Advanced Thermal Barrier Coatings for Operation in High Hydrogen Content Gas Turbines

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Center for Thermal Spray Research

DOE NETL UTSR
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Program Manager: Dr. Briggs while

Dwivedi et al., JACerS, DOI: 10.1111/jace.13021
Viswanathan et al., JACerS, DOI: 10.1111/jace.13033

Dwivedi et al., JTST, Under Review
Viswanathan et al., JACerS, Under Review
DOE UTSR Meeting, Oct 2014, Purdue University, IN

Snapshot of accomplishment under UTSR program

- 50+ coating conditions
- 40+ architectures
- 600+ FCT samples

- Adequate erosion resistance
- Significantly higher durability
- CMAS resistance
- Mechanisms and Methodology to incorporate any new composition

2010

Single Layer YSZ

600 hrs

4 years

2014

1,200 hrs

Layer-1

Layer-2

Layer-3
Interplay between TBC durability and “manufactured” coating properties

- Ceramic strength/toughness
- Coating density
- Ceramic coating compliance and ceramic chemistry
- Coating porosity/cracks

Stresses originated from Thermal Expansion Mismatch

Particulate Erosion

Foreign Object Damage

Phase change at elevated temp

Sintering related Compliance loss

Oxidation (TGO) induced coating delamination

Molten CMAS penetrations

Bond coat chemistry, Roughness
- Ceramic coating toughness
- Bond coat roughness
- Coating thickness

Ceramic coating composition
- Pore architecture
- Coating thickness
Multilayered architecture to combat multifunctional requirements

Plasma spray is naturally suited for such layered manufacturing
Multilayered architecture to combat multifunctional requirements

- Erosion Resistance
- Sinter Resistance
- Low Thermal Conductivity
- Transition Layer
  Mitigates Zirconate/TGO Reactions
- Oxidation Protection/Adhesion

- Nickel Superalloy

- Erosion, FOD, CMAS/Ash
- Low-K material, Porosity, Lower sintering rate
  Remains complaint
- Compatibility with Bondcoat
  Mostly traditional TBC, High toughness

- Adequate roughness, oxidation resistant (dense), environmental effects
Impact of water vapor on conv. & new TBC materials

*Initial Results*

No significant difference found at this temperature, and long term exposures

Collaborative partnership with ORNL - Materials selection

- HVOF bond coats (**NiCoCrAlY & NiCoCrAlYHfSi**) for ORNL testing
- ORNL is investigating the interactions with several different substrate materials
**Figure 7:** This process map relates NiCr (a surrogate for NiCrAlY) particle states, achieved during liquid and gas fuel HVOF (Woka and Diamond Jet) and plasma spray (Triplex) to resultant microstructures and roughness. Significant difference among the TS bond coats exist in terms of microstructure, density and internal oxidation. These differences can dramatically affect performance. It is critical to understand these effects to optimize NiCrAlY bond coats. Maps allow for systematic tailoring of coating properties.

Not all bond coats are the same! Processing plays a role.
**Processing Effects on HVOF Bond Coats**

HVOF process type and spray conditions significantly affect deposition stresses and final stress state of the coating.

**JP5000 chosen due to microstructure and compressive stress state.**
Down selection of bond coat material

Pint et al., AMP May 2012

XPT: NiCoCrAlY
AMDRY: NiCoCrAlY-HfSi

Reactive element bondocat showed higher life under all the conditions

Collaboration with Dr. Bruce Pint and Dr. Allen Haynes at ORNL
BC roughness effects may overshadow chemical effects?

