Correlating Thermal Barrier Coating Microstructure Between Engine Run Combustion Hardware and Furnace Cycle Testing

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Abstract
Microstructural investigation was performed on thermally cycled buttons as well as on engine run combustion hardware with operating hours from ~30,000-40,000 hours. The thermally grown oxide (TGO) layers of both were compared, and it was found that TGO composition as well as morphology differed significantly. Thermally cycled buttons showed a relatively thick and uniform TGO layer comprised of alumina above the bond coat with a layer of mixed oxide spinel forming directly above the alumina layer. However, engine run hardware had thin, non-uniform TGO layers with large clusters of mixed oxides scattered throughout the bond coat. Based on TGO thickness only, the engine run combustion liners would still have over 50% remaining life before coating failure. However, the ability to predict remaining life based solely on TGO thickness is uncertain due to the difference in oxide formation. Further analysis is recommended to better understand the impact of TGO growth and the presence oxide clusters on coating life for engine run hardware.

Background
The Materials and Processes Group at Solar Turbines Incorporated is located in San Diego, California, and is responsible for gas turbine materials development, quality assurance, product support, and failure analysis. This report is focused on product support for thermal barrier coated (TBC) combustor liners. Combustion liners are inspected visually and by non-destructive methods when an engine returns for an overhaul, where a combustor can be repaired and successfully operated for another overhaul cycle. As part of the repair, the TBC coating is typically removed and reapplied, even though the condition of the coating presently has been in excellent condition. To determine if the coating can be used for another overhaul cycle, condition assessment of the coating from overhaul engines is needed. This project has two main objectives: 1. to determine the condition of combustor liner TBCs at overhaul intervals to establish a more accurate coating lifetime prediction, and 2. to compare the coatings on engine run hardware with microstructural characteristics found in laboratory furnace cycle testing.

Thermal barrier coatings are applied to parts in the hottest sections of the turbine that see above ~1100°C such as combustor liners and turbine components. These parts are coated with multilayer systems consisting of two main coating layers, and a third developing in service. Hot section parts are typically made of nickel superalloys because of their high strength and creep resistance. However, these superalloys undergo severe degradation at high temperatures in oxidizing environments and therefore require coatings for protection. The first coating layer, which is called a bond coat, reduces oxygen diffusion, improves adhesion, and is a reservoir for aluminum. These coatings are typically MCrAlY (where M is Co and/or Ni) or PtAl compositions. The top layer is the thermal barrier coating, which is typically made of tetragonal yttria stabilized zirconia (YSZ), because of its high toughness and low thermal conductivity. During service, a third layer develops between the bond coat and ceramic topcoat called the thermally grown oxide (TGO) layer. The bond coats are designed to slowly form a thin layer of α-Al2O3 TGO as oxygen readily diffuses through the YSZ TBC and reacts with the Al in the bond coat. This TGO prevents rapid oxidation of the bond coat and superalloy beneath it. The TGO is often the life limiting layer as the evolution of this coating creates substantial strain in the system with continued engine cycling\textsuperscript{1,2}.
Introduction
Currently at Solar, TBC lifetime estimates are based on TGO thickness when the ceramic topcoat has separated from the bond coat on thermally cycled buttons. However, the environments that TBCs experience in a turbine versus in a laboratory thermal cycling furnace are very different. The main difference being the exposure of the nickel alloy and bond coat to higher temperatures during laboratory thermal cycling versus in a turbine environment, where the base metal and bond coat are protected by the TBC from high temperatures with appropriate backside cooling. This will change the diffusion kinetics of the metal elements in the bond coat, therefore changing TGO composition and growth.

It is known that when the TGO reaches a certain thickness, the strain in the multilayer system becomes too great causing spallation of the ceramic topcoat from the base layers\(^2\). This critical TGO thickness is defined as the life-limiting thickness and is used when comparing TBC coated parts from the field\(^3\). However, the life limiting thickness is strongly influenced by the