

Integrated TBC/EBC for SiC Fiber Reinforced SiC Matrix Composites for Next Generation Gas Turbines

DoE UTSR DEFE0031281 Kickoff meeting

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- Engine efficiency increases with a higher turbine surface temperature.
- The combustion temperature in next generation turbines is expected to reach ~1700°C.
- Will require SiC/SiC CMC as the turbine material with coatings
- Significant challenge for thermal barrier coating (TBC) and environmental barrier coating (EBC) development including:
 - CTE mismatch
 - Protect CMC from oxidation
 - Prevent material volatilization under hot steam



- Currently Ni-based superalloys have almost reached their intrinsic temperature limit.
- SiC continuous fiber reinforced SiC ceramic matrix composites (SiC/SiC CMCs) are the most promising material system for use in next generation turbine engines.
 - low density, high strength and toughness
 - high temperature stability
 - high temperature creep resistance
 - high-temperature oxidation resistance in dry air



- However, SiC/SiC CMCs can have catastrophic recession under high velocity steam.
- SiC can be oxidized to SiO₂ to form a protective scale

$$SiC + \frac{3}{2}O_2(g) \rightarrow SiO_2 + CO(g)$$

Silica reacts with water vapor to form volatile hydroxide species

$$SiO_2 + 2H_2O(g) \rightarrow Si(OH)_4(g)$$

• At high temperatures, silica can also directly react with SiC to form gas species

$$2SiO_2 + SiC \rightarrow 3SiO(g) + CO(g)$$



The lack of stability in steam environment requires environmental barrier coatings

The requirements for EBC/bond coat (BC)

- Good thermal expansion coefficient (CTE) match with CMC
- Good CMC adhesion
- Stable in water vapor and oxygen
- Phase stability and chemical compatibility,
- High strength and toughness



Current EBC developed at NASA Glenn Research Center¹

 Zhu, D., Harder, B., Hurst, J. B., Good, B., Costa, G., Bhatt, R. T., and Fox, D. S. (2017). Development of Advanced Environmental Barrier Coatings for SiC/SiC Ceramic Matrix Composites: Path Toward 2700 F Temperature Capability and Beyond.



Technical Approach



The concept of integrated TBC/EBC/BC



- Dense Y_2O_3 or Yb_2O_3 top layer ensures low oxygen diffusion and volatilization rates under high temperature high velocity steam environment.
- Graded composition allows smooth transition from SiC to SiBCNO with increasing amount of embedded Y₂O₃ particles.
 - Graded structure avoids sharp CTE mismatch
 - Tolerant to oxidation; further increase TBC lifetime
 - PDC SiC bond coat/SiC substrate interface provides excellent adhesion



Advantages

- The advantages of the design are
 - Good bonding with CMC;
 - Graded compositions without sharp interfaces to mitigate thermal stresses from CTE mismatch;
 - Low oxygen transport rate, low oxidation rate and low volatility in high temperature, high velocity steam environment;
 - Tolerant to certain degree of oxidation thereby preventing catastrophic failure;
 - Chemically stable and compatible with CMC and TBC (TBC to be developed in future projects)



• Good bonding with CMC:

Si-based PDC precursors yield ceramics with the same composition as the substrate composite.

• Graded compositions without sharp interfaces to mitigate thermal stresses from CTE mismatch:

Flexibly adjustable ratios between the SiBCN/ Y_2O_3 (or Yb_2O_3), the C:N ratio and the Si:B ratio in Si-B-C-N makes PDC precursors most useful in fabricating our graded coating.



Advantages

• Low oxygen transport rate, low oxidation rate and low volatility in high temperature, high velocity steam environment:

 $\rm Y_2O_3$ has an extremely low oxygen diffusion coefficient that is two orders of magnitude lower than that of undoped $\rm HfO_2$ or $\rm ZrO_2$

Y₂O₃ has very good resistance to volatilization under the steam environment



Advantages

• Tolerant to certain degree of oxidation thereby preventing catastrophic failure:

 Y_2O_3 reacts with SiO₂ and forms a mixture of Y_2SiO_5 and $Y_2Si_2O_7$ at 1400°C. The yttrium silicates themselves have been found to have very low oxygen diffusion coefficient and volatilization rate.

