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

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Thermal Barrier Coatings in Hydrogen-Fired IGCC Turbines

**CHALLENGE:** Improved reliability and lifetime of coatings in IGCC gas turbines

- Increased mass flow of syngas fuel
- Increased heat transfer from water vapor
- Impact of water vapor on oxidation
- Contaminants

**APPROACH:** Tailored and optimized plasma-sprayed thermal/environmental barrier coating

- Material requirements and selection
- Processing impacts on microstructure and properties
- Iterative coating design and testing
- Industry feedback and knowledge transfer

Courtesy of GE
Degradation in IGCC Gas Turbine TBCs

Can lead to degradation of top coat and also leads to increased bond coat oxidation

**Approach:** Investigate microstructure-degradation mechanism links in novel zirconates and bond coat materials

Water Vapor
High Sulfur Content

Leads to localized coating spallation and reduced thermal protection

**Approach:** Increase TS coating toughness through use of materials and controlled processing of splat interfaces

Higher Turbine Inlet Temperatures

Leads to increased sintering rates and higher temperatures at the TBC/Substrate interface

**Approach:** Integrate novel zirconates (e.g. Gd₂Zr₂O₇) which have increased sintering resistance and low thermal conductivity

Particle Impact

Erosion

Particle Adhesion

Deposits

Residual Stress from Thermal Expansion Mismatch

Ceramic Top Coat

Oxidation & Cracking at Interface

Crack Initiation Sites Could Lead to Enhanced Degradation

Diffusion of Corrosion Species

Stresses develop during TS processing and also result from thermal expansion mismatch between the TBC and substrate

**Approach:**
1. Evaluation of deposition stresses using in situ sensing and ex situ X-ray diffraction techniques
2. Tailoring of coating stresses through process control which influences structural effects

Nickel Superalloy Substrate

Diffusion of coal ash species (e.g. Si, Al, Ca, Mg, Na, K, sulfate ions) into the top coat can lead to local spallation and can increase bond coat oxidation

**Approach:** Systems-level evaluation of processing-microstructure-property relationships for multilayer TBCs exposed in controlled atmospheres with simulated ash deposits
Proposed IGCC Coating Architecture

**Development/Evaluation Plan**

**Erosion Resistant Top Coat**
- Produce dense YSZ and Gd$_2$Zr$_2$O$_7$ top coat layers
- Evaluate erosion resistance of dense materials
- Develop density-graded structure for top coat

**Thermal Barrier Layers**
- Determine Gd$_2$Zr$_2$O$_7$ properties (thermal/mechanical) under thermal gradients
- Assess IGCC environmental effects on degradation of zirconates

**Bond Coat**
- Evaluate processing (HVOF/LPPS + anneal) effects on microstructure and phase composition of MCrAlY (where M = Ni, Co, Si, Hf, and/or La)
- Determine IGCC environmental effects on long-term oxidation of bond coat materials

**Performances Attributes**

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

**Layer Microstructures**

- APS Dense Gd$_2$Zr$_2$O$_7$
- APS Gd$_2$Zr$_2$O$_7$
- APS YSZ
- HVOF/LPPS MCrAlY

**Nickel Superalloy**
(Rene 80 or CMSX4)
Overall UTSR Program Approach

Advanced Thermal Spray TBCs for IGCC Turbine Systems

**Bond Coat**
- Materials: MCrAlY, $M = \text{Ni, Co, Si, Hf, La}$
- Processing Effects on Microstructure (HVOF/LPPS/Anneal)
- Isothermal Exposures in water vapor
- Property Evaluation: Oxidation behavior in high temperature water vapor

**Top Coat**
- Materials: YSZ, $\text{Gd}_2\text{Zr}_2\text{O}_7$
- Processing Effects on Microstructure (APS)
- Isothermal Exposures in water vapor
- Property Evaluation: Thermal conductivity, sintering, compliance, erosion, thermal expansion

**System Level**
- Rig Testing: Thermal gradient exposure with water vapor
- Isothermal Exposures with ash deposits
- Property Evaluation: Bond coat oxidation, through-thickness residual stress and composition, erosion

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Thermal spray is a complex process

- Melting, quenching and consolidation in single process
- Splat based build-up and state induced properties
  - High velocity & temperature (melting/softening)
  - Impact & rapid solidification
  - Quenching, thermal stresses

Layered and graded architectures through successive splat quenching

- Layered Thick Films
- Graded Porosity In ceramics
Common Approach for TBC Manufacturing

