Final Scientific/Technical Report

University of Maryland College Park
Final Sicentific/Technical Report
New Environmental-Thermal Barrier Coatings for Ultrahigh Temperature Alloys
Contract Number: DE-AR0001424

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Lead Recipient:	University of Maryland College Park (UMD)
Project Team Members:	Prof. David Clarke, Prof. Liangbing Hu, Dr. Yunhui Gong
Project Title:	New Environmental-Thermal Barrier Coatings for Ultrahigh Temperature Alloys
Program Director:	Dr. Philseok Kim
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Contract Administrator:	Stephanie Swann
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Public Executive Summary

Provide an executive summary, which should contain information with unlimited rights **but NOT contain proprietary or protected information**. ARPA-E may use this section to respond to requests for information about your project after its conclusion or may otherwise determine that it needs to make this information immediately available to the public.

This section should include a discussion of 1) how the research adds to the understanding of the area investigated; 2) the technical effectiveness and economic feasibility of the methods or techniques investigated or demonstrated; and 3) how the project is otherwise of benefit to the public. The discussion should be written in terms understandable by an educated layman.

Our ARPA-E funded project, New Environmental-Thermal Barrier Coatings for Ultrahigh Temperature Alloys, has made significant strides in advancing the understanding of design and fabrication of novel thermal barriers coatings. Through rigorous research and innovative approaches, our team has explored new frontiers, pushing the boundaries of knowledge in this critical field.

1. Advancing Understanding.

The challenge that still remains unresolved is how to accelerate the coating composition selection and conduct diverse tests on the coatings. In this project, we introduced an ultrafast high temperature sintering (UHS) method to accelerate the coating iteration process, which offers a rapid method of producing ETBCs, at a small but realistic scale, for empirical evaluation. We have built a coefficient of thermal expansion (CTE) database of various coating and substrate candidates, which helps guide the coating composition selection together with other considerations like melting point, thermal stability, phase compatibility, and high temperature mechanical properties. This not only enables a much larger repertoire of compositional variables and combinations to be assessed qualitatively but, just as important, determines ones that could lead to failure so that certain combinations can be eliminated. Together with approaches like ink spraying, tape casting, or a slurry dip technique, UHS is conducted to sinter the thermal barrier coatings on various alloy and ceramic substrates within minutes. As an example, we have fabricated TBCs on Nb-based C103 substrate by UHS treatment. The results show that YMS/$NbSi_2$ coatings were well adhered to the C103 substrate after UHS treatment, demonstrating that UHS process is effective for fabricating TBCs on a refractory alloy. We have evaluated the performance of the coatings, using room temperature to 1300°C thermal cycling tests and measured thermal conductivity, by which the coating compositions can be further evaluated and re-adjusted to refine the iteration steps for more robust results. These findings not only contribute to the academic community's knowledge and understanding but also pave the way for future research, offering a foundation upon which others can build and expand.

2. Technical Effectiveness and Economic Feasibility.

We have developed the manufacturing flow and predicted the cost model for ETBCs fabrication by the UHS process. The technical flowchart delineates multiple crucial stages, including Non-Destructive Testing (NDT) inspection of the incoming substrate, substrate surface cleaning, bond coating, sequential top coating, ultrafast sintering, and final product inspection. This manufacturing flow serves as the foundation for estimating capital investment, materials consumption, energy usage, and operational costs. It enables the comparison of ETBCs produced by different processes, such as electron beam physical vapor deposition (EB-PVD) and plasma spray, and assesses sensitivity to potential changes in operational and market conditions.

The cost of coating an actual part with a modern TBC system is multifaceted and falls into three primary cost categories:

a. One-time cost factors, which include application development, tooling development and design, processing qualification and approval, and production process documentation.

b. Direct coating-related cost factors, comprising direct materials (such as powder, ingot, plating salt, and aluminizing donor alloy), auxiliary materials (like grit, cleaning agents, and gloves), labor for various tasks (including incoming inspection, cleaning, surface preparation, and post-coating processing), equipment amortization, energy, and process gases.

c. Indirect cost factors, encompassing materials preparation and recycling, preventive maintenance and spare parts, strip and rework in case of non-conformance, tooling cleaning and rework, tooling replacement, and packing and shipping.

The cost of coating an actual part significantly depends on the part's volume and its product life cycle. Higher volumes and longer production life cycles tend to reduce the relative percentage of one-time costs. Additionally, the efficiency of the coating process balances process uniformity requirements and the process window. A broader coating specification, within a reasonable range, can make the coating process more economical, particularly in multi-part batch operations.

