



Degradation of TBC Systems in Environments Relevant to Advanced Gas Turbines for IGCC Systems—University of Pittsburgh

Background

The conditions inside integrated gasification combined cycle (IGCC) systems, such as high steam levels from hydrogen firing, high carbon dioxide steam mixtures in oxy-fired systems, and different types of contaminants, introduce complexities associated with thermal barrier coating (TBC) durability that are currently unresolved. In this work the University of Pittsburgh will team with Praxair Surface Technologies (PST) to determine the degradation mechanisms of current state-of-the-art TBCs in environments consisting of deposits and gas mixtures that are representative of gas turbines using coal-derived synthesis gas (syngas).

This project was competitively selected under the University Turbine Systems Research (UTSR) Program that permits academic research and student fellowships between participating universities and gas turbine manufacturers. Both are managed by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL). NETL is researching advanced turbine technology with the goal of producing reliable, affordable, and environmentally friendly electric power in response to the nation's increasing energy challenges. With the Hydrogen Turbine Program, NETL is leading the research, development, and demonstration of these technologies to achieve power production from high hydrogen content (HHC) fuels derived from coal that is clean, efficient, and cost-effective; minimizes carbon dioxide (CO₂) emissions; and will help maintain the nation's leadership in the export of gas turbine equipment.

Project Description

This project will determine the degradation mechanisms of current state-of-the-art TBCs in environments comprised of particulate matter and gas mixtures which are representative of gas turbines using coal-derived synthesis gas (syngas). The observed degradation processes will be used to guide the development of improved coatings for hot section components in the potentially harsh gas turbine environments in which fuels derived from coal and even perhaps biomass are burned. The unresolved complexities associated with TBC durability include enhanced attack of yttria-stabilized zirconia (YSZ) top coating by chemical reaction, physical damage of the topcoat by molten deposit penetration, and accelerated bond coat corrosion. This work is investigating how the interaction between the ash and oxidants affect TBC degradation by using lab-scale testing. Important outcomes from this study will include understanding TBC degradation; modeling IGCC environments to develop better coatings; and extending the service life of TBCs by mitigating degradation.

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PROJECT DURATION

Start Date	End Date
10/01/2011	09/30/2014

COST

Total Project Value
\$562,702

DOE/Non-DOE Share
\$434,324 / \$128,378

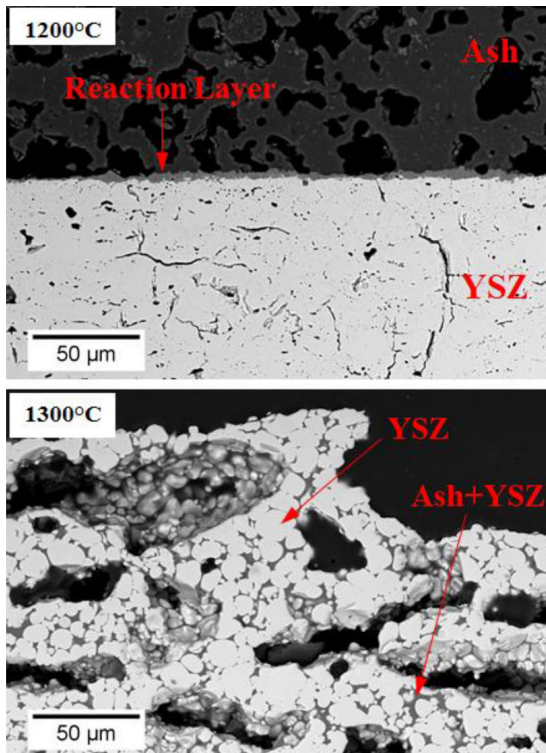
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This research is using the high-temperature corrosion testing facilities at the University of Pittsburgh. The deposits currently being used are based on fly ash, and accordingly, consist of calcium oxide (CaO), aluminum oxide (Al_2O_3), silicon dioxide (SiO_2) and iron oxides (FeO_x). Additions of potassium sulfate (K_2SO_4) and iron sulfide (FeS) are used to simulate other ash constituents. The tests are being conducted on two different TBC system types provided by PST of Indianapolis, Indiana. PST will also conduct thermal gradient tests for assessing TBC durability with and without deposits. Both exposed and unexposed test samples are being extensively characterized using the suite of capabilities available at the University of Pittsburgh.



