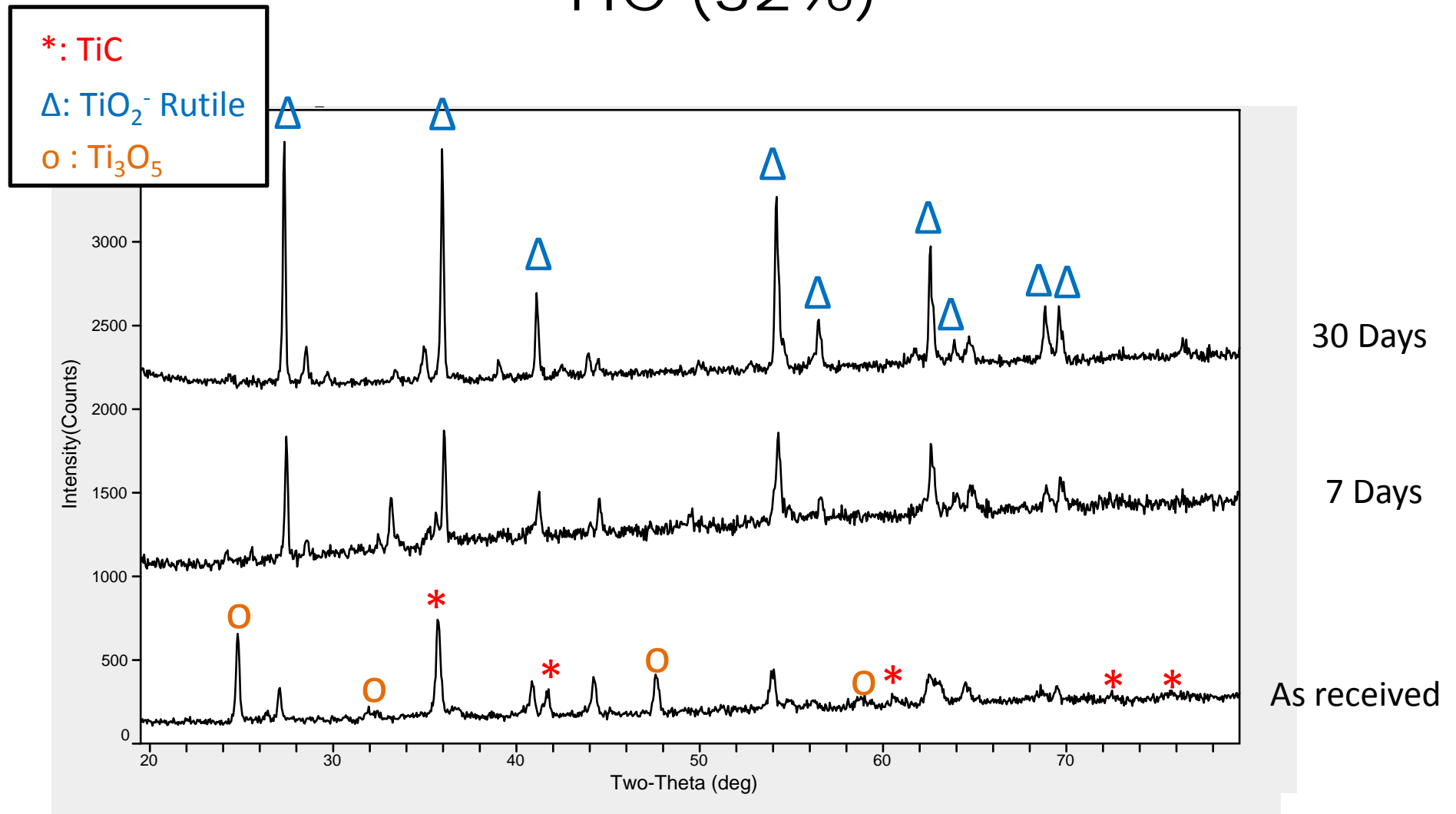
30 Days  
750°C  
Simulated Flue Gas Test



