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







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<u>CHALLENGE</u>: Improved realiability 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

<u>APPROACH</u>: Tailored and optimized plasmasprayed thermal/environmental barrier coating

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



TBC degradation in IGCC is more complex than in natural gas turbines ³







TBC degradation in IGCC is more complex than in natural gas turbines 4



Multilayered architecture to combat multifunctional requirements ⁵



Plasma spray is naturally suited for such layered manufacturing





Status of today's TBCs

Plasma spraying is the principle approach for TBC manufacturing

- YSZ by atmospheric plasma spray and variants
- CoNiCrAIY bond coat via LPPS or HVOF

Salient facts:

- 2 M pounds of YSZ was plasma sprayed in 2010
- Multitude to spray cells within OEM and throughout the supply chain all over the world

The TBC system of today was started almost 40 years ago







Life cycle of a TBC



What is the difference in these TBC coatings?





15% Porosity

16% Porosity



20 % Porosity



Understanding, optimizing and controlling microstructure is critical for design, performance and reliability.



Thermal spray is a complex process



Sprayed coatings are complex, layered, high defect density materials ¹⁰



How to design based on the defect architecture ? How to precisely manufacture coatings with defects ? What are the relevant and true properties for design ? How to measure them and How to assess reproducibility ? What processing protocols do we follow for control ?

APS TBC fabrication involves numerous variables



& parameters

locations

Multitude of evaluation

Criteria and variants



Intrinsic

- Engine design variants, operating environment
- Material system and components
- Part geometry
- Location specific performance attributes

Extrinsic

- Feedstock materials (chemistry/morphology/size /homogeneity)
- Coating processing location and equipment attributes (control !)
- Spray Process parameters
- Deposition parameters (robotic manipulation, dep.temp., flux etc.)
- Part handling and management (prep, heating, cleaning)

Evaluation criteria, specification, semantics !





How can modern TS science enhance TBC requirements?







Advances in Process Monitoring and Control



Relevant properties for plasma sprayed thermal barrier coatings¹⁵





All these properties are governed by coating architecture, commonly called as "porosity"
 can be tailored by processing...



How do defect architecture affect thermal conductivity ?

Thermal conductivity



Recent work has demonstrated non-linear elastic effects 17



Quantifying compliance for different processing/microstructure



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







Identification of compliance parameters



The two parameters are unique to a coating.



Non-linear parameters and FCT life







It has been a moving target to define properties...



Integration of processing science with properties and performance



Overall UTSR Program Approach







- Evaluate oxidation characteristics of different types of bond coat materials in water vapor containing atmospheres in order to select the most viable material and processing condition.
- Develop processing strategies and maps for plasma spraying of emerging zirconate materials.
- Optimize engineered coating architectures for the ceramic top coat of the TBC system to simultaneously provide erosion resistance, thermal and environmental protection, low thermal conductivity, sintering resistance and compliance.
- Determine the degradation mechanisms in multilayer TBCs after controlled-atmosphere furnace tests & erosion tests.





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Not all bond coats are the same ! Processing plays a role 27



Processing Effects on HVOF Bond Coats



JP5000 chosen due to microstructure and compressive stress state.



Impact of water vapor on conventional and new TBC materials



No significant difference found at this temperature

Ongoing collaborative partnership

HVOF bond coats have been sprayed (NiCoCrAlY & NiCoCrAlYHfSi) for ORNL testing



ORNL is investigating the interactions with several different substrate
 materials





Down selection of bond coat material



XPT: NiCoCrAIY

AMDRY: NiCoCrAIY-HfSi

Reactive element bondocat showed higher life under all the conditions



Collaboration with Dr. Bruce Pint and Dr. Allen Haynes at ORNL



Bond coat roughness effects may overshadow chemical effects?



