Improved Performance Thermal Barrier Coatings Using The Solution Precursor Plasma Spray Process

Maurice Gell*, Eric Jordan*, Jeffrey Roth, Rishi Kumar
University of Connecticut

Jiwen Wang, Chen Jiang
Balky Nair*
HiFunda LLC

UTSR SBI

STTR Phase IIA Presentation
November 4, 2015
BACKGROUND
TBC Applications

Blades and Vanes

Combustor Case
Topcoat requirements:

- Low thermal conductivity,
- High use temperature,
- High durability:
  - Toughness
  - Strain tolerance
Solution Precursor Plasma Spray (SPPS) Process

Solution Precursors
- A, B or A+B
- Multiple composition

Liquid reservoir

Solution Precursors

Temperature control unit

Plasma gun

Liquid injector

Droplets

Coating

Substrate
Solution Precursor Plasma Spray: Unique Microstructural Features

Through-thickness vertical cracks

Varied nano/micro-scale porosity: 0~40%

Layered porosity: inter-pass boundaries.

Splat diameter < 2 μm
Splat thickness < 1 μm
Splat area is 1/2500 of that in APS TBCs
Thick SPPS Thermal Barrier Coatings

Substrate

Surface

4mm

500 µm
Effect of SPPS TBC Thickness On Durability

Thermal Cycle: 1121° C/1 hour

Spallation Life, Cycles

Substrate A
Substrate B

Coating Thickness (mm)

Normalized Crack Spacing

Coating Thickness (mm)
In-Plane Fracture Toughness

In Plane Fracture Toughness (MPa\(\cdot\)m\(^{1/2}\))

- APS TBC
- SPPS TBC

Graph showing the in-plane fracture toughness for APS and SPPS TBCs.
SPPS YSZ With IPBS: Thermal Conductivity

- 50% Reduction Demonstrated
Engineered SPPS YSZ TBC Architecture

- Vertical cracks for strain tolerance/thermal cycle durability
- Planar pores (IPBs) for low thermal conductivity
SPPS can Make Thin Dense Layers 10 Micron
YAG A CHALLENGE AND OPPORTUNITY
## Properties Of YSZ and YAG

<table>
<thead>
<tr>
<th>Material Property</th>
<th>YSZ</th>
<th>YAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (°C)</td>
<td>2680</td>
<td>1950</td>
</tr>
<tr>
<td>Maximum Operating Temperature (°C)</td>
<td>1200-1300</td>
<td>1800</td>
</tr>
<tr>
<td>Thermal Conductivity at 1350 °C (W/mol-K)</td>
<td>2.0-3.0 (measured)</td>
<td>2.5 (extrapolated)</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (ppm/K)</td>
<td>$9.5 \times 10^{-6}$</td>
<td>$7.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>6.10</td>
<td>4.55</td>
</tr>
<tr>
<td>Vickers Hardness</td>
<td>1200</td>
<td>1700</td>
</tr>
<tr>
<td>Fracture Toughness</td>
<td>Highest</td>
<td>Less</td>
</tr>
</tbody>
</table>
3 SPPS TBCs Developed

- **YSZ**
  - Benefits: High Durability

- **YSZ with IPBs**
  - Benefits: Lower K, High Durability

- **YAG**
  - Benefits: Higher Temp., Similar K, High Durability, Lower Density
SPPS YAG TBCs: Project Objectives

• Develop a Higher Temperature (+200°C), Lower Thermal Conductivity Thermal Barrier Coating Using Yttrium Alumina Garnet (YAG) and the Solution Precursor Plasma Spray Process (SPPS)
• Phase IIa Objective Improve Performance/Cost
  • Lower Thermal Conductivity
  • Increase deposition rate $ and efficiency
  • Radically improve CMAS resistance
Anticipated Benefits

• A New TBC That Can Tolerate Surface Temperatures of 1500°C Can Be Game-Changing For the Gas Turbine Industry Due to Higher Turbine Efficiencies and Lower Fuel Consumption
Yttria-Alumina Phase Diagram