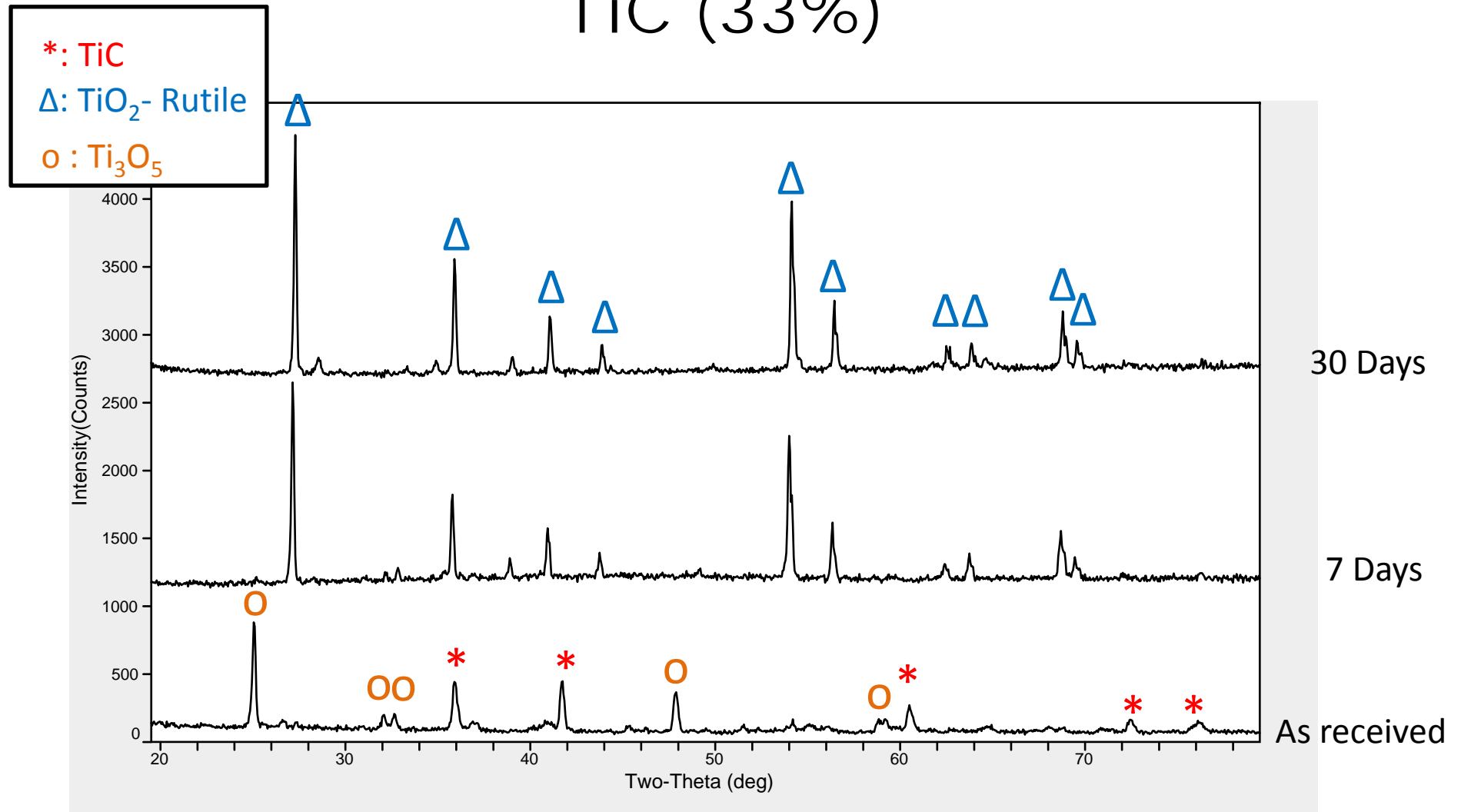
# Impact of simulated flue gas at 750°C 430 Substrate