This yttrium silicate formation, in addition to the hermetic Y_2O_3 top layer, will further increase the lifetime of EBC/BC at extremely high temperatures.

• Chemically stable and compatible with CMC and TBC (TBC to be developed in Phase II of this project)



Project Objectives



Overall Goals

- Develop an integrated and graded EBC/BC that is:
 - Good bonding with CMC;
 - Graded compositions without sharp interfaces to mitigate thermal stresses from CTE mismatch;
 - Low oxygen transport rate, low oxidation rate and low volatility in high temperature, high velocity steam environment;
 - Tolerant to certain degree of oxidation thereby preventing catastrophic failure;
 - Chemically stable and compatible with CMC and TBC (TBC to be developed in Phase II of this project)
- Create a strong collaborative team with complementary expertise and state-of-the-art facilities
 - The Clemson University team of PIs Bordia and Peng.
 - The GE team, led by John Delvaux



Objectives

- Investigate the effect of composite stoichiometry (i.e. Si/B/C/N ratio in the precursor and the ratio of the Sibased precursor to yttrium oxide (Y_2O_3) (or ytterbium oxide (Yb_2O_3)) particle filler and processing conditions on the size of the resultant phases and nanostructure of the composite ceramics.
- Investigate the effect of the composition and nanostructure on the thermal properties and oxidation and volatilization behavior in oxidizing and high velocity steam environments. The control parameters are the stoichiometry of the precursor (e.g. Si/B/C/N ratio) and the volume fraction of the oxide particles Y2O3 (or Yb2O3) and range of microstructures produced as part of the first objective



Objectives

- Process the graded Y₂O₃ (or Yb₂O₃) particulate /silicon boron carbon nitride (SiBCN) matrix composite coating and investigate the phase and microstructure stability during high velocity steam exposure at temperatures up to 1500°C.
- Develop a method to create Y₂O₃ (or Yb₂O₃) and SiBCN powders with predetermined compositions suitable for atmospheric plasma spraying (APS). The powders will be provided to the industrial collaborators for the fabrication of integrated environmental barrier coating/bond coating (EBC/BC) using APS.
- Evaluate the performance of integrated BC/EBCs from APS under high velocity steam environments at temperatures up to 1500°C.



Project Structure



Project Tasks

- Task 1.0: Project management and planning
- Task 2: Processing and stability of Y₂O₃-Si-B-C-N and Yb₂O₃-Si-B-C-N composites
- Task 3: Thermal and oxidation response of Y₂O₃-Si-B-C-N and Yb₂O₃-Si-B-C-N composites
- Task 4: Processing and performance of graded coatings processed using cold spray and pyrolysis
- Task 5: Processing and performance of graded coatings processed using atmospheric plasma spraying (APS)



Project Tasks – Task 2

Processing and stability of Y_2O_3 -Si-B-C-N and Yb_2O_3 -Si-B-C-N composites

Goal: to develop a rational approach to process composites with the desired phases and microstructure.

- Subtask 1: Determine the effect of composition and processing temperature on the phase and microstructure of composites
- Subtask 2: Investigate the effect of temperatures on the phase-stability phase and microstructure of composites during oxidation at temperatures up to 1500°C



Rationale for Task 2



PDC is very flexible in controlling the final compositions¹



We have abundant experience in fabricating and characterizing PDC ceramic coatings (example above is for oxidation resistant coatings)²

1. Riedel, R., Mera, G., Hauser, R., and Klonczynski, A. (2006). Silicon-based polymer-derived ceramics: synthesis properties and applications-a review dedicated to Prof. Dr. Fritz Aldinger on the occasion of his 65th birthday. Journal of the Ceramic Society of Japan, 114(1330), 425-444.