Free-standing YSZ coupons reacted with commercial fly ash. A thin reaction layer formed at 1200 °C, while the ash melted and severely degraded the YSZ at 1300 °C.

Goals and Objectives

The main goal of this project is to use lab-scale testing to systematically reveal the interplay between prototypical deposit chemistries (i.e., ash and its constituents, K_2SO_4 and FeS) and environmental oxidants (i.e., oxygen, water, and CO_2) on the degradation behavior of advanced TBC systems. Specific objectives are as follows:

- To characterize and determine the main factors governing the degradation of a state-of-the-art nickel-cobalt-chromium-aluminum-yttrium (NiCoCrAlY) bond coats and two differently processed YSZ TBCs in gaseous atmospheres that are increasingly relevant to IGCC systems.

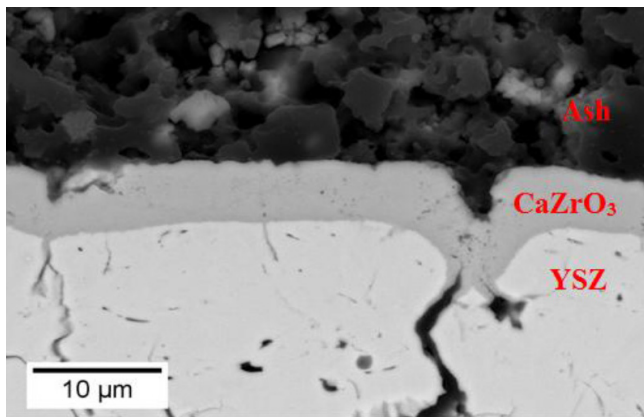
- Add to the complexity by including synthetic surface deposits based on coal fly ash, with particular emphasis on the fly-ash components calcium oxide and silicon dioxide.
- Establish an effective experimental procedure for assessing high-temperature, deposit-induced degradation in IGCC-relevant environments.
- Study the further complexity of adding K_2SO_4 or FeS to the synthetic ash deposit.

The fundamental relevance of these objectives lies in the need to better understand the chemical, physical, and kinetic factors that can lead to accelerated degradation of TBCs used in IGCC systems. The practical significance lies in the guidance provided for predicting TBC degradation behavior and for designing TBCs that exhibit adequate degradation resistance.