# Impact of simulated flue gas at 750°C TiC (32%)

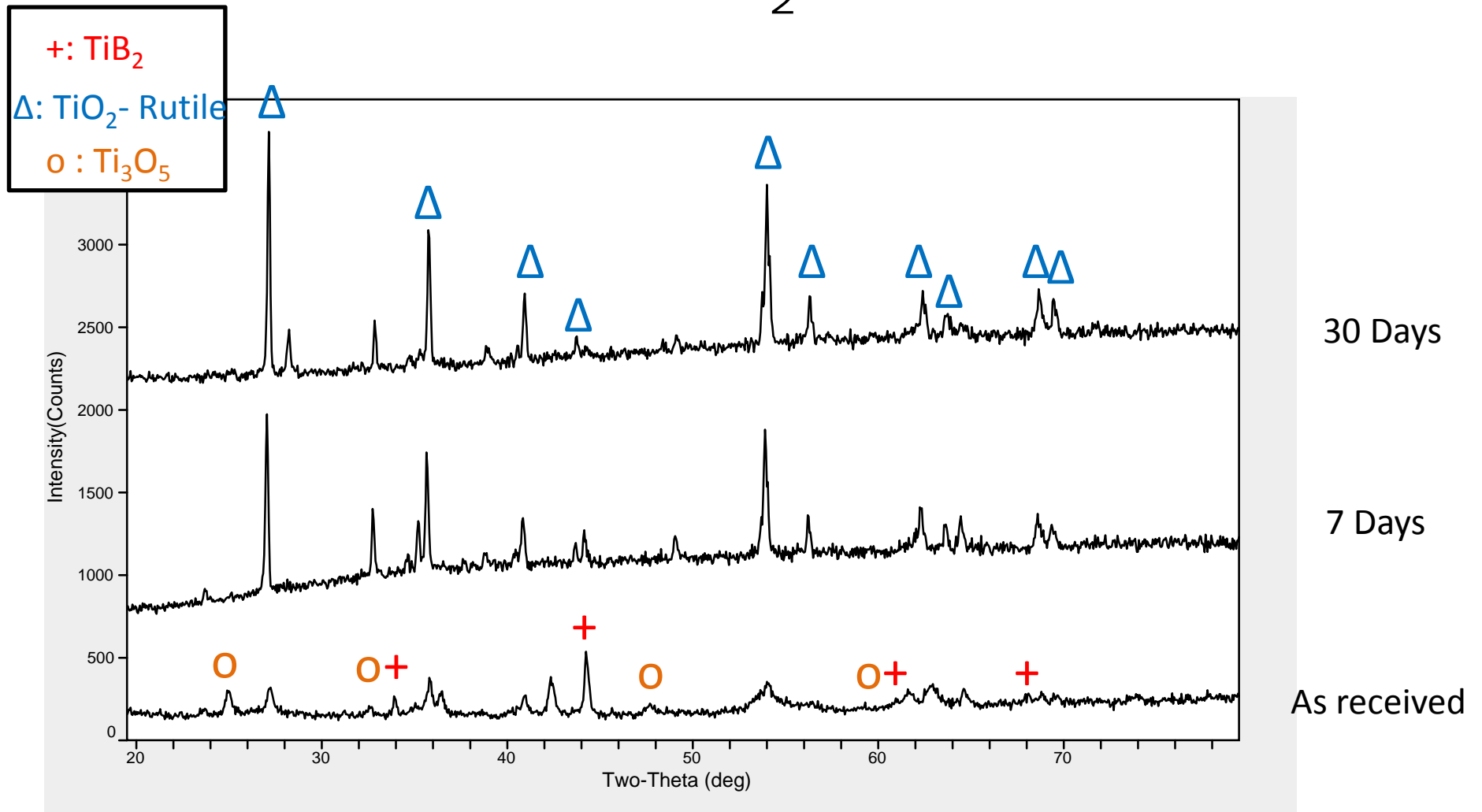


# Impact of simulated flue gas at 750°C TiC (33%)





# Impact of simulated flue gas at 750°C $TiB_2$



# Summary of Coated 430 Samples after Simulated Flue Gas Tests

	750°C- 7 Days	750°C- 30 Days
TiC (32%)	<p>O - Slight concentrate (Interface) - Lower (beyond interface)</p> <p>TiO<sub>2</sub> - (surface)</p>	<p>O - Increased amount (Interface) - Lower (beyond interface)</p> <p><b>Chromium Oxide</b> - (Interface)</p> <p>TiO<sub>2</sub> - Sharper XRD peaks</p>
TiC (33%)	<p>O - Slight concentrate (Interface) - Lower (beyond interface)</p> <p><b>Chromium Oxide</b> - (Interface)</p> <p>TiO<sub>2</sub> - (surface)</p>	<p>O - Less (Interface) - Lower (beyond interface)</p> <p><b>Chromium Oxide</b> – Thinner layer (Interface)</p> <p>S - concentrated (at Fe, surface)</p> <p>TiO<sub>2</sub> - Sharper XRD peaks</p>
TiB <sub>2</sub>	<p>O - Slight concentrate (Interface) - Lower (beyond interface)</p> <p><b>Chromium Oxide</b> - (Interface)</p> <p>TiO<sub>2</sub> - (surface)</p>	<p>O - Less (Interface) - Lower (beyond interface)</p> <p><b>Chromium Oxide</b> – Thinner layer (Interface)</p> <p>TiO<sub>2</sub> - Sharper XRD peaks</p>
430	<p><b>Magnetite</b></p>	<p><b>Hematite</b></p> <p>Cr<sub>2</sub>O<sub>3</sub> – (Surface)</p>