Approaches for roughness improvement via processing



Two layer bond coat: roughness results

Coating #	#Spray Run #Spray Run #Fine Powder (AMDRY 386-2)Coarse Powder (AMDR		Roughness , Ra (µm)
1	R860	R863	7.3 - 9.7
2	R861	R864	8.1 - 8.5
3	R862	R865	7.9 - 8.5



R860: Densest bottom layer

R863: Poor splat cohesion



R861: Denser bottom layer

R864: Poor splat cohesion and some cracking



R862: least dense bottom layer

R865: good particle melting and splat cohesion



Selected parameters

- □ R860 for dense layer (100µm)
- □ R865 for coarse layer (50µm)



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Process development for multilayer top coats is critical







Need for higher operating temperature and severe environments

		Traditional YSZ	New TBC Requirement
-	Phase Stability	Good < 1200C	Good<1300-1400C
	Thermal Expansion	Fair	Challenging
	Thermal Conductivity*	Low	Lower
	Sintering Resistance*	Fair	Good
	Erosion Resistance*	Good	Challenging
	Fracture Toughness*	Good	Challenging
	Mechanical Compliance	known	To be explored

Materials' intrinsic properties

Can be optimized via processing strategies*





TBC Materials under considerations

Material	Composition	Advantages	Powder
YSZ	7-8wt% YSZ	Stable below 1200 C, cost effective, properties well-characterized	Various sources, different levels of purity
Zirconate	La ₂ Zr ₂ O ₇	Pyrochlore, low thermal conductivity, phase stability to 1400 C	Julich
Zirconate	Gd ₂ Zr ₂ O ₇	Pyrochlore, low thermal conductivity, phase stability to 1400 C, compatible with YSZ	Saint Gobain, Julich,
Co-doped	1.5mol%Yb2O3 1.5mol% Gd2O3 2.1mol% Y2O3 ZrO2	t' phase, low thermal conductivity, sintering resistant, compatible with MCrAIY bond coat, high erosion resistance	NASA













Processing challenges with new materials

General processing challenges

Different melting temperature than YSZ

- Optimization of Plasma condition
- Optimization of powder cut
 - Different conditions for several layers

Properties driven processing challenges

- Poor erosion resistant of new materials
 - Denser yet sufficient compliance
- Lower fracture toughness than YSZ
 - Microstructural optimization

Cost driven processing challenges

- Minimum use of the material
 - Traditional or alternative materials
 - **Compatibility issue**

Multi-directional integrated approach to address the challenges



Extend knowledge gained with YSZ to new ceramics







Process enabled tailoring of microstructure & properties







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Comparing process space between YSZ and Gd₂Zr₂O₇







Process Maps for new materials: case study $Gd_2Zr_2O_7$



Process Map

Coating Deposition

Multidimensional characterization to achieve desired properties

- Evolving Stress
- Coating Modulus
 - Non-linearity/Compliance
 - Thermal Conductivity
- Erosion
- Fracture Toughness



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ICP: Evolving stress



Stoney's formula for <u>Evolving stress</u>

$$\sigma_{\rm Ev} = \frac{E_S' t_S^2}{6\Delta t_D} \Delta \kappa$$



ECP: E, ND and HD



Insitu and Exsitu curvature characterization of coating stresses ⁴⁶



Gd₂ZrO₇ generally shows lower stress evolution than YSZ



Lower toughness ?

Poorer splat-splat bond ?



Comparison of non-linear elastic properties for range of process conditions 47



Correlation between thermal and mechanical properties







GdZ is significantly more sinter resistant and related to starting microstructure 49



UH-GdZ-Fine

- GDZ: Showed Low-K
- The sintering rate can be controlled via processing
 - Important for multilayer TBC development

Sintering behavior of new materials



Erosion performance of new material (**Gd₂ZrO₇**)





Process monitoring and other observations for **Gd₂ZrO₇**



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Understanding for individual layer Step to multilayer coatings

Step-1: Bi-layer













Gd₂ZrO₇/YSZ double layer



Sintering compatibility of bi-layers

Isothermal exposure at 1200°C for 24 hours



Matching compliance of GdZ with that of YSZ



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Sintering compatibility of bi-layers via processing



Lignite ash exposure @ 1200C for 24 hours

Low-Low

High-High



Med-Med

Simulated Lignite ash was provided by Prof. Nitin Padture, Brown University



NASA Co-doped materials





Comp. 1	1.5mol% Yb2O3 1.5mol% Gd2O3 2.1mol% Y2O3 Balance ZrO2		t' phone
Comp. 2	1.2mol% Yb2O3 1.2mol% Gd2O3 1.7mol% Y2O3 Balance ZrO2	□low K □sintering resistant	t phase
Comp. 3	1.9mol% Yb2O3 2.0mol% Gd2O3 6.0mol% Y2O3 Balance ZrO2	Compatible with MCrAIY BC Indext provide the second strain of	Lower K
Comp. 4	3.0mol% Yb2O3 3.0mol% Gd2O3 3.0mol% Y2O3 Balance ZrO2		cubic