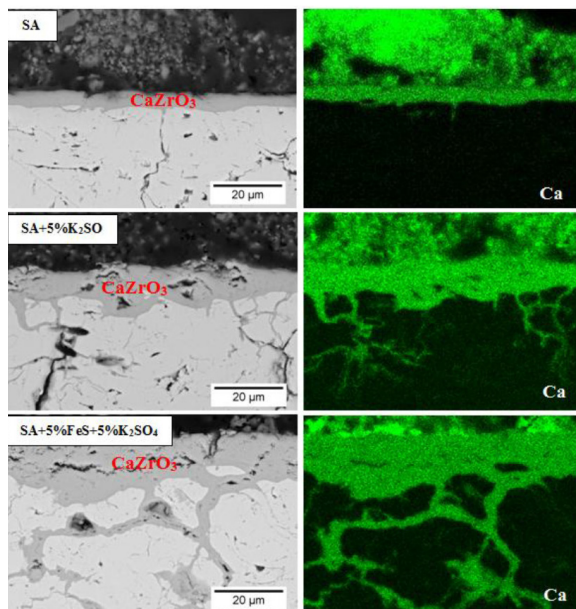
Accomplishments

- Commercial fly ash was found to cause extensive degradation of the YSZ top coat material at temperatures above 1300 °C. At relatively lower temperatures, a solid-state reaction occurred between the YSZ and ash which was less detrimental, but still relevant to TBC durability.
- Synthetic fly ash of varying compositions was used to assess TBC degradation at the lower temperatures. Solid-state reaction to form calcium zirconate (CaZrO_3) was found to occur only if a minimum level of CaO was present in the ash.
- Realistic synthetic fly-ash compositions with additions of K_2SO_4 and FeS caused extensive damage, resulting in thicker reaction layers and much deeper infiltration into cracks within the YSZ. Using synthetic mixtures will provide an understanding of the specific role(s) of each ash constituent in accelerating the degradation process.
- Testing done in $\text{CO}_2 + 20\%\text{H}_2\text{O}$ environments showed very little difference in the formation of the CaZrO_3 layer as compared to experiments in dry air. These initial results suggest that this particular attack on YSZ may not depend greatly on the gas atmosphere.
- The presence of CO_2 or H_2O in the reacting atmosphere was not found to alter the protective oxidation of state-of-the-art NiCoCrAlY bondcoat alloys at 1100 °C.
- A study of the reactive element level in NiCoCrAlY alloys revealed that while harmless in air, slightly excessive Y doping is detrimental in the presence of commercial fly ash, as Y-rich oxide inclusions in the scale act as initiation sites for rapid alloy degradation.
- Upon exposure of various NiCoCrAlY alloys to commercial fly ash, as well as synthetic ash mixtures (oxides with/without FeS or K_2SO_4) in air and in $\text{O}_2\text{-SO}_2$, the extent of metal loss could be directly related to the relative amounts of $\beta\text{-NiAl}$ and $\gamma\text{-Ni}$ phases in the alloy structure.

- Exposure of selected alloys to individual oxide deposits (CaO , MgO , Al_2O_3 , SiO_2 , Fe_2O_3 , Cr_2O_3) in air showed that, while all oxides altered the extent of Al_2O_3 growth, only CaO caused significant alloy degradation.
- CaO was shown to react preferentially with the Al-lean γ phase through the formation of a liquid calcium chromate. The β - γ phase distribution was found to be critical to the establishment of a continuous Al_2O_3 layer, which effectively mitigates alloy degradation. These observations provide an understanding for the better resistance of β -rich alloys in the presence of more complex ash deposits, and offer guidance for coating design.



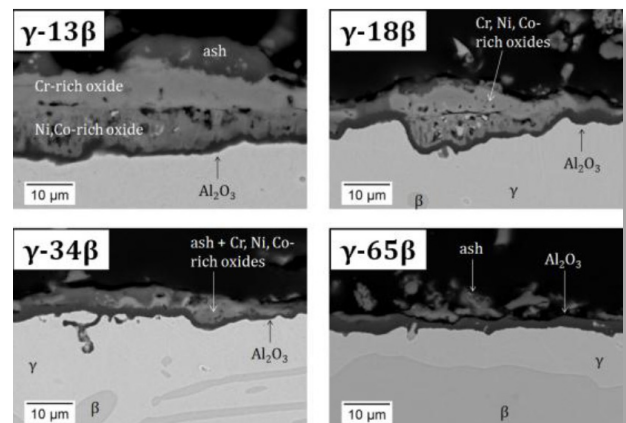
YSZ reacted with a synthetic ash at 1100 °C for 72 hours showing a continuous reaction layer. Synthetic ash mixtures with lower amounts of CaO did not form this reaction product, showing that there is a minimum CaO activity necessary in the ash to react with the YSZ.



