HVOF Thermal Spray TiC/TiB₂ Coatings for AUSC Boiler/Turbine Components for Enhanced Corrosion Protection

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Southern Illinois University Carbondale

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Chinbay Q Fan
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Powder Synthesis

Kanchan Mondal
Particle Characterization
Corrosion Studies

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HVOF coating

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PhD Student
HVOF, Flame Spray Coatings

GTI project number 21397
Chinbay Fan and Ronald Stanis
• 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

Synthesis of TiC/ TiB₂ Powders

Coated SS

Corrosion Tests

SEM/ EDS

TEM

XRD

H₂/Air

H₂/O₂

C₂H₂/Air

Air Oxidation

Simulated Ash

Steam Corrosion
Powder Physical Properties

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

<table>
<thead>
<tr>
<th></th>
<th>Melting Temp</th>
<th>Density</th>
<th>Hardness</th>
<th>Young’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>3070 °C</td>
<td>4.65 g/cm³</td>
<td>28 GPa</td>
<td>456 GPa</td>
</tr>
<tr>
<td>TiB₂</td>
<td>2900 °C</td>
<td>4.5 g/cm³</td>
<td>34 GPa</td>
<td>570 GPa</td>
</tr>
<tr>
<td>B₄C</td>
<td>2500 °C</td>
<td>2.52 g/cm³</td>
<td>38 GPa</td>
<td>450 GPa</td>
</tr>
</tbody>
</table>
Carbothermal Process for TiC and TiB₂ 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

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

Fuel Flexible: Acetylene, H₂, Kerosene...
Oxidant Flexible: Air or O₂

Stainless Steel As received  After surface roughening

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

Water honing
**Spray Deposition**

**Just Flame**

**Flame with Powder**

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon (C)</th>
<th>Silicon (Si)</th>
<th>Manganese (Mn)</th>
<th>Phosphorus (P)</th>
<th>Sulfur (S)</th>
<th>Chromium (Cr)</th>
<th>Nickel (Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS 304H</td>
<td>(0.04-0.1)</td>
<td>(0.75)</td>
<td>(2)</td>
<td>(0.045)</td>
<td>(0.03)</td>
<td>(18-20)</td>
<td>(8-10.5)</td>
</tr>
<tr>
<td>SS 430</td>
<td>(0-0.12)</td>
<td>(0-1)</td>
<td>(0-1)</td>
<td></td>
<td></td>
<td>(16-18)</td>
<td>(0)</td>
</tr>
<tr>
<td>P91</td>
<td>(0.08-0.12)</td>
<td>(0.2-0.5)</td>
<td>(0.3-0.6)</td>
<td></td>
<td></td>
<td>(8-9.5)</td>
<td>(0.4 max)</td>
</tr>
</tbody>
</table>

**Partially Covered Samples**

**Southern Illinois University**
Corrosion Test Setup

- 2% SO\(_2\) in N\(_2\)
- 0.5% HCl in N\(_2\)
- CO\(_2\)
- N\(_2\)
- Moist N\(_2\)
- Thermocouple
- Furnace
- Exhaust
- Crucibles with samples
- 50 – 60 °C

SIU Carbon Dale
Southern Illinois University
# Summary of Coated 304H Samples after Simulated Flue Gas Tests

<table>
<thead>
<tr>
<th>Material</th>
<th>500°C</th>
<th>600°C</th>
<th>650°C</th>
<th>700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>No noticeable oxidation or sulfurization (coated)</td>
<td>S - Less (coated)</td>
<td>S, O – Less (coated)</td>
<td>O -Less (coated)</td>
</tr>
<tr>
<td>TiB₂</td>
<td>S - Significantly less (coated)</td>
<td>O -slightly less (coated)</td>
<td>S - Significantly less (coated)</td>
<td>O -Less (coated)</td>
</tr>
<tr>
<td>TiC</td>
<td>S - Significantly less (coated)</td>
<td>O - Significantly less (coated)</td>
<td>S, O – concentrated (around coated)</td>
<td>S - Significantly less (coated)</td>
</tr>
</tbody>
</table>
Coated 430 Substrates: Simulated Flue Gas Test - 750 °C

| TiC (32%) | TiC (33%) | TiB₂ | 430 |

- **As Received**
- **7 Days**
- **30 Days**
Simulated Flue Gas Test: 7 Days

430

TiC 32%

TiC 33%

TiB₂
Simulated Flue Gas Test: 30 Days

430 Ti

Fe

Cr

O

Mn

TiC 32%

TiC 33%

TiB₂
Oxidation resistance from coating: TiC (32%)
Oxidation resistance from coating: TiC (32%)
Oxidation Resistance: Oxygen Penetration