Fracture in topcoat

Furnace cycle test

Bondcoat layer require adequate roughness for high TBC life

NiCoCrAlYHfSi

Top coat life (hours)

Commercial

CTSR

Roughness, Ra (mm)

Commercial

CTSR

Fracture in TGO

Fracture in topcoat
Processing Strategies

Rough bond coat surface

Particle size → Processing Control → Two layered architecture

Strategy

- Utilize the **Fine** particle size for *Dense Oxidation Resistant* initial layer
- Utilize the **Coarse** particle size to tailor the topography for high *surface roughness*

Feedstock

- AMDRY 386-2 $D_{50}$: 32.31 μm
- AMDRY 386-4 $D_{50}$: 62.72 μm
Deposition Scheme

Two layers bond coat deposition

Layer-2: ~50µm Coarse powder (Rough Surface)
Layer-1: ~100µm Fine powder (Dense microstructure)

Substrate

Densest bottom layer
Denser bottom layer
Least dense bottom layer

Poor splat cohesion
Poor splat cohesion and some cracking
Good particle melting and splat cohesion
Performance of the Two Layered Bond Coat

Similar top coats on 3 different bond coats
FOCUS : Two Layered Bond Coat

Improved bond coat roughness

![Graph showing FCT Hours for NiCrAlYHfSi, NiCrAlYHfSi (Two Layered), and Commercial bond coats.](image)

- NiCrAlYHfSi
- NiCrAlYHfSi (Two Layered)
- Commercial
Failure mechanism of TBCs: Occurring at BC-TC interface

With extending service hours

- **TGO Growth**: Additional Stress build up at the interface. (limited control)
- **Sintering**: loss in compliance => higher stress build up. Higher driving force for crack propagation. Process optimization to design coating with large compliance in as sprayed condition.

Majority of TBC failure occur at the BC-TC interface. **Parameter of interest is Fracture Toughness.**
Is the toughness sensitive to microstructure of TBCs?

The defect architecture governs Thermal conductivity and Coating compliance

Some defects present more tortuous path to a crack than others.

These defects can be controlled via processing.

Plasma spray can be utilized to produce significantly different microstructures.

Can we manipulate the effective fracture toughness of these structure?
Fracture Toughness: Double Torsion Technique

Max. Load for fracture

\[ K_{IC} = \frac{P_{IC} S_m}{S t^4 \xi} \left[ 3(1+\nu) \right]^{1/2} \]

- \( P_{IC} \): Maximum load at failure
- \( \nu \): Poisson’s ratio
- \( S \): Specimen width
- \( S_m \): Moment arm
- \( t \): Specimen thickness
- \( \xi \): Thickness correction factor

\[ \xi = 1 - 1.26(t/S) + 2.4(t/S) \exp(-\pi S/2t) \]

Advantages:
- Does not require crack length monitoring
- Can be performed a low thickness specimen (~600μm).
Case Study: Effect of particle size distribution

D_{50}: Mean particle size

- D_{50} = 96.11 µm
- D_{50} = 59.75 µm
- D_{50} = 24.01 µm

Fract. tough, K_{IC} (MPa√m)

Fine

Ensemble

Coarse

Fine powder cut

Ensemble powder cut

Coarse powder cut

50µm

50µm

50µm
Fracture toughness and modulus relationship

- With sintering or densification of microstructure, fracture toughness increases.
- Toughness is more sensitive towards sintering

Fracture toughness is sensitive to coating microstructure

Fracture toughness, $K_{IC}$ (MPa$\cdot$m$^{1/2}$)

Indentation modulus, $E_{ind}$ (GPa) \( \propto \frac{1}{\text{porosity}} \)
In order to limit the compliance loss

1. Porous coatings
   
   Generally, it has been believed that the porous TBCs last longer.

2. DVCs

   ![Typical APS coatings](image)

   FCT carried out at 1100°C, 24 hrs cycle

   ![FCT Life (Hours)](image)
Multiple requirements from a thermal barrier coating

**Design requirements**

1. **High toughness**: Improved Cyclic Life
2. **Low modulus**: Less driving force to failure
3. **Low thermal conductivity**: Low substrate temperature

Need a strategic approach towards coating design for multi-functionality
Multiple requirements from a thermal barrier coating

