Low Thermal Conductivity, High Durability Thermal Barrier Coatings for IGCC Engines

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Microstructure & Requirements For TBCs

**TBC Requirements**

- Low Thermal Conductivity
- High Use Temperature
- High Durability

- Toughness
- Strain Tolerance

**Requirements**

- Low Thermal Conductivity
- High Use Temperature
- High Durability

**Microstructure**

- Superalloy
- Bond Coat
- EB-PVD 7YSZ
- Gas Film
- Hot Gas

**Temperature**

100 µm
TBC Applications

- Combustor Case
- Blades and Vanes
Goals

• Reduce the thermal conductivity of TBCs to 0.5 watt/m-K by Optimal Porosity Structuring

• Increase the allowable surface temperature of the TBC from the current approximately 1200\textdegree{} C for YSZ to 1300\textdegree{} C. By a more stable top layer.

• Improve the durability of the TBC in the face of Contaminants (CMAS) and Moisture compared to current YSZ coatings.
Accomplishments

• SPPS Process with IPBs reduces YSZ thermal conductivity to half of normal values.
• Thermal conductivity of 0.5 W/m-°K attained.
• SPPS YSZ TBCs can replace advanced low K TBCs with expensive rare earth content.
• Under DOE STTR program high temperature low CTE YAG TBCs rendered durable by SPPS microstructure with vertical cracks.
Presentation Outline I

• Introduction to Solution precursor Plasma Spray (SPPS)
• Importance of vertical cracks in SPPS and our exciting new STTR program results.
• Development of process parameter-microstructure (IPB) relationship
• Failure of Image analysis to determine conductivity and introduction of laser flash methods
Presentation Outline II

• Success in reducing thermal conductivity by a factor of 2.
• GdZr layer for higher temperature operation and contaminant (CMAS) resistance.
• Addition of aluminum to YSZ for improved CMAS resistance
• Addition of CaSO2 for CMAS resistance
• Summary
Goals will be accomplished by making and Testing TBC systems Using:

• Solution Precursor Thermal Spray in UConn thermal spray facility
• TBC Testing Facility
• Moist Environment Testing (being built for this program)
## Program Plan

<table>
<thead>
<tr>
<th>TASK</th>
<th>YEAR 1</th>
<th>YEAR 2</th>
<th>YEAR 3</th>
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<tbody>
<tr>
<td>1. Manage/Plan/Report</td>
<td>🟥</td>
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<tr>
<td>2. SPPS of Low K TBC</td>
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<tr>
<td>3. Test Low K TBC</td>
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<tr>
<td>4. Fabricate Gd-Zr Layer</td>
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<td>5. Fab. Al-Ti Doped TBC</td>
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<tr>
<td>6. Fab. CaSO₄ Additive</td>
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<tr>
<td>7. CMAS Testing</td>
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<tr>
<td>8. Moisture Testing</td>
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<tr>
<td>9. Define Mechanisms</td>
<td></td>
<td></td>
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<tr>
<td>10. Gradient Cyclic Testing</td>
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</table>
Air Plasma Spray (APS)

- Cathode
- Anode
- Gas
- 50 micron Particles
- Powder Injector
- Plasma Jet
- Coating
- Substrate

Particles Melt and Build Splat Structure => 7YSZ
Solution Precursor Plasma Spray Process (SPPS)
SPPS Deposition: Process Flexibility

Precursor Droplet Evaporation

Breakup, Gelation, Precipitation

Pyrolysis Sinter

Melt

Spray Pyrolysis

Spray Pyrolysis Deposition: Process Flexibility
Liquid Delivery Options

Standard Liquid Delivery System

Unique High Pressure System (33 atm)
Cyclic Furnace Test Facility
Specimen Shape & Furnace Cycle

- **Disk-Shape Samples**

- **Thermal Cycling Life Test**

- Put the TC on the sample, furnace TC is 20 °C low
- Rotate Sample to average hot spots

![Diagram of disk-shape sample with layers labeled Top-Coat (~250 μm), Substrate (~125 μm), and Bond-Coat (~125 μm) with dimensions 5 mm x 2 mm x 12.52 mm]

![Temperature-time graph showing a flat line at 1121 °C from 0 to 50 minutes, followed by a steep decrease to 0 °C at 60 minutes]

[Graph showing temperature-time relationship with peak at 1121 °C]
SPPS TBCs Have Unique Features