Tooling costs vary according to the process and the part. For instance, stainless steel tooling materials are generally sufficient for thermal spray processing, while processes like EB-PVD and platinum aluminide diffusion require superalloys due to higher operating temperatures. Tooling wear depends on the tooling stripping process, with grit blasting being generally more aggressive than wet stripping.

Given the variability in cost elements, stating precise coating costs can be misleading. Instead, it is more practical to provide a typical range of costs based on various processing factors. In the following sections, we evaluate these cost elements for selected examples, which highlights the primary cost groups (b and c) as mentioned earlier.

For the cost breakdown, we assume a 10-year equipment amortization scheme with a 10% annual interest rate, material costs ranging from \$30 to \$70 per kg for ceramic powder and ingot, and \$50 to \$100 per kg for MCrAlY powder. The price of 1 oz of Pt exceeds \$900. Energy costs are based on US averages, with gas prices estimated at approximately \$0.1 to \$0.2 per kg for CO_2, \$0.5 per m3 for argon, and \$1 to \$2 per liter for kerosene.

In this project, we primarily focused on the processing of multilayer coatings and ultrafast sintering to estimate the costs associated with materials and operations. Technical and economic information regarding inspection, cleaning, and bond coating steps were provided by potential industrial collaborators. We have estimated materials costs and the cost of coating/sintering operations. Materials costs are estimated to be $11.12 based on coating materials and chemical stoichiometry.

Based on our estimation, the methods and techniques investigated in this project have proven to be highly effective and potentially economically feasible. Through meticulous experimentation and analysis, we have developed robust solutions that address the challenges of highly efficient developing novel environmental thermal barrier coatings. These solutions are not only technically sound but also economically viable, offering a practical pathway for implementation in real-world scenarios. Our leadership estimates that achieving a marketable product, refining production methods, securing manufacturing and distribution partners, and executing a go-to-market strategy can be accomplished within the next 4–5 years.

3. Public Benefit.

Beyond the realm of scientific discovery, our project holds substantial benefits for the public. First of all, developing new environmental thermal barrier coatings for 1300°C-capable refractory alloys for harsh turbine environments can enhance the efficiency of air turbines, leading to reduced fuel consumption. This efficiency improvement translates into lower carbon emissions, contributing to cleaner air and mitigating climate change impacts. In the context of aircraft engines, advanced thermal barrier coatings can significantly reduce fuel consumption and carbon emissions from air travel, which represents 2% of all global carbon emissions. Reduced fuel consumption in aviation not only lowers operational costs for airlines but also decreases the carbon footprint associated with air travel, benefiting the environment on a global scale. As regard to electricity generation, gas turbines produced approximately 35% of the total electricity generation in the US. Improving their efficiency would significantly reduce the energy usage and carbon emissions. It is estimated that the 1700°C-capable ETBCs on the 1300°C-capable alloys could improve the efficiency of natural gas turbines and jet engines by 7%. Such an efficiency improvement in natural gas turbine used for U.S. electricity generation could save up to 15-16 quads of energy; in civilian aircraft turbines, 3-4 quads of energy could be saved.

Secondly, high performance ETBCs can protect turbine components from high temperatures and oxidation, extending the lifespan of air turbines. This longevity reduces the frequency of replacements and maintenance, saving resources and reducing industrial waste, which is beneficial for both the environment and the economy.

Meanwhile, the advancements in development of new ETBCs described in this project also lead to breakthroughs in materials science and manufacturing technologies. These innovations can have broader applications beyond gas turbines, influencing various industries and leading to the development of new materials and manufacturing processes.

Last but not least, research, development, and implementation of novel ETBCs stimulate innovation in the aerospace and energy sectors. This innovation, in turn, fosters economic growth by creating jobs, supporting research institutions, and attracting investments in related industries.

In summary, our ARPA-E funded project represents a significant leap forward in the understanding highly efficient developing new environmental-thermal barrier coatings. The technical effectiveness and economic feasibility of our methods underscore their practical applicability, promising tangible benefits for society. The project directly contributes to our sustainable future, by improving gas turbine's efficiency and decreasing fuel consumption and CO_2 emission. Furthermore, the knowledge generated by our research serves as a valuable educational resource, fostering a greater understanding of developing thermal barrier coatings among the public and inspiring future generations of scientists and innovators.

Acknowledgements

We extend our sincere gratitude to the Advanced Research Projects Agency-Energy (ARPA-E) for their invaluable financial support, which made this research possible. Their commitment to advancing innovative energy technologies has been instrumental in driving our project forward.

Accomplishments and Objectives

This award allowed University of Maryland College Park to demonstrate a number of key objectives. The focus of the project was on building a New Environmental-Thermal Barrier Coatings for Ultrahigh Temperature Alloys.