Primary Requirement

- Compliance
- Durability
- Thermal Performance

Function of coating microstructure

Processing strategies can control layer by layer coating properties

Substrate

Bond Coat
Focus on need for high toughness ceramic at failure location

- Focus on need for high toughness ceramic at failure location
- Ni based Superalloy Substrate
- Multilayer Topcoat
- Bondcoat
- Oxidation protection
- Strength/creep resistant
- High fracture toughness layer
- Erosion and CMAS Resistant
- Phase stability
- Sinter Resistant
- Low thermal conductivity
- Low thermal conductivity
- Erosion and CMAS Resistant
- Low thermal conductivity
- Phase stability
- Teixeira et al., JTST, 9(2), 2000—191
- Padture et al., vol. 296, Science, 280, 2002

\[ \sigma_i^s \geq \sigma_c : \text{Failure} \]
Elastic Energy approach to optimize coating architecture

Approach: Higher toughness with denser coatings…

Total Elastic Energy available for interfacial crack propagation

\[ U_{\text{isothermal}} = \frac{(1+\nu)}{2(1-\nu)} (\Delta \alpha_c \Delta T_{sub})^2 (E_c h_c) \]

Levi et al., MRS Bulletin, 2012

For constant \( h_c \)

\( U_{\text{interface}} \propto E \) (modulus)

Failure occurs when

\( U_{\text{interface}} \geq G_c \)

\( E_{\text{Dense}} > E_{\text{Porous}} \)

\( U_{i\text{Dense}} > U_{i\text{Porous}} \)
Elastic Energy approach to optimize coating architecture

Total Elastic Energy available for interfacial crack propagation

\[
U_{isothermal} = \frac{(1 + \nu)}{2(1 - \nu_c)}(\Delta \alpha_c \Delta T_{sub})^2(E_c h_c)
\]

Levi et al., MRS Bulletin, 2012

For constant \( h_c \)

\[ U_{interface} \propto E \text{ (modulus)} \]

Failure occurs when

\[ U_{interface} \geq G_c \]

For multilayer coatings

\[
U_{isothermal} = \frac{(1 + \nu)}{2(1 - \nu_c)}(\Delta \alpha_c \Delta T_{sub})^2(E_{c1} h_{c1} + E_{c2} h_{c2} + E_{c3} h_{c3}....)
\]

Derived from Levi et al., MRS Bulletin, 2012
Typical APS TBC

Functionally Optimized TBC with high fracture toughness interface layer

Structural Compliance

Crack initiation due to TGO growth

Porous layer for lower modulus

High Toughness Layer

Fracture toughness, $K_{IC}$ (MPa$\cdot$m$^{1/2}$)

Indentation modulus, $E_{ind}$ (GPa)

Substrate

Bond Coat

High Plasma Power

Sintered for 24 hours

YSZ sintered

YSZ as-sprayed

Fine Particles

Crack initiation due to TGO growth
Revised TBC Architecture

- **Porous architecture**
  - Bondcoat
  - Substrate

- **Layer 2**: Low modulus
  - Layer 1**: High toughness
  - Bondcoat
  - Substrate

- **Layer 2**: High toughness
  - Layer 1**: Low modulus
  - Bondcoat
  - Substrate

**Conventional TBC**
- Porous single layer

**Optimal bi-layered TBC**
- Bi-layer with tough near-interface layer

**Inverse bi-layered TBC**
- Bi-layer with inverse architecture

Images showing microstructures with 50µm scale bars.
**FCT durability of revised TBC Architecture**

- **Single layer TBCs**
- **Bi-layer TBCs**

**Consistent improvement in TBC life for bi-layer coatings**

With high toughness interface layer
The failure location for all the architectures remains the same

<table>
<thead>
<tr>
<th>Porous architecture</th>
<th>Layer 2: Low modulus</th>
<th>Layer 2: High toughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bondcoat</td>
<td>Layer 1: High toughness</td>
<td>Layer 1: Low modulus</td>
</tr>
<tr>
<td>Substrate</td>
<td>Bondcoat</td>
<td>Substrate</td>
</tr>
</tbody>
</table>

**Failed Specimens**

- Conventional porous single layer
- Conventional TBC Substrate
- Bondcoat
- Layer 1: High toughness
- Layer 2: Low modulus

- Bi-layer with dense near-interface layer
- Optimal bi-layered TBC Substrate
- Bondcoat
- Layer 1: Low modulus
- Layer 2: High toughness