Material courtesy: Dongming Zhu, NASA Glenn



Non-linear parameter space



Thermal properties

G-L	Gd ₂ ZrO ₇ Low Cond			
G-M	Gd ₂ ZrO ₇ Medium Cond			
G-H	Gd ₂ ZrO ₇ High Cond	C#1	Co-doped # 1 Med Cond	
G-UH-F	G-UH-F Gd ₂ ZrO ₇ Ultra High C#2 Cond (Fine powder) C#2		Co-doped # 2 Med Cond	
			Co-doped # 3 Med Cond	
Y-L	YSZ Low Cond	0#3		
Y-M	YSZ Med Cond			
Y-H	YSZ High Cond			





Performance assessment of co-doped powders



Co-doped powder#2 and 3: Reaction with Lignite at high temperature



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Co-doped powder: summary



Task update summary

Task Discription	% Progress	Status	Comment
Project Management and Planning			
1.1 Revise and Maintain Project Management Plan	100	Completed	
1.2 Quarterly Assessment and Reporting	100	Completed	
1.3 Annual Meetings	100	Completed	
1.4 Final Report	0	On schedule	
ond Coat Processing and Evaluation			
2.1 Bond Coat Processing and Microstructural Evaluation	90	Completed	Additional characterization
2.2 Determination of Bond Coat Oxidation Behavior in High Temperature Water Vapor	60	Completed/revisiti	Working w ith ORNL
2.3 Final Selection of Bond Coat Material for System-Level Coating	90	Completed/revisiti	Collaboration with
			Working with ORNL + Setup develop
MILESTONE: Determination of bond coat oxidation behavior in controlled atmospheres	60	Completed/revisiti	at CTSR
MILESTONE: Down-selection of optimum bond coat material and processing for			
	80	Completed/revisiti	In progress, working with ORNL
nermal Barrier Processing and Evaluation			
			Additional process conditions are bei
3.1 Process Optimization of Zirconates Using Diagnostics and In Situ Property Sensing	100	Completed	considered
3.2 Evaluate Sintering Behavior of Bilaver TBC	100	Completed	More work is being done
3.3 Determine Thermal Conductivity Changes Due to Thermal Gradient Exposure	50	Behind Schedule	Burner rig test setup is completed
3.4 Determine Coefficient of Thermal Expansion for Gd27r2O7	100	Completed	More measuremnets will be conducte
3.5 Frosion Testing of Dense Top Coat	100	Completed	
MILESTONE: Process maps will be completed relating processing conditions to			
properties for plasma sprayed Gd2Zr2O7	100	Completed	
MILESTONE: Development of gradient thermal conductivity model for plasma sprayed			Application of the model for various
Gd2Zr2O7	80	Completed	lavers is being considered
			Additional processing conditions are
MILESTONE: Development of erocion-resistant Gd27r2O7 top layer for TBC	100	Completed	being explored
stom-Level Evaluation of Multifunctional Coating	100	Completed	
	50	On schedule	
4.2 Rig Testing	10	On schedule	Burner rig test setup is completed
4.3 System Level Oxidation and Hot Corrosion Testing	30	On schedule	ECT test setup is completed and start
4.4 Residual Stress and Composition Evolution in Multilaver Coatings	30	On schedule	
4.5 Additional Ex Situ Characterization of Multilayor Coatings	35		
4.5 Additional EX Situ Characterization of inditilayer Coatings			
million of oxidation and not contrain behavior of	20		FCT and Burner rid setup
MILESTONE: Determination of residual stress state and compositional evolution in	20		
multilayer coatings exposed to high temperature water vapor atmospheres	NA	On schedule	
MILESTONE: Determination of thermal and mechanical properties in multilover TBCs after	14/4		
hine temporature, controlled atmosphere exposures	ΝΔ	On schodulo	
Ingritemperature, controlled attrosphere exposures	11/4	On schedule	BR

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STATE: UNIVERSI

Collaboration Efforts: Industrial Partnerships



Working with them regarding Gd₂Zr₂O₇ commercial thermal spray powder development



Anand Kulkarni of Siemens for Substrate and FCT testing



Bruce Pint/Allan Haynes ORNL

A.Shyam, E.Lara-Curzio ORNL HTML