Microstructure Of SPPS TBCs

Unique Features

- 3D Nano & Micrometer Porosity
- Through-Thickness Cracks
- Ultra-Fine Splats
SPPS Coating have 7X higher In Plane Toughness
Structured Planar Porosity (IPBs) Leads to Lower Thermal Conductivity
Advantages of Solution Precursor Plasma Spray

• Vertical stress relieving cracks
• Higher Fracture Toughness
• Rapid Composition Exploration (100X)
• Structured Porosity (IPBs) leading to low K coatings
Work Done under HiFunda/UConn STTR DOE Program

Patcharin Burke Program Manager
Thermal Expansion Mismatch Drive Cyclic Stresses

• TBC Stress=$E_{tbc}(\alpha_{tbc}-\alpha_{metal})(T-T_{stress\ free})/(1-v)$
• The lower the coefficient of expansion $\alpha_{tbc}$ higher the stress
• Many Ceramics ruled out because of low CTE that otherwise have desirable properties. Vertical cracks can lift this restriction.
• Example: Yttrium Aluminum Garnet (YAG)
# Properties of YSZ and YAG

<table>
<thead>
<tr>
<th>Material Property</th>
<th>YSZ</th>
<th>YAG</th>
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<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>
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<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>**</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>
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Thermal Cycling Test Results
(1180ºC/12 hrs)
--Failure Lives To 50% Spallation--

<table>
<thead>
<tr>
<th>APS YSZ</th>
<th>SPPS YAG TBCs Type I</th>
<th>SPPS YAG TBCs Type II</th>
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<tbody>
<tr>
<td>Baseline**</td>
<td></td>
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<tr>
<td>1. 72 hrs</td>
<td>1. 300 hrs*</td>
<td>1. 300 hrs*</td>
</tr>
<tr>
<td>2. 120 hrs</td>
<td>2. 300 hrs*</td>
<td>2. 300 hrs*</td>
</tr>
<tr>
<td>3. 300 hrs*</td>
<td>3. 300 hrs*</td>
<td></td>
</tr>
</tbody>
</table>

*Intact, still running

**Baseline: IN939, NiCoCrAlY Bond Coat, YSZ Top Coat
Prior Test Experience With Variety of Advanced TBCs: 60-200 hrs
Returning to SPPS YSZ
Initial SPPS Trials/Thermal Conductivity Measurements

• Taguchi DOE Spray Trials to optimize IPBs for minimum thermal conductivity (0.5 watt/m-°K).

• Access Outcome Using Image Based Finite Element (OOF) Calculated Thermal Conductivity.

• Image Based Thermal Conductivity Determination (OOF) was not Reliable
Modified Plan

• Use a Lesser Number of Laser Flash Measured Thermal Conductivity and Heuristically Understanding to Reach the Thermal Conductivity Goal of cutting in half the conductivity to 0.5 watt/meter- °K
Development of Heuristics Needed to Make Optimal IPBs

By Modeling and Testing
Artificial Microstructures for Insight Analyzed by OOF

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</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td>0.198</td>
<td><img src="mesh1.png" alt="Mesh" /></td>
<td>0.963</td>
<td>0.05653</td>
<td>0.04</td>
<td>1.413</td>
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<tr>
<td><img src="image2.png" alt="Image" /></td>
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<td><img src="mesh2.png" alt="Mesh" /></td>
<td>0.974</td>
<td>0.04689</td>
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<td><img src="image3.png" alt="Image" /></td>
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<td>0.20</td>
<td><img src="mesh4.png" alt="Mesh" /></td>
<td>1.0</td>
<td>0.004126</td>
<td>0.04</td>
<td>0.103</td>
</tr>
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</table>

1. Circuitous Path with as narrow as possible bridge points
Over 100 Different Spray Conducted

• 25 have had thermal conductivity measured
• 10 have been measured in LFA prior to selecting ideal substrate
• 15 have been measured with ideal substrate thickness.
Figure 6. TBC #1, a Low K SPPS YSZ TBC using IPBs and porosity
Effects of Processing Variables On IPB Formation

• Spray Distance
• Precursor Injection Method
• Precursor Feed Rate
• Raster Scan Step Height
Formation of Inter-Pass Boundaries
Effect of Spray Distance on IPBs

Atomizing Bete with 2 mm index. 1 min cooling/15 passes. Stainless steel substrate.