# On-going Task: P91 Steel Substrates

<b>HVOF Spray coating</b>	
<b>Spray Parameters</b>	
<b>H2 Flow rate</b>	76 LPM
<b>O2 Flow rate</b>	13 LPM
<b>N2 Flow rate</b>	1.8 LPM (Low Flow)/ 3.6 LPM (High Flow)
<b>Spray Distance</b>	27cm

Samples		Coating Time (min)	Coating Powder	Coating Conditions
A		0	Control, no coating	Glass blasted, then surface ground
B	Side A	12	TiC 32%C 1500C 2hr	Low N2 carrier flow
	Side B	3	TiC 32%C 1500C 2hr	High N2 carrier flow
C	Side A	12	Ti Metal	Low N2 carrier flow
	Side B	3	Ti Metal	High N2 carrier flow
D	Side A	12	TiC 32%C 1500C 2hr	High N2 carrier flow
	Side B	12+12	TiC 32%C 1500C 2hr	High N2 carrier flow
E		0	Glass Blasted Control	As-received metal had heavy surface corrosion
F	Side A	12	TiC 32%C 1500C 2hr	Glass blasted, Low N2 carrier flow
	Side B	12	TiC 32%C 1500C 2hr	Glass blasted, High N2 carrier flow

# Achievements

- Facile synthesis of sub micro TiC and TiB<sub>2</sub> powders.
- HVOF thermal spray coating of the prepared powders on 304H, 430, and P91 substrates.
- Corrosion test analysis of coated 304H and 430 substrates.
- Increased longevity and corrosion resistance of the coated substrates subjected to fireside corrosion in AUSC SH/RH tubes and boiler tubes.