Feedstock Characteristics

Process Variables

Plasma Spray Grey Box

Component Performance

CTSRR Approach for TBC Development

Feedstock Characteristics
- Composition
- Morphology
- Size Distribution

Spray Stream Characteristics
- Plume Orientation
- Plume Spread
- Particle State

Deposition Conditions
- Feed rate
- Raster / Rotation Rate
- Angle of Deposition

Coating Structure
- Defect (Cracks & Pores)
- Crystal (Phase & Composition)
- Layering (Splat Characteristics)
- Grain (Size)
- Anisotropy

Coating Property
- Structural
  - Adhesion, Residual Stress,
  - Toughness, Stiffness, Elastic Modulus
- Functional
  - Electrical / Thermal transport,
  - Wear / Erosion / Corrosion Resistance

Process Variables
- Equipment related
  - (Gun, Gases, Power)
- Particle Injection

Substrate Conditions
- Chemistry
- Adsorbates
- Temperature
- Roughness

Component Performance

How can modern TS science enhance TBC requirements?

Properties dominated by defects, nanoscale grains, splats interfaces and interphases

Temperature-Dependent Thermal Conductivity

Nonlinear Stress-Strain

Integrated Process Diagnostics

Neutron-based Assessment of Pore Distribution (3D)

Thermal Aging Effects on Properties

2nd Order Process Map
Elastic Modulus Contours
What is the difference in these TBC coatings?

Understanding, optimizing and controlling microstructure is critical for design, performance and reliability.
Thermal spray microstructure has significant influence on material properties.

Clarke and Phillpot, Materials Today, June 2005

Nakamura et al., Acta Met, 2004
Integrated Study of Thermal Spray TBCs

- Understand and control the plasma spray process to tailor and optimize the microstructure
- Develop methodologies for diagnostics, control, microstructure and property quantification
- Establish correlations among process-microstructure-properties so as to affect
  - Microstructure, thermal conductivity and compliance
- Achieve repeatability and reliability in microstructure and properties
- Assess changes in properties at time and temperature

⇒ Provide input for design
⇒ Reduce infant mortality and improve reliability
⇒ Quantify microstructure evolution for life prediction
Integrated Studies of TS Coatings Including TBCs

- Fundamental process science and property evaluation at CTSR

3D Particle In Flight Diagnostics

In Situ Curvature Sensor
Integrated Studies of TS Coatings Including TBCs

- Fundamental process science and property evaluation at CTSR
- Collaborative studies with Consortium members including field trips to industrial sites
Many parameters can be considered for tailoring a microstructure

- Starting powder morphology
- Particle size distribution
- Particle injection
- Plasma torch, power and gases
- Substrate temperature
- Particle flux
- Robot motion

- Examine process/coating repeatability
- Examine testing repeatability

Start the Gun

Set Parameters

Low Feed Rate

Diagnostics

Collect Splats

High Feed Rate

Diagnostics

Coating for In-situ Curvature

Stop

+ Pore Architecture
  Modulus (two orientations)
  Indentation
  Stress-Strain
  Thermal Conductivity
  (in-plane and through-thickness)
Example 1: Effect of Starting Powder Morphology

Each Powder Optimized to Produce the Same Average T & V
Example 1: Effect of Starting Powder Morphology

Each Powder Optimized to Produce the Same Average T & V

Similar Total Porosity and Higher % ILP
Example 1: Effect of Starting Powder Morphology

HOSP shows consistently lower E and K

Each Powder Optimized to Produce the Same Average T & V
Example 1: Effect of Starting Powder Morphology

Temperature-dependent K and mechanical behavior differences are observed.
Example 2: Changing T-V process space via torch parameters
Example 2: Changing T-V process space via torch parameters

Changing torch parameters effects particle temperature distribution
Example 2: Changing T-V process space via torch parameters

Changing torch parameters effects microstructure, elastic modulus and thermal conductivity.
Example 2: Changing T-V process space via torch parameters

Process map allows for distinguishing processing effects

2\textsuperscript{nd} Order Process Map

Low K & Compliant

Stiff

Poor efficiency
Example 2: Changing T-V process space via torch parameters

Total amount and type of porosity can be controlled
Example 2: Changing T-V process space via torch parameters

Mechanical behavior is influenced by processing.
Example 2: Changing T-V process space via torch parameters

Detailed process maps can be created for use by process and design engineers.
Microstructural Effects on Mechanical Behavior