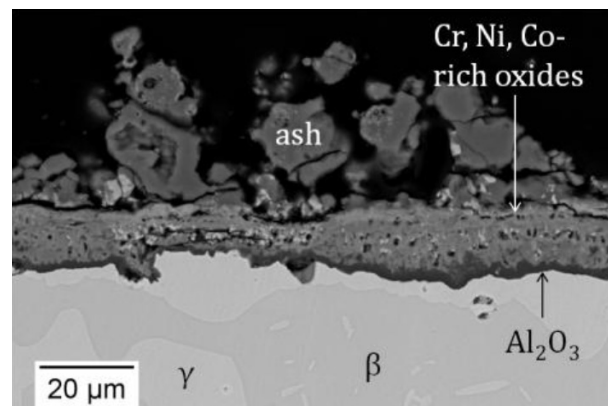
YSZ reacted with synthetic ash (SA) with and without additions of K_2SO_4 and FeS . The reaction product formed with only synthetic ash does not infiltrate the cracks in the YSZ. The degradation is more aggressive with the additives: the reaction product is thicker and the infiltration is more significant.

Benefits

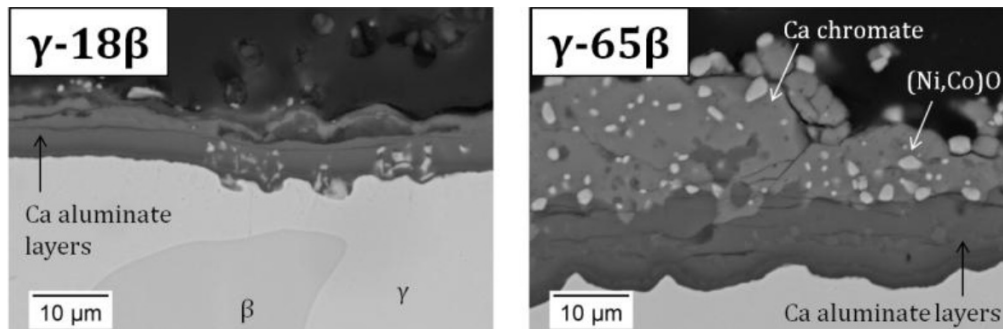
This UTSR project supports DOE's Hydrogen Turbine Program that is striving to show that gas turbines can operate on coal-based hydrogen fuels, increase combined cycle efficiency by three to five percentage points over baseline, and reduce emissions. The outcome of this study will help define cost-effective IGCC specifications, performance modeling, and directions for new coating/blade alloy compositions.



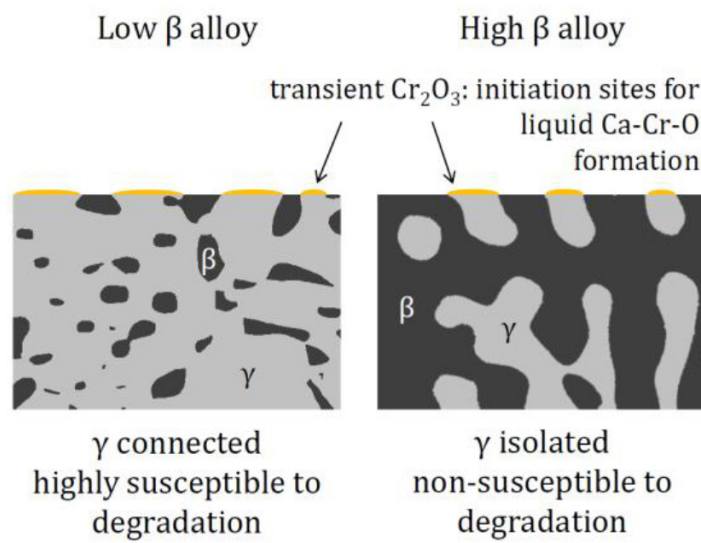
NiCoCrAlY alloys after 50 hours exposure to class C fly ash in CO_2 - H_2O at 1100 °C. Alloy degradation is mitigated when increasing the β phase fraction.



Ni-19Co-15Cr-24Al-0.3Y (atomic %) after 50 hours exposure to class C fly ash in CO_2 - H_2O at 1100 °C. Excessive doping caused extensive alloy degradation.



NiCoCrAlY alloys after 50 hours exposure to CaO in air at 1100 °C. Reaction of CaO with the Cr-rich γ -phase to form a calcium chromate causes extensive alloy degradation.



Role of phase distribution in CaO-induced degradation of β - γ NiCoCrAlY alloys.