2. Wang, K., Unger, J., Torrey, J. D., Flinn, B. D., and Bordia, R. K. (2014). Corrosion resistant polymer derived ceramic composite environmental barrier coatings. *Journal of the European Ceramic Society*, 34(15), 3597-3606.



Project Tasks – Task 3

Thermal and oxidation response of Y_2O_3 -Si-B-C-N and Yb_2O_3 -Si-B-C-N composites

Goal: to develop the needed database for the rational design of graded coatings.

- Subtask 1: Effect of composition and microstructure of composites on thermal expansion coefficient, elastic modulus and thermal conductivity
- Subtask 2: Effect of composition and microstructure of composites on oxidation and volatilization during exposure to high velocity steam at temperatures up to 1500°C.



Rationale for Task 3



Peng, F., Erdman, R., Van Laningham, G., Speyer, R. F., and Campbell, R. (2013). Thermal Conductivity of ZrB₂-SiC-B₄C from 25 to 2000° C. *Advanced Engineering Materials*, 15(6), 425-433.



Rationale for Task 3



(a). Illustration of the high velocity testing apparatus used in the oxidation study^{1.} (b) Our home-build TGA unit to characterize oxidation behavior up to $2000 \ ^{0}C^{2}$.

- 1. Golden, R. A. and Opila, E. J. (2016). A method for assessing the volatility of oxides in high-temperature high-velocity water vapor. Journal of the European Ceramic Society, 36(5), 1135-1147.
- 2. Peng, F., Van Laningham, G., and Speyer, R. F. (2011). Thermogravimetric analysis of the oxidation resistance of ZrB₂-SiC and ZrB₂-SiC-TaB₂-based compositions in the 1500-1900 °C range. Journal of Materials Research, 26(1), 96-107.



Processing and performance of graded coatings processed using cold spray and pyrolysis

Goal: to demonstrate a graded BC/EBC system for effective oxidation protection of SiC based CMC

- Subtask 1: Processing of optimized composition graded coatings
- Subtask 2: Characterization of the oxidation and volatilization during exposure to high velocity steam at temperatures up to 1500°C and performance in burner rig and under thermal cycling



Graded composition coatings using atmospheric plasma spraying (APS)

Goal: to demonstrate the feasibility of using APS to make graded coatings and their properties.

- Subtask 1: Processing of powders suitable for APS
- Subtask 2: Processing of graded coatings using APS
- Subtask 3: Characterization of the oxidation and volatilization of APS coatings during exposure to high velocity steam at temperatures up to 1500°C and performance in burner rig.



Project Schedule



Original Timeline – will be Modified

TA[3] Integrated TBC/EBC for Next Generation Gas Turbines (Clemson col. with GE



UNIVERSITY

Original Milestones- will be Modified if needed

- Year 1
 - M1: Selection of polymers and acquisition of the needed materials.
 - M2: Establish the effect of composition and processing temperature on the phase and microstructure of Y₂O₃-Si-B-C-N and Yb₂O₃-Si-B-C-N composites.
 - M3: Design and fabrication of the cold spray processing of coatings and high velocity steam oxidation equipment.
 - M4: Establish the effect of temperatures on the phase stability during oxidation at temperatures up to 1500°C.



Original Milestones- will be Modified if needed

- Year 2
 - M5: Determine thermal expansion coefficient, elastic modulus and thermal conductivity for select composite coating compositions.
 - M6: Determine the effect of composition on oxidation and volatilization during exposure to high velocity steam at temperatures up to 1500°C.
 - M7: Processing of composition graded coatings using cold-spray and pyrolysis.
 - M8: Determine the effect of exposure to high velocity steam at temperatures up to 1500°C on graded coatings made using cold spray and pyrolysis.



Original Milestones- will be Modified if needed

- Year 3
 - M9: Investigate the effect of thermal cycling on graded coatings made using cold spray and pyrolysis.
 - M10: Supply powders for APS to GE Power.
 - M11: Complete Fabrication of graded coatings using APS.
 - M12: Establish the effect of exposure to high velocity steam at temperatures up to 1500°C on graded coatings made by APS.
 - M13: Investigate the effect of thermal cycling on graded coatings made by APS.
 - M14: Phase 1 completion including final report.