- Intra-splat columnar grains
- Inter-splat interfaces

- Fractured Surface
  Cross-section APS-YSZ

- Polished Surface
  Cross-section APS-YSZ

- Globular Pores
- Inter-splat Spacing
- Cracks within a splat
- Cracks between the splats
Microstructural Effects on Mechanical Behavior

**Upon Mechanical Loading**

- **Mechanism 1:** Opening/closure of pores or spacings, the source of Non-linearity
- **Mechanism 2:** Sliding of defect surfaces causes frictional energy loss, Hysteresis behavior

Non-linearity of the coating represents the compliance present in it
**Microstructural Effects on Mechanical Behavior**

**In-situ: Curvature Monitoring**

Measurement tells the evolution history of a deposited coating. Each local peak corresponds to a pass (deposition of one layer). The slope of the curvature evolution is referred as “Evolving stress”.

**Ex-situ: Thermal Cycle of the Coated Specimen**

After spraying, the coating (with substrate) is heated inside a furnace. The temperature change induces mismatch strain, and the curvature of coating changes. The continuous recording of one thermal cycle provides an ANELASTIC curv-temp plot, which is then converted to a stress strain curve to quantify the coating compliance.
Microstructural Effects on Mechanical Behavior

Case study: three coatings deposited at three different spray distances

**In-situ**

Curvature evolution during spray

**Ex-situ**

Curv–temp relationship obtained from post deposition thermal cycling

In-situ

Ex-situ
Microstructural Effects on Mechanical Behavior

Case study: three coatings deposited at three different spray distances

Estimated stress-strain curves

Non-linear parameters of the three coatings

Elastic Modulus, $E$ (GPa)

Non-linear Degree, $ND$

0.99 W/m-K
60 mm

0.82 W/m-K
100 mm

0.69 W/m-K
150 mm

Elastic Modulus, $E$ (GPa)
How could deposits impact mechanical behavior?

**Coating with salt solution treatment** was 30% stiffer than as sprayed one. It also showed more hysteresis in it.

Salt mist was introduced between some selective passes during coating deposition.

The presence of salt at defect surfaces made the coating stiffer, with increased non-linearity and hysteresis.
IGCC Turbine Coating Properties: Material Effects

Material choice influences thermal properties

Thermal Conductivity of As-Sprayed Coatings

As-sprayed Coatings

Thermal Conductivity (W/m.K)

- La$_2$Zr$_2$O$_7$
- Gd$_2$Zr$_2$O$_7$
- Co-doped YSZ
- YSZ
IGCC Turbine Coating Properties: Material Effects

**Erosion of As-Sprayed Coatings**

Material choice influences erosion properties with $\text{Gd}_2\text{Zr}_2\text{O}_7$ having high erosion rates.
**IGCC Turbine Coating Properties: Material Effects**

**Mechanical Behavior of As-Sprayed Coatings**

Material choice influences mechanical properties.
Gadolium Zirconate $\text{Gd}_2\text{Zr}_2\text{O}_7$

In-flight Particle Velocity (m/s)

In-flight Particle Temperature (°C)

Condition 1
Condition 2
Condition 3
Condition 4

Thermal conductivity (W.m$^{-1}$.K$^{-1}$)

Cond. 1 Cond. 2 Cond. 3 Cond. 4

0.6
0.7
0.8
0.9
1.0

0.6
0.7
0.8
0.9
1.0

IGCC Turbine Coating Properties: Processing Effects
IGCC Turbine Coating Properties: Processing Effects

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

Thermal conductivity (W.m$^{-1}$.K$^{-1}$)

- Condition 1
- Condition 4
- Condition 3

Time at 1200 °C isothermal exposure (hours)

0 20 40 60 80 100 120

**Microstructure influences thermal properties**
Thermally Sprayed Multilayer TBC

Multilayer coating demonstration
Modeling of Thermal Conductivity Evolution in a Gradient

Schematic of the model used to predict temperature gradients in TBCs from thermal conductivity values determined isothermally.

Comparison of isothermal and thermal gradient models with rig test thermal conductivity and temperature change across the TBC data showing good agreement.
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.
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**Thermal spray microstructures are complex with multiscale features that heavily influence material properties.**

**Advanced thermal spray processing science allows for a greater understanding between parameters, particle state, microstructure, and coating properties.**

Through the UTSR program, CTSR will assess multilayer TBCs for coal-gas-derived systems by investigating new materials and process-induced properties and their impact on degradation mechanisms.