# Acknowledgement

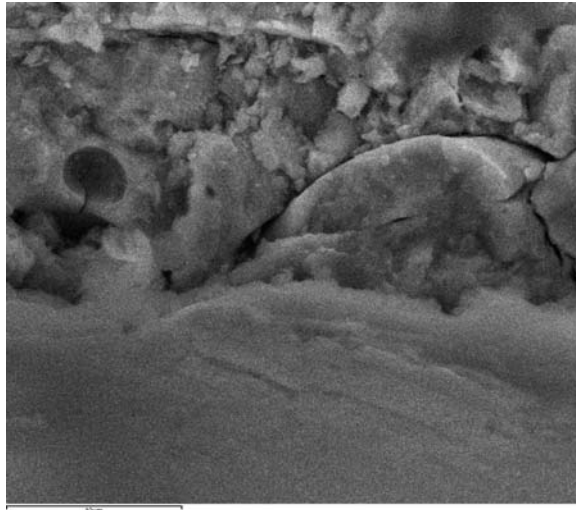


US DOE Project Number: DE-FE0008864  
Project Officer: Richard Dunst

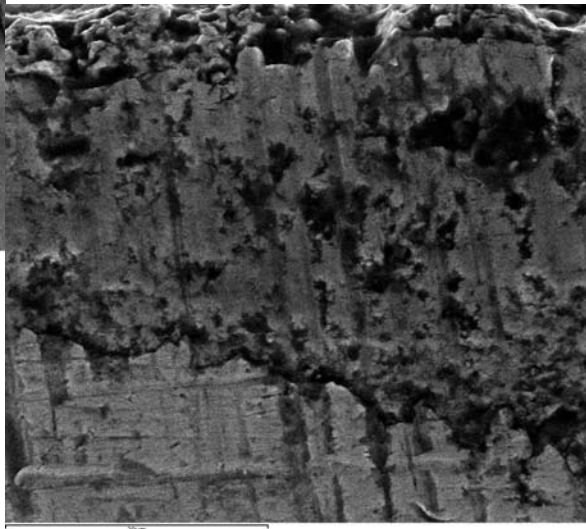


# Thank You.

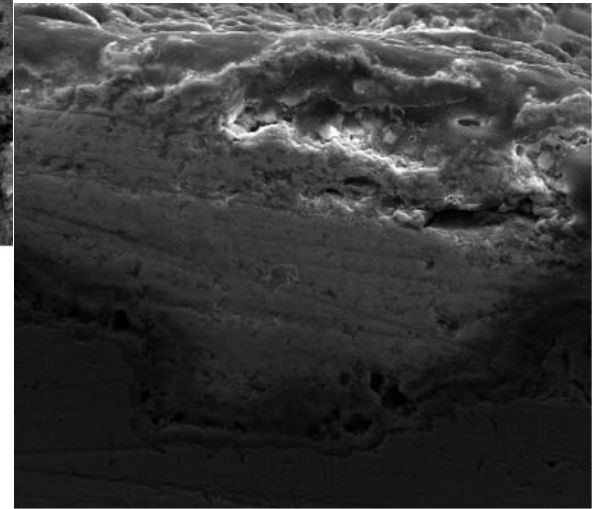




As received

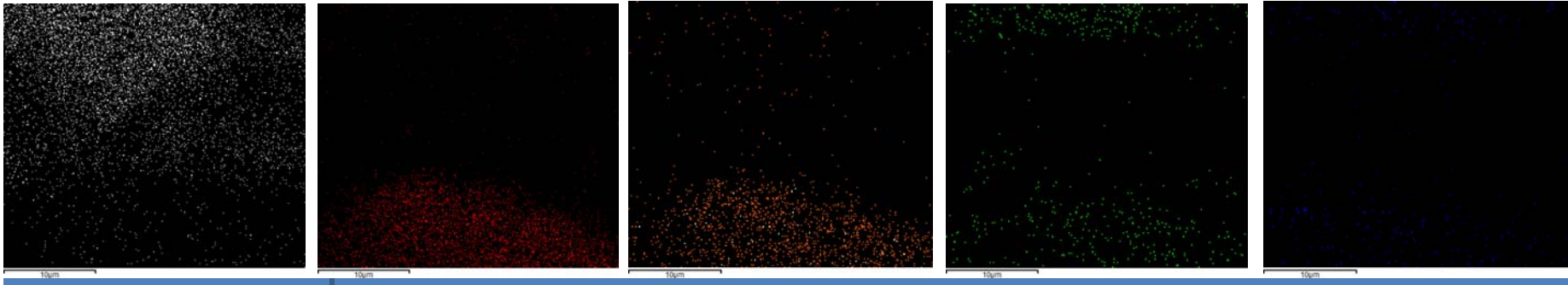


7 Days

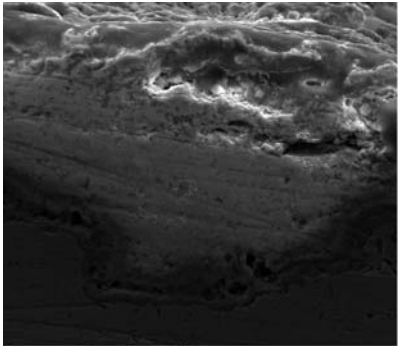
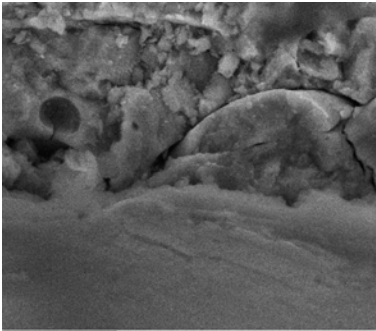