- Bi-layer with inverse architecture
- Inverse bi-layered TBC Substrate
- Bondcoat
- Layer 1: Low modulus
- Layer 2: High toughness

Failed Specimens Images:
- Conventional porous single layer: C1 (50 µm)
- Bi-layer with dense near-interface layer: B5 (50 µm)
- Bi-layer with inverse architecture: B3 (50 µm)
Process optimization strategies

Conventional TBCs

- Porous YSZ
  - Low K
  - Low E

Overlay BC

Superalloy Substrate

Enhanced Durability TBCs

- Porous YSZ
  - Low K
  - Low E

- High $K_{IC}$ TBC Layer

- Overlay BC enhanced roughness

Layer 2

Layer 1

Superalloy Substrate

Property based design map for coatings with enhanced durability

Simultaneous optimization of coating durability and functionality

Effective in-plane elastic modulus, $E$ (GPa)

Near-interface layer $K_{IC}$, (MPa$\sqrt{m}$)

TBC lifetime (hours)

RT Thermal conductivity (W/m-K)
<table>
<thead>
<tr>
<th></th>
<th>Traditional YSZ</th>
<th>New TBC Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Phase Stability</strong></td>
<td>Good &lt; 1200C</td>
<td>Good&lt;1300-1400C</td>
</tr>
<tr>
<td><strong>Thermal Expansion</strong></td>
<td>Fair</td>
<td>Challenging</td>
</tr>
<tr>
<td><strong>Thermal Conductivity</strong>*</td>
<td>Low</td>
<td>Lower</td>
</tr>
<tr>
<td><strong>Sintering Resistance</strong>*</td>
<td>Fair</td>
<td>Good</td>
</tr>
<tr>
<td><strong>Erosion Resistance</strong>*</td>
<td>Good</td>
<td>Challenging</td>
</tr>
<tr>
<td><strong>Fracture Toughness</strong>*</td>
<td>Good</td>
<td>Challenging</td>
</tr>
<tr>
<td><strong>Mechanical Compliance</strong></td>
<td>known</td>
<td>To be explored</td>
</tr>
</tbody>
</table>

Materials’ intrinsic properties

Can be optimized via processing strategies*
### Candidates for top coat composition under consideration

#### TBC Materials under considerations

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Advantages</th>
<th>Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>7-8wt% YSZ</td>
<td>Stable below 1200°C, cost effective, properties well-characterized</td>
<td>Various sources, different levels of purity</td>
</tr>
<tr>
<td>Zirconate</td>
<td>La$_2$Zr$_2$O$_7$</td>
<td>Pyrochlore, low thermal conductivity, phase stability to 1400°C</td>
<td>Julich</td>
</tr>
<tr>
<td>Zirconate</td>
<td>Gd$_2$Zr$_2$O$_7$</td>
<td>Pyrochlore, low thermal conductivity, phase stability to 1400°C, compatible with YSZ</td>
<td>Saint Gobain, Julich</td>
</tr>
<tr>
<td>Co-doped</td>
<td>1.5mol%Yb$_2$O$_3$ 1.5mol% Gd$_2$O$_3$ 2.1mol% Y$_2$O$_3$ ZrO$_2$</td>
<td>t' phase, low thermal conductivity, sintering resistant, compatible with MCrAlY bond coat, high erosion resistance</td>
<td>NASA</td>
</tr>
<tr>
<td>YSZ-Al-Ti</td>
<td>YSZ+20mol%Al+5mol%Ti</td>
<td>CMAS resistant</td>
<td>Ohio State Univ</td>
</tr>
</tbody>
</table>
Exploring and processing new materials

YSZ

La$_2$Zr$_2$O$_7$

Gd$_2$Zr$_2$O$_7$

Cluster-doped
Transitioning to low K TBC: $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlores

**Challenges:**

1. CMAS mitigation
2. High erosion/FOD resistance
3. Compatibility with YSZ

All have significant dependency on processing.
Coating microstructure for enhanced CMAS resistance