M. Shojaiie-Bahaabad et al,
Ceramics Intl., Vol 35, 2009
Thermal Spray Optimization

Many Variables

• Stand off Distance
• Precursor Composition
• Atomizing Gas Pressure
• Scan Speed and Step Height
• Injection Method, Stream vs. Atomizing
• Feed Rate
• Gun Power
• Gas Mix
• Gun Type
Increased Spray Distance at Lower Atomizing Pressure

6/27/2013 spray trials, 10 psi atomizing pressure
Performance
SPPS YAG TBCs: Standard Microstructure
--Used for Engine-Critical Properties Tests--

- Vickers Hardness: 200-400
- Porosity: 15-20%
Thick SPPS YAG TBCs Can Be Readily Fabricated

- 800 microns (33 mils) thick strain-tolerant microstructure
- Can be used for vanes, combustors and turbine outer air seals

Proprietary & Confidential
Stoichiometric YAG Deposited By SPPS Process

- Predominantly YAG Phase with Minor Amounts of YAM and YAP
- Pure YAG phase
SPPS YAG TBCs: Phase Stability

- SPPS YAG TBCs Are Phase Stable To At Least 1600°C
Thermal Conductivity of SPPS YAG TBCs

- Measured by Netzsch Instruments Using Laser Flash
- 1 mm thick sample with Vickers Hardness of 246
Flash Method

Error

Thermal Conductivity of different YAG samples

- Porosity ~15%
  
  HV = 249 ± 175

- Porosity ~33%
  
  HV = 260 ± 33

- Porosity ~23%
  
  HV = 324 ± 60
Thermal Conductivity Reduced by 1/3 SPPS YAG with Heavy IPBs
SPPS YAG TBCs: Sintering Resistance

Sintering Effects Are Small Up to 1600ºC
SPPS TBCs: Sintering & Thermal Conductivity

- SPPS YAG TBCs More Sinter Resistant Than SPPS and APS YSZ


Phase Stability: 50:50 w/o YAG/CMAS Powder

- YAG Phase Stable To 1500°C In Presence of CMAS
SPPS YAG TBCs: Thermal Cycle Life vs Hardness

- SPPS Strain-Tolerant Microstructure Overcomes Higher Thermal Expansion Mismatch Stresses
SPPS YAG TBCs: Erosion Rate vs Hardness
(Tests Performed at Penn State Univ. By Dr. D Wolfe)

90°, 80 m/s

Coating Mass Loss (g)

- APS YSZ Baseline
- SPPS YAG #9, 230 VHN
- SPPS YAG #8, 290 VHN
- SPPS YAG #11, 500 VHN

Erodent Feed (kg)

y = 0.6x + 0.0022
y = 0.39x + 0.0005
y = 0.23x + 0.0004
y = 0.175x + 0.0004
SPPS YAG TBCs: Erosion Rate vs Hardness

(Tests Performed at Penn State Univ. By Dr. D Wolfe)

90º, 80 m/s

Coating Loss Rate (mm/kg)

YSZ

SPPS YAG, #9, 230 VHN

SPPS YAG, #8, 290 VHN

SPPS YAG, #11, 500 VHN
SPPS YAG TBCs: Erosion Rate vs Hardness

-30º Impingement-

(Tests Performed at Penn State Univ. By Dr. D Wolfe)

- SPPS YAG Has Superior Erosion Resistance To APS YSZ In Both 30º 90º Impingement Erosion Tests.
Spritz/Atomizer Test Conditions

- 1 wt% CMAS Aqueous Solution
- 0.1 mL/spray

### 4-CMAS (M.P. ~1200 °C)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>52.3</td>
<td>37.1</td>
<td>7.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Mol.%</td>
<td>51.5</td>
<td>39.2</td>
<td>4.1</td>
<td>5.2</td>
</tr>
</tbody>
</table>