30 Days

TiC (33%) Coated 430



As Prepared



Treated at 750 °C  
for 1 month

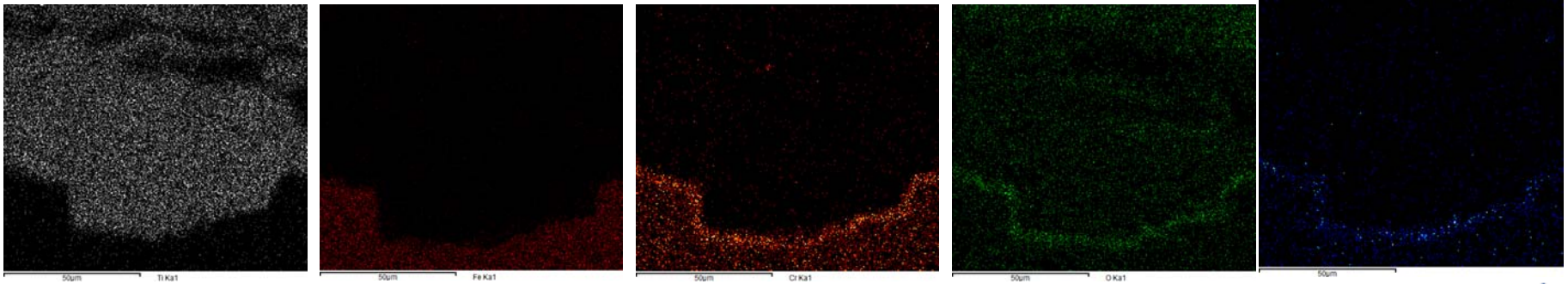
Ti

Fe

Cr

O

Mn



TiC (33%) Coated 430

Ti

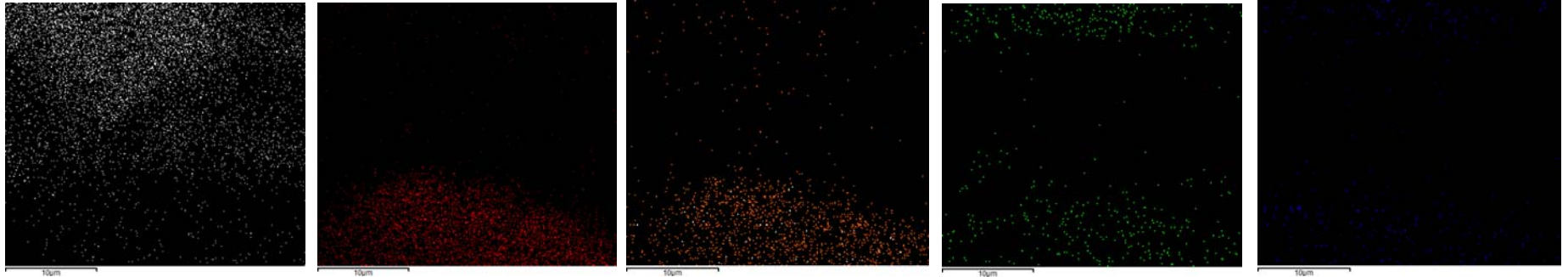
Fe

Cr

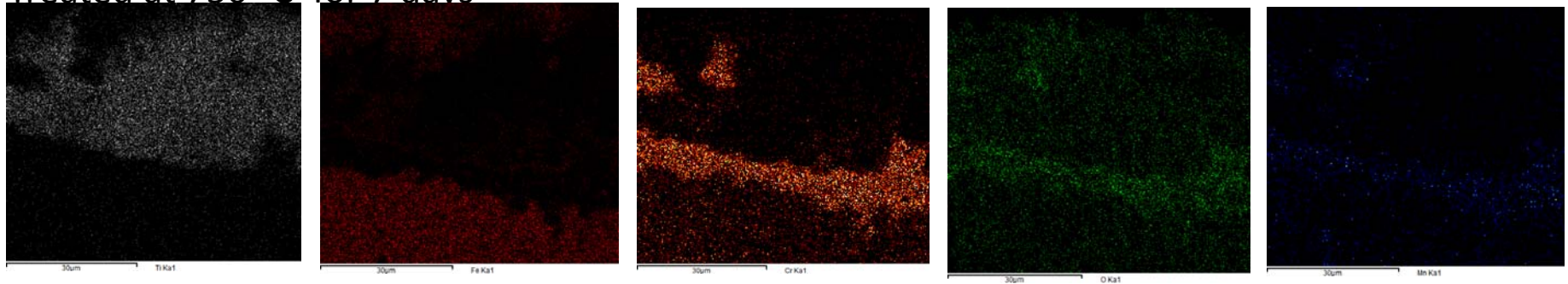
O

Mn

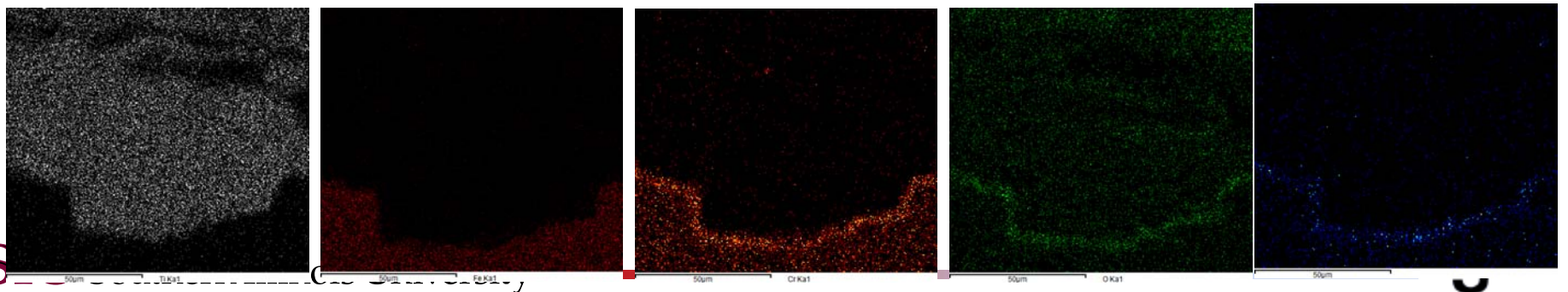
As Prepared



Treated at 750 °C for 7 days