- Dense GDZ seems to offer lesser Lignite ash penetration depth.
- It also offer benefits in terms of erosion resistance.
- However, it has high modulus, which will increase the overall strain energy.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>CaO</th>
<th>FeO</th>
<th>Al₂O₃</th>
<th>Cr₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>TiO₂</th>
<th>SrO</th>
<th>MnO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>P₂O₆</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>29.7</td>
<td>25.4</td>
<td>14.8</td>
<td>14.7</td>
<td>5.1</td>
<td>3.6</td>
<td>1.8</td>
<td>1.1</td>
<td>1.0</td>
<td>0.9</td>
<td>0.8</td>
<td>0.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Courtesy: Prof. Nitin Padture
Coating microstructure for enhanced CMAS resistance

Dense GDZ seems to offer lesser Lignite ash penetration depth.

It also offer benefits in terms of erosion resistance.

However, it has high modulus, which will increase the overall strain energy.

Potential candidate for Top layer

Isothermal treatment under CMAS like conditions

- Porous GDZ
- Dense GDZ

SiO₂: 29.7
Na₂O: 0.6
P₂O₆: 0.2

Reaction zone ~100 µm

100 µm

DVC GZO

Molten ash wicking

Dense GDZ seems to offer lesser Lignite ash penetration depth.

It also offer benefits in terms of erosion resistance.

However, it has high modulus, which will increase the overall strain energy.

Courtesy: Prof. Nitin Padture
Larson Miller Parameter (LMP): Temp and Time for thermal exposure

LMP = T(ln t + C)

Various duration at 1100°C and 1200°C

YSZ

New TBC

High K, Low Sintering rate

Sintering behavior of new materials: Challenges
Free standing bi-layer coatings
Isothermal exposure at 1200°C for 24 hours

Big difference in sintering rates require microstructural modifications
Toughness is an issue with Cubic pyrochlore, GDZ

- YSZ more sensitive to processing than GDZ
- Equivalent sintering affects YSZ fracture toughness more than GDZ

Fracture toughness, $K_C$ (MPa$\cdot$√m)

Indentation modulus, $E_{ind}$ (GPa) → $E \alpha 1/\text{porosity}$
Larger microcracking in GDZ due to low toughness

Introduces processing challenges

SEM

YSZ

20µm

GDZ

20µm

Filtered

Y3

20µm

G3

20µm
FCT durability of bi-layered YSZ and $\text{Gd}_2\text{Zr}_2\text{O}_7$ coatings

Failed microstructure (C)

Spalled GDZ layer

YSZ layer

TBC Lifetime (Hours)

- Single Layer Porous YSZ
- Porous
- Med. Porosity
- Low Porosity

Failed At YSZ-GDZ interface

DOE UTSR Meeting, Oct 2014, Purdue University, IN
Big difference in sintering rates require microstructural modifications

Free standing bi-layer coatings
Isothermal exposure at 1200°C for 24 hours

Before

After

Conductivity (W/mK)

0.8
1.0
1.2
1.4
1.6
1.8

LMP (Larson Miller Parameter)

42000 44000 46000 48000 50000 52000 54000 56000

YSZ

Tan et. al

Toughness of GDZ!!!
Systematic progress over past four years

- **Y1**
  - YSZ and GDZ process property relationships
    - Process Map development
    - Toughness, Lignite ash penetration depth, erosion

- **Y2**
  - Rough bond coat process optimization with 40% increase in FCT life
    - Two layer dense BC layer

- **Y3**
  - Bi-layer YSZ coating with two fold increase in FCT life, and maintaining low $K$
    - High toughness interface layer, Elastic energy model

- **Y4**
  - Multilayer YSZ-GDZ coating system
    - Enhanced life, Lignite ash penetration minimization, erosion resistance
CTSR
Further reduction in the cost- Bondcoat processing, other TBC materials

CTSR
Burner rig testing with CMAS attach

CTSR
TBC overhaul: reclaimed substrates

CTSR
Deposition and testing on an actual component

GE Aviation
Different FCT cycling time

Praxair
Gradient Jet-test

Siemens
FCT

ORNL
Various cycling time and substrate material

Extension and evaluation of multilayer YSZ-GDZ coatings
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