4.13 cm SD
IPB 021412 A

4.44 cm SD
IPB 021412 B

4.76 cm SD
IPB 021412 C
Precursor Injection Method & IPBs

Standard 7YSZ precursor solution. 2 mm index. 4.44 cm SD 40 s cooling/5 passes. Stainless steel substrate.

Bete Atomizing

Stream Injection
Precursor Feed Rate & IPBs

Standard 7YSZ Precursor Solution. Stream Injection. 4.44 cm SD. Stainless steel substrate.

#6: 38 mL/min
IPB 013112 E

#8: 106 mL/min
IPB 010512 C
Raster Scan Height & IPBs-I

Standard 7YSZ Precursor Solution. Bete Atomzing. 4.44 cm SD. 40 s cooling/5 passes. Stainless steel substrate.

1 mm index
IPB 012512 H

2 mm index
IPB 012512 E

3 mm index
IPB 012512 B
Effect of Raster Scan On IPBs-II

Standard 7YSZ Precursor Solution. Stream Injection. 4.44 cm SD. 40 s cooling/5 passes. Stainless steel substrate.

2 mm index
IPB 013112 B

3 mm index
IPB 013112 E

4 mm index
IPB 013112 H

6 mm index
IPB 013112 K
Calculating Thermal Conductivity
Finite Element Mesh Generated from Micrograph Using OOF Program
### Image Based (OOF) Conductivity NOT Reliable

<table>
<thead>
<tr>
<th>Sample</th>
<th>LFA</th>
<th>OOF</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temp</td>
</tr>
<tr>
<td>Stainless steel substrate</td>
<td>100 C</td>
<td>16.5</td>
<td></td>
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<tr>
<td>IPB#042412-C</td>
<td>150 C</td>
<td>0.72</td>
<td>150 C</td>
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<tr>
<td>IPB#042412-D</td>
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<td>0.99</td>
<td>150 C</td>
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<tr>
<td>IPB#060412-G</td>
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<td>0.55</td>
<td>150 C</td>
</tr>
<tr>
<td>IPB#060412-I</td>
<td>150 C</td>
<td>0.32</td>
<td>150 C</td>
</tr>
</tbody>
</table>

*Note: Single-layer model, 3mm substrate, 6mm piece.*

*Note: Two-layer model, 3mm substrate, 6mm piece.*

*Note: Two-layer model, 2mm substrate, 1" disk.*

*Note: Two-layer model, 3mm substrate, 1" disk.*

Table 1. Thermal conductivity of YSZ TBCs with interpass boundaries determined by laser flash analysis (LFA) vs. finite element calculations using SEM images and OOF software.
1. Porosity not Easily Distinguished from Other Regions
2. Is only 2-D
Laser Flash Apparatus

Figure 2: Schematic of the NETZSCH LFA 447
Laser Flash Schematic

Figure: Diagram of the flash method for measuring thermal diffusivity.
Creating Low Thermal Conductivity

By Structuring the Porosity via Inter-pass boundaries (IPBs)
Thermal Conductivity of SPPS YSZ TBCs With IPBs
Laser Flash- Twelve Specimens

1.47
1.31
1.12
1.09
1.08
0.97
0.90
0.83
0.82
0.67
0.66
0.65
0.53
Significant Program Achievement

- Reduced YSZ TBC Thermal Conductivity by >50% to 0.53 watt/m-oK
- Further Reduction Likely With IPB Optimization
- Low Thermal Conductivity Now Possible Without Scarce, Expensive Rare Earth Oxides
Contaminants Affect TBC Failure

Calcium, Magnesium, Aluminum
Silicon= CMAS
A 387 MW (H Machine) Engine processes about $2 \times 10^{10}$ Kg\(^1\) of Air/ year

- Jeffrey Bons gets fractional sticking of solids roughly 1%-10%
- 1 PPM of solids would be 20,000 Kg if it sticks even at 10% = 2000 Kg it is very bad at 1% bad.
- To be a small problem you need about 1 PPB (20Kg) clean up. **CMAS will be a Problem.**

- \(^1\)Chiesa, P. et al, Using Hydrogen as a Gas Turbine Fuel, J. of Engineering for Gas Turbine and Power 127, 73, 2005
CMAS Infiltration of 7YSZ Thermal Barrier Coating