7 Days
750°C
Simulated Flue Gas Test

Normalized Oxygen Atomic Amount

Depth (μm)

TiB₂
TiC (33%)
TiC (32%)
430
30 days

Fe 430 10μm

Cr

O

Mn

Ti

TiC 32%

TiC 33%

TiB₂
Oxidation Resistance: Oxygen Penetration

30 Days
750°C
Simulated Flue Gas Test

Normalized Oxygen Atomic Amount

Depth (μm)

TiB₂
TiC (33%)
TiC (32%)

430
Impact of simulated flue gas at 750°C

430 Substrate

X: Fe-Cr
□: Magnetite
◊: Hematite
●: Cr₂O₃

As received
7 Days
30 Days

SIU
Southern Illinois University

Southern Illinois University

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

*: TiC
Δ: TiO₂ - Rutile
○: Ti₃O₅

As received
7 Days
30 Days

Southern Illinois University
Impact of simulated flue gas at 750°C
TiC (33%)

*: TiC
Δ: TiO₂· Rutile
ο: Ti₃O₅

As received
7 Days
30 Days

Impact of simulated flue gas at 750°C on TiC (33%). The diagram shows the change in crystallographic phases over time due to exposure to flue gas at 750°C. The markers * represent TiC, Δ represents TiO₂· Rutile, and o represents Ti₃O₅.
Impact of simulated flue gas at 750°C

TiB₂

+ : TiB₂
Δ : TiO₂ - Rutile
○ : Ti₃O₅

As received
7 Days
30 Days

Southern Illinois University
## Summary of Coated 430 Samples after Simulated Flue Gas Tests

<table>
<thead>
<tr>
<th></th>
<th>750°C- 7 Days</th>
<th>750°C- 30 Days</th>
</tr>
</thead>
</table>
| **TiC (32%)** | O - Slight concentrate (Interface)  
- Lower (beyond interface)  
TiO₂ - (surface) | O - Increased amount (Interface)  
- Lower (beyond interface)  
Chromium Oxide - (Interface)  
TiO₂ - Sharper XRD peaks |
| **TiC (33%)** | O - Slight concentrate (Interface)  
- Lower (beyond interface)  
Chromium Oxide - (Interface)  
TiO₂ - (surface) | O - Less (Interface)  
- Lower (beyond interface)  
Chromium Oxide – Thinner layer (Interface)  
S - concentrated (at Fe, surface)  
TiO₂ - Sharper XRD peaks |
| **TiB₂** | O - Slight concentrate (Interface)  
- Lower (beyond interface)  
Chromium Oxide - (Interface)  
TiO₂ - (surface) | O - Less (Interface)  
- Lower (beyond interface)  
Chromium Oxide – Thinner layer (Interface)  
TiO₂ - Sharper XRD peaks |
| **430** | Magnetite | Hematite  
Cr₂O₃ – (Surface) |
## On-going Task: P91 Steel Substrates

### HVOF Spray coating

<table>
<thead>
<tr>
<th>Spray Parameters</th>
<th>H2 Flow rate</th>
<th>O2 Flow rate</th>
<th>N2 Flow rate</th>
<th>Spray Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.8 LPM (Low Flow)/ 3.6 LPM (High Flow)</td>
<td>27cm</td>
</tr>
</tbody>
</table>

### HVOF Spray coating Spray Parameters

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

- Facile synthesis of sub micro TiC and TiB$_2$ 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
TiC (33%) Coated 430

TiC (33%) Coated 430

As Prepared

Treated at 750 °C for 7 days

Treated at 750 °C for 30 days
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 TiB₂ powder.
- Optimization for HVOF spray coating of the TiC and TiB₂ 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 TiB₂ powder synthesis

Task III: Sample Acquisition

Task IV: HVOF Spray Coating

Task V: Corrosion Studies

Task VI: Post Exposure Characterization