A number of tasks and milestones were laid out in Attachment 3, the Technical Milestones and Deliverables, at the beginning of the project. The actual performance against the stated milestones is summarized here:

Table 1. Key Milestones and Deliverables.

Tasks	Milestones and Deliverables
Task 1: Go/No-Go: Refine Tasks and milestones (if applicable)	Q1: Refine tasks and milestones for the work plan (if applicable) **Actual performance:** (07/01/2021-09/30/2021) We have successfully refined tasks and milestone outlined in the initial work plan on 07/22/2021-08/15/2021. During this period, the project team conducted extensive consultations, research reviews, and technical assessment. As a result of this refinement, the project team was able to establish clear and quantifiable objectives for each task, ensuring alignment with overall project goals.
Task 2: Design of 200 ETBCs (compositions and layer combinations) 2.1 Identified viable oxides for coating constituents 2.2 Design of coating architectures completed (oxides, layer sequence, thickness, porosity level,…)	Q1: Identified viable oxides for coating constituents. **Actual performance**: (10/01/2021-12/31/2022) During 09/30/2021-02/10/2022, we examined the coefficient of thermal expansion, elastic moduli and melting temperature of various substrate and coating materials. These data help guide oxide selections for surrogate substrates including polycrystalline SiC, disilicide-coated Nb and alumina. These substrates provide a range of CTEs and oxide scales (SiO_2 and Al_2O_3) to cover potential new alloy substrates to developed under ULTIMATE. We have identified 30 oxide compositions. Q2: Design of coating architectures completed (oxides, layer sequence, thickness, porosity level,…) **Actual performance**: (01/01/2022-03/31/2022) Utilizing the expertise of the PIs, we have made substantial progress in the composition selection process before 03/31/2021. Our focus was on chemical compatibility, coefficient of thermal expansion matching, and phase diagrams. In addition, we conducted advanced micromechanics modeling for the development of multilayer structures. This modeling effort allowed us to gain valuable insights into the structural behavior and mechanical properties of the coatings. This modeling task was completed on 02/10/2022. Furthermore, we dedicated significant effort to design coating architecture. We have designed 200 coating formulations, including different thickness, sequences, and porosity levels. Based on the knowledge gained from the above task and the results of UHS synthesis and tests, we have further refined the designs of ETBCs.

Tasks 3: UHS synthesis of 200ETBCs 3.1 Develop and optimize UHS processing for single oxide coating layer. 3.2 Synthesized multilayer ETBCs using UHS on flat coupons 3.3 Synthesize multilayer ETBCs using UHS on 3D shapes	Q1: Develop and optimize UHS processing for single oxide coating layer. **Actual performance**: (09/30/2021-01/01/2022) During this period, we have systematically studied the UHS synthesis conditions to achieve single layer coatings of 30 oxide compositions on 10 × 10 mm substrates with full density and tailored porosity on surrogate substrates including polycrystalline SiC, disilicide-coated Nb and alumina. Q2: Synthesized multilayer ETBCs using UHS on flat coupons **Actual performance**: (04/01/2022-06/30/2022) Our team developed a procedure to synthesis multilayer ETBCs using UHS on flat coupons. It was demonstrated that multilayer was successfully achieved under our synthesis condition, as confirmed by metallography and X-ray analysis. Q3: Synthesize multilayer ETBCs using UHS on 3D shapes. **Actual performance**: (07/01/2022-09/30/2022) During this period, we have optimized the UHS processes to demonstrate adherent coatings on airfoil shapes with at least 1 square inch surface area.
Task 4. Coating performance tests 4.1 Perform sequential tests and data analysis 4.2 Complete performance tests to down select coatings 4.3 Complete thermal conductivity measurements for 30 oxide compositions 4.4 Coordinate key ETBC performance	Q1: Perform sequential tests and data analysis. **Actual performance**: (10/01/2021-12/31/2022) We have established and refine the fast-fail experimental procedures during 10/01/2021-12/31/2022. Q2: Complete performance tests to down select coatings. **Actual performance**: (07/01/2021-09/30/2022) We have prepared a series of coatings, and performed fast cooling and glass formation tests, furnace cycle tests on coating, which survived the glass-formation test. Q3: Complete thermal conductivity measurements for 30 oxide compositions. **Actual performance**: (04/01/2022-06/30/2022) We have acquired thermal diffusivity of the 30 oxide compositions. Q4: Coordinate key ETBC performance tests with resource teams. **Actual performance**: (07/01/2022-09/30/2022) We conducted more thorough property tests for 3 promising candidates with the resource teams in this period.