Treated at 750 °C for 30 days

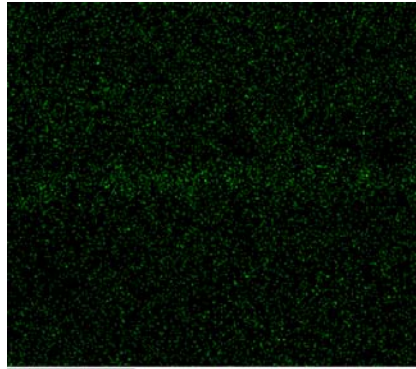




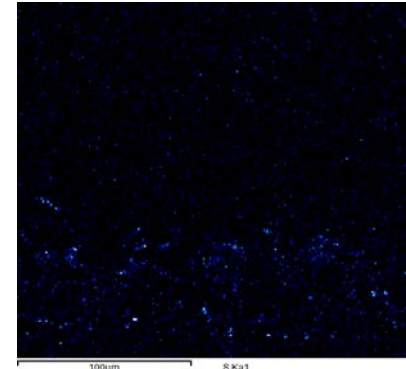
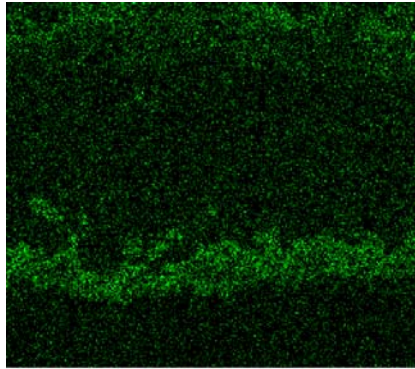
O

S

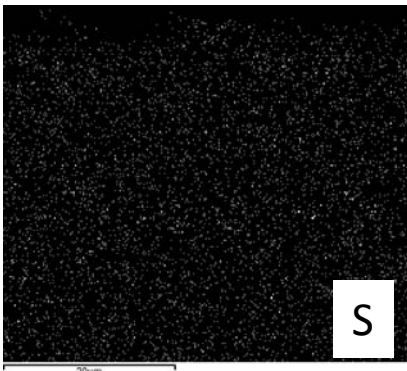
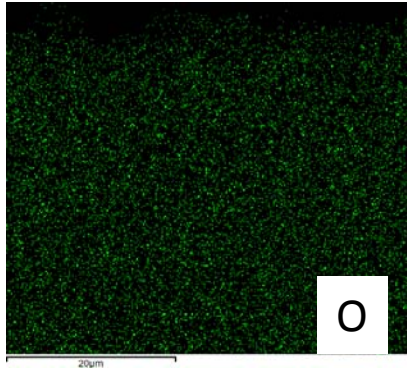
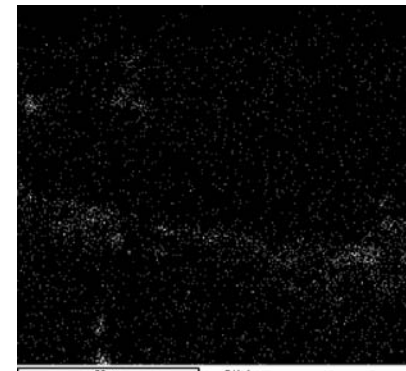
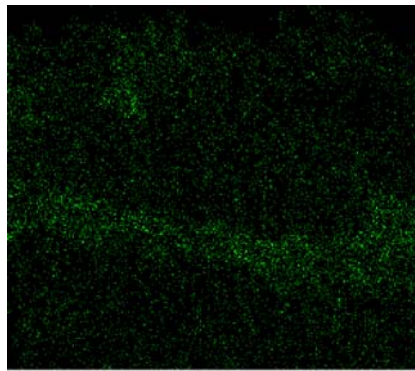
TiC  
32%