### 9-CMAS (M.P. ~1180 °C)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>CaSO₄</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>42.00</td>
<td>31.57</td>
<td>1.54</td>
<td>16.50</td>
<td>2.66</td>
<td>1.54</td>
<td>1.54</td>
<td>1.33</td>
<td>1.32</td>
</tr>
<tr>
<td>Mol.%</td>
<td>26.75</td>
<td>45.56</td>
<td>2.38</td>
<td>14.03</td>
<td>5.72</td>
<td>0.84</td>
<td>1.42</td>
<td>1.44</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Spritz Test: Cyclic Lives

4 Component CMAS

No. of Cycles to Failure

21 33 31 61
APS YSZ SPPS YSZ SPPS GZO/YSZ SPPS YAG

9 Component CMAS

No. of Cycles to Failure

30 35 36 59
APS YSZ SPPS YSZ SPPS GZO/YSZ SPPS YAG
CMAS Paste test - 2.5mg/cm²

Number of Cycles to failure

- APS YSZ: 2
- APS GZO: 21
- SPPS GZO: 3
- SPPS YAG: 135
- SPPS YAG with different structure: 130
CMAS Paste test - 10 mg/cm²

Number of Cycles to failure

- APS YSZ: 1
- APS GZO: 20
- SPPS GZO: 1
- SPPS YAG: 8
- SPPS GZO - Double Layer: 40
- SPPS YAG with different structure: 130
SPPS YAG TBCs: Critical Engine Properties

200°C Temperature Advantage
• Phase Stability
• Sinter Resistance
• CMAS Resistance

Improved Durability
• Thermal Cycle Resistance
• Erosion Resistance

Other Significant Properties
• Lower Thermal Conductivity
• Reduced Density
• Surface Smoothness
Cost Reduction - Utility Improvements
Phase IIA Industry Partners

- Solar Turbines
- Siemens Energy
- Pratt & Whitney
- Praxair
- Progressive Surface
- Chromalloy
- General Electric Power
- Rolls-Royce
- Oerlikon-Metco
Industrial Partners Activities

- Olikon Metco spray trials done
- Praxair spray trials done
- Solar Engine Parts sprayed and tested
- Progressive Spray trials done
- Outside of Phase IIa we are involved in Tech Transfer
Goals Related to Industrialization

Benefits Cost Ratio

• Lower Thermal Conductivity (less thickness)
• Higher Deposition Efficiency
• **Higher Deposition Rate
• Larger Stand off Distance
Conductivity reduction via rare earth Doping

- SPPS YAG coatings were produced with 1 atm.% doping of a Rare Earth
- ~24% reduction in thermal conductivity was achieved at RT

**Graph:**
- XRD showing phase stability
- Comparison of Thermal conductivity

**Images:**
- SEM images of SPPS YAG coatings with 1 atm.% doping
Modified Precursor + Sinplex Gun Nearly 30 % Deposition Efficiency Improvement
Sinplex Gun with Modified Precursor Increases Deposition Rate 30%
Deposition Rate Deposited (Feedrate * g/ml * 60 / 454 * DE/100) **Doubled**

Have done 0.67 but working on microstructure
Improved Using Acetate Vs. Nitrate Precursor

- Substantial increase in DE and DR leads to a 45% reduction in production cost of SPPS YAG coatings with Acetate precursor
- Lower Viscosity helps in more uniform flow, less clogging and buildup at the nozzle
- Stronger exothermic peaks during decomposition aids in melting of YAG particles in plasma

DSC

Crystallization of YAG

YAG peaks are visible (in red) with some YAP phase (in blue)