tests with resource teams 4.5 Exposure test	Q5: Exposure test **Actual performance**: (07/01/2022-12/31/2022) Coated samples are to be exposed to a temperature (T_{exp}) greater than >1500°C in laboratory air for sufficiently long time to test the effectiveness of the coating. Following thermal exposure, the samples should meet the following criteria: (1) no glass formation at T_{exp}, (2) minimal spallation during ultrafast cooling from T_{exp}, (3) >50 cycles with 90% coating intact in 1300 °C (30 minutes per cycle) furnace cycle tests; (4) RT tensile ductility of ETBC coated base alloy such as Nb silicide ≥ 90% of base alloy after T_{exp} air exposure, (5) adherent ETBCs on 3D shapes through furnace cycle tests.
Task 5. Tech-2-market (T2M) analysis 5.1 Tech-2-market (T2M) plan 5.2 Techno-economic Analysis 5.3 Phase I Final T2M plan	Q1: Tech-2-market (T2M) plan. **Actual performance**: (01/01/2022-03/31/2022) During this period, we have completed an initial T2M plan that includes an overview of IP strategy and management plan, lays out the preferred commercialization pathway and identifies relevant industrial partners to assist in transition efforts. The initial plan has been submitted to ARPA-E. Q2: Techno-economic Analysis. **Actual performance**: (04/01/2022-06/30/2022) We have provided an estimate of the costs and benefits of the proposed process for ARPA-E acceptance, along with sensitivity analysis of key cost drivers. Q3: Phase I Final T2M plan. **Actual performance**: (07/01/2022-09/30/2022) A final T2M plan was submitted that includes product requirements, analysis of manufacturing risks, strategy for transition of process to Phase 2 and potential licensing plan (or equivalent, if another commercialization pathway is selected).

For projects involving computer modeling, provide a brief description of the model, key assumptions, how the model was validated, and whether or not the model and results were presented in peer-reviewed publications.

This project doesn't involve any computer modeling.

Project Activities

The project's primary focus was to address the growing demand for more efficient gas turbines, necessitating the development of advanced environmental-thermal barrier coatings (ETBCs) for refractory alloys used in challenging environments. Conventional coating methods face hurdles due to materials uncertainty in next-generation superalloys and the time-consuming process adjustments required for specific coating compositions. To expedite the development process, we implemented an innovative strategy integrating coating design, synthesis, and evaluation through ultrafast high-temperature sintering (UHS). Leveraging a coefficient of thermal expansion (CTE) database, we meticulously analyzed and planned coating designs, targeting substrates with a range of CTE values. Our approach, combining spray painting/tape casting with UHS, enabled high-throughput and cost-effective synthesis of multi-layer coatings, showcasing diverse compositions, stacking sequences, and thicknesses. Thorough thermal cycling tests up to 1300°C confirmed the coatings' resilience after 50 cycles, providing essential insights for adjustments and further evaluation. Notably, our strategy enabled coatings on complex geometries, periodic multi-layer ETBCs, and tailored porosity, showcasing its versatility. This accelerated iteration strategy proved remarkably cost-effective, offering rapid screening, lower capital costs, and significantly higher throughput than conventional methods. Ultimately, the project's outcomes pave the way for 1700°C-capable coatings, exceeding performance metrics and illuminating a path for rapid synthesis applicable to a wide array of applications.

If there was a modification to the award as a result of changes in tasks or milestones, state when that occurred and provide a brief narrative describing the change.

There were no modifications to the award during the project's course.

Project Outputs

A. Journal Articles

Design, Fabrication and Screening of Environmental-Thermal Barrier Coatings Prepared by Ultrafast High Temperature Sintering. *Advanced Functional Materials* (In revision)

B. Papers

None

C. Status Reports

None

D. Media Reports

None

E. Invention Disclosures

None

F. Patent Applications/Issued patents

Ultrafast High Temperature Sintering (UHS) Systems and Methods for Fabricating Environmental-Thermal Barrier Coatings. US patent filed.

G. Licensed Technologies

None

H. Networks/Collaborations Fostered

None

I. Websites Featuring Project Work Results

None

J. Other Products (e.g. Databases, Physical Collections, Audio/Video, Software, Models, Educational Aids or Curricula, Equipment or Instruments)

None

K. Award, Prizes, and Recognition

None

Follow-On Funding

Additional funding committed or received from other sources (e.g. private investors, government agencies, nonprofits) after effective date of ARPA-E Award.

Table 2. Follow-On Funding Received.

Source	Funds Committed or Received
ARPA-E	DE-AR0001809