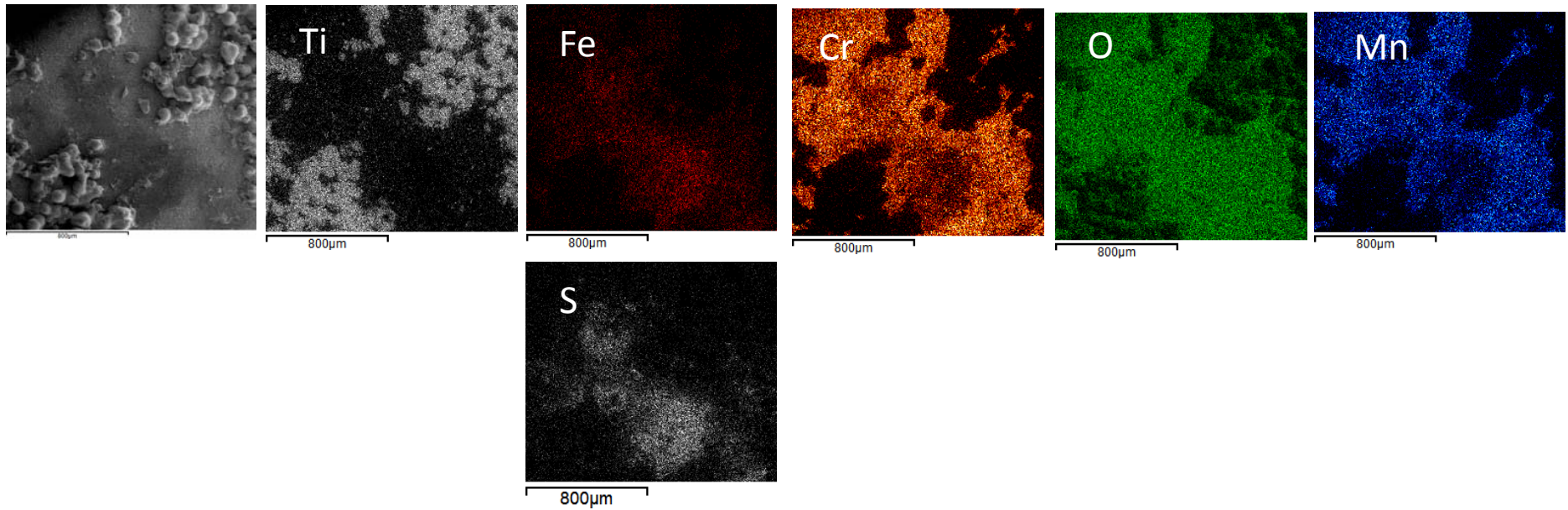
TiB<sub>2</sub>



TiC  
33%



# Simulated Flue Gas Test: 30 Days



# Objectives and Tasks

## Major Project Objectives

- Synthesis of nanoparticles of TiC by a patented process.
- Extension of the process to synthesize nano sized TiB<sub>2</sub> powder.
- Optimization for HVOF spray coating of the TiC and TiB<sub>2</sub> on select ferritic, austenitic and nickel alloy samples generally used for water wall tubing, high temperature boiler sections, turbine blades and USC tubing applications.
- Laboratory evaluation of the corrosion resistance of the coatings employing simulated flue gas and simulated ash.
- Selection of optimum alloy protection system in different temperature/chemical regimes
- Field evaluation of fabricated probes of select coating in actual boiler/turbine environment

***Task I: Project Management and Planning.***

***Task II: TiC and TiB<sub>2</sub> powder synthesis***

***Task III: Sample Acquisition***

***Task IV: HVOF Spray Coating***

***Task V: Corrosion Studies***

***Task VI: Post Exposure Characterization***