XRD of heat treated precursor for 5 hours at 1200°C
# Standoff Distances

<table>
<thead>
<tr>
<th>Industrial Partner Visits</th>
<th>STTR Phase</th>
<th>Plasma Gun Used</th>
<th>Standoff Distance (inch)</th>
<th>Results/ Comments</th>
<th>Future work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Praxair 11/2014</td>
<td>2</td>
<td>F-4</td>
<td>1.5-3.0</td>
<td>Poor-Fair initial results</td>
<td>F-4, 100HE, Plazjet, HE1100</td>
</tr>
<tr>
<td>Progressive 02/2015</td>
<td>2</td>
<td>100HE</td>
<td>2.0-2.75</td>
<td>Fair initial results</td>
<td>100HE itself</td>
</tr>
<tr>
<td>Progressive 05/2015</td>
<td>2a</td>
<td>100HE</td>
<td>2.0-2.75</td>
<td>Good, Columnar structure, Vickers Hardness-400</td>
<td>Spray B/C, APS YSZ and SPPS YAG for Thermal Cycling</td>
</tr>
<tr>
<td>Metco 09/2015</td>
<td>2a</td>
<td>Sinplex Pro</td>
<td>2.25-2.75</td>
<td>Initial testing with YSZ, Good results</td>
<td>Spray YAG</td>
</tr>
<tr>
<td>Praxair 11/2015</td>
<td>2a</td>
<td>F-4</td>
<td>2.0-3.25</td>
<td>Will explore parameters of F-4 gun to deliver acceptable microstructure and hardness</td>
<td>HE1100</td>
</tr>
</tbody>
</table>

![Different Plasma guns](image-url)
Solar Turbines: SPPS YAG Tests

- Solar In-House Thermal Cycle Tests (2100°F/10 hr) Confirm Thermal Cycle Durability

- 1st Rig Test to 3000°F In 10 Cycles Showed No Distress

- 2nd Rig Test Showed Temperature Drop For 10 mils of SPPS YAG Comparable to 20 mils of APS YSZ
Summary & Conclusions-I

- SPPS YAG TBCs Show Potential For >1500°C Operation Based On Phase Stability, and Sinter Resistance
- This Represents >200°C Advantage Over APS YSZ
- Durability of SPPS YAG TBCs ≥ APS YSZ In Thermal Cycle and Erosion Tests
- Thermal Conductivity of SPPS YAG TBCs with IPBs is 0.7 Watt/m°K at room temperature extrapolates to 0.58 at 1300 C Measured by Netzsch.
Summary & Conclusions-II

- Deposition Efficiency increased from 43% up to 70% using a different Precursor and Sinplex Gun.
- *Deposition Rate to part doubled cutting cost in half.
- Standoff distance improved from 1.6 inches to 3 inches Further Improvement sought.
- **More than an order of magnitude improvement in CMAS cyclic life a high doses. Out performs Gadolinium Zirconate so far.
- Has been applied to Engine parts with excellent durability and thermal performance.
- Separate arrangements for Tech Transfer to a fortune company.
Summary & Conclusions-II

• Engine Manufacturers Show Strong Interest In SPPS YAG TBCs; Are Conducting In-House Testing

• Technology Transfer Being Conducted With TBC Coating Suppliers; They Will Conduct Demonstration Trials and Provide Process Economics

• SPPS YAG Continues to Show Strong Promise As Higher Temperature (200°C), Sinter-Resistant, CMAS-Resistant, Low K, Low ρ, Durable TBC
SPPS TBC Commercialization

- Solution Spray Technologies (SST) LLC Formed To Further Develop & Commercialize SPPS TBCs
- SST Has Exclusive License to University of Connecticut SPPS TBC Patents
- SST Is Working With Engine OEMs to Qualify SPPS TBCs
- SST is Working With TBC Producers To Optimize & Commercialize SPPS Process
Acknowledgements

• Dr. Briggs White, DOE Program Manager, UTSR Program on SPPS YSZ with IPBs

• Dr. Patcharin Burke, DOE Program Manager, STTR Phase I, II & IIA Programs on SPPS YAG TBCs

• Our Industrial Partners for Phase II SPPS YAG TBCs: Solar Turbines, Siemens Energy, Pratt & Whitney, Praxair and Progressive Surface
Questions ?