Project Budget



Summary Budget

From the Proposal

SUMMARY OF BUDGET CATEGORY COSTS PROPOSED The values in this summary table are from entries made in subsequent tabs, only blank white cells require data entry						
Section A - Budget Summarv						
		Federal	Cost Share	Total Costs	Cost Share %	Proposed Budget Period Dates
		\$389,993	\$210,000	\$599,993	35.00%	Example!!!01/01/2014 - 12/31/2014
	Total	\$389,993	\$210,000	\$599,993	35.00%	
Section B - Budget Categories	Totai	\$309,993	φ2 10,000	\$J99,995	55.00%	
CATEGORY	Federal	Cost Share		Total Costs	% of Project	Comments (as needed)
a. Personnel	\$247,670	\$35,070	\$0	\$282,740	47.12%	
b. Fringe Benefits	\$78,612	\$10,907	\$0	\$89,519	14.92%	
c. Travel	\$6,000	\$0	\$0	\$6,000	1.00%	
d. Equipment	\$29,630	\$0	\$0	\$29,630	4.94%	
e. Supplies	\$25,129	\$0	\$0	\$25,129	4.19%	
f. Contractual						
Sub-recipient	\$0	\$0	\$0	\$0	0.00%	
Vendor	\$0	\$140,000	\$0	\$140,000	23.33%	
FFRDC	\$0	\$0	\$0	\$0	0.00%	
Total Contractual	\$0	\$140,000	\$0	\$140,000	23.33%	
g. Construction	\$0	\$0	\$0	\$0	0.00%	
h. Other Direct Costs	\$17,028	\$0	\$0	\$17,028	2.84%	
Total Direct Costs	\$404,069	\$185,977	\$0	\$590,045	98.34%	
i. Indirect Charges	\$195,924	\$24,023	\$0	\$219,947	36.66%	
Total Costs	\$599,993	\$210,000	\$0	\$809,992	135.00%	



Project Management Plan



Project Goal

The overall goal of this project is to design an integrated and graded bond coat/environmental barrier coating/thermal barrier coating system that can effectively protect and lead to use of SiCf/SiC matrix CMCs in next generation gas turbine with combined cycle energy efficiency of above 65% and life time needed for gas turbines (HGP components: up to 32,000 operating hours before overhaul).



Risk Management

- Scheduling risk (Task not being completed in the allotted time).
 - allow ample scheduling flexibility.
 - at any given point in time, the post-doc and the students will be working on two or three different tasks.
 - regularly (once every two weeks) discuss the progress of the project with our collaborators at GE Power.
- The project's high technological value.
 - both PIs and our collaborators at GE have a rich background in their field of expertise and can tackle conceptual difficulties associated with the project using alternative approaches and strategies.



Risk Management

- Human resources
 - Typically we have advance notice of post-doc/student leaving and will move immediately to recruit a new postdoc/student.
 - As a last resort, we will request a no-cost extension on the project and recruit another researcher to work on the project.
- Hardware related failure.
 - repair it using our discretionary funds or by reallocating the budget in this project.
 - If the failure is major, we will use our network of collaborators at other institutions and national labs who have similar pieces of equipment in their lab.



Risk Management

- Since the proposed research is transformative, it is possible that the basic hypothesis (i.e. improvement of coating performance using graded composite coatings) is not correct.
 - in the proposed research, we plan to investigate a broad spectrum of composites (in the early stages); thus, the research will provide ample opportunities to fundamentally explore this possibility and determine its technical usefulness and limitations.
- Not possible to optimize the microstructure for maximizing all the needed properties for this application.
 - in consultation with our collaborators at GE, we will determine a rank order and weighing factors for the relevant properties and using this metrics, select the best coating system.









Thank you very much for your attention