Field Observation of CMAS Attack

CMAS Deposits

Transverse Cracks that Lead to Shedding of Topcoat

Coating Loss Due to CMAS Infiltration

Most Aggressive Attack Tends to Occur in Hottest Regions

Mercer et al. 2005
1. Loss of Strain Tolerance-Mechanical Effect

Fig. 1. Examples of delaminations in thermal barrier coatings obtained from components removed from engines subjected to CMAS penetration: (a) Sub-surface mode I delaminations in an airfoil with a TBC made by electron beam physical vapor deposition; the delaminations are within the penetrated zone [9]. (b) Delaminations at several locations within a shroud penetrated by CMAS; the TBC is 1 mm thick and deposited by air plasma spray (APS) [10].
Mechanics Modes for Loss of Strain Tolerance Developed by Hutchinson and Evans

Fig. 10. A map for deep delamination in an APS–TBC on a superalloy substrate with CMAS infiltration to depth, $h/H$. The mixed mode toughness parameter is, $\lambda = 0.25$. 
2. Many types of chemical and Phase Effects for example Y loss and destabilization of t phase ZrO2 to Monoclinic with a destructive volume change.
CMAS Damage Mitigation and Increased Temperature Capability to be Implemented

Three Approaches
1. Add Gd-Zr to baseline system for higher temperature phase stability and CMAS

![Diagram of TBC system #2 with low conductivity solution plasma sprayed YSZ with IPBS and CMAS resistant high temperature tolerant Gc-Zr protective surface layer (PSL).]

**Figure 7.** TBC system #2 with low conductivity solution plasma sprayed YSZ with IPBS and CMAS resistant high temperature tolerant Gc-Zr protective surface layer (PSL).
Why Gd$_2$ Zr$_2$O$_7$ ?

• **Higher Temperature Phase Stability limit
  YSZ 1150 °C vs. 1550 °C  For GdZr

• Half the Conductivity of YSZ

• Better CMAS Resistance
CMAS Resistance of GdZr

From Carlos Levi, UCSB
Analysis of Gd$_2$Zr$_2$O$_7$/CMAS Reaction Product

Sealant Layer Identified as Hexagonal Apatite Phase, CaGd$_4$(SiO$_4$)$_3$O

Coating System Needs to be Designed Such That Coating/CMAS Constituents Form Stable Refractory Compound

From Levi, UCSB
Gadolinium Zirconate Sample Spray
Conditions Developed at UConn
Add Metastable Al2O3 to block CMAS in the YSZ layer

Figure 9. TBC system #4 has features of TBC #1-3 with calcium sulfate infiltration.
2. Addition of metastable Al

1121 °C, 24 h

APS 7YSZ

SPPS 7YSZ

SPPS YSZ + 20 mol% Al₂O₃ + 5 mol% TiO₂

TBCs Destroyed

CMAS-Front Arrest
How it Works


CMAS Glass

Substrate

Heat-Treatment

CMAS Glass Comp. in Psuedowollastonite Field

ZrO$_2$ with Y$^{3+}$+Al$^{3+}$+Ti$^{4+}$ Solute

ZrO$_2$ depleted in Y$^{3+}$, Al$^{3+}$, Ti$^{4+}$ Solute

Glass Comp. in Anorthite Field

Pores
Microscopy Shows Anorthite phase is blocking
3. Infiltration of CaSO$_4$ via a low melting eutectic of NaSO$_4$-CaSO$_4$-MgSO$_4$
3. Infiltration with CaSO4 found in the field by Braue

Fig. 3 a middle section of the YSZ top coat displaying CaSO4 infiltration of open porosity (suction-surface/region B, SEM, secondary electron image), b and c elementary mapping (Ca_k, S_k) proving that CaSO4 is continuous within the intercolumnar pore network of the coating.
Summary & Plans

• **Project Goals:**
  – Reduce conductivity to 0.5 Watt/M-°K
  – Increase surface temperature allowable to 1300 °C
  – Significantly improve CMAS resistance

• Structured Porosity (IPBs) will be used and optimized to lower thermal conductivity to < 0.5 Watt/M-°K

• A top layer of GdZr will be used to:
  – Allow 1300 C surface temperature
  – Reduce CMAS attack

• Al-Ti Metasable solutes will be added to the YSZ to reduce CMAS infiltration

• CaSO$_4$ will be used for the first time to arrest CMAS infiltration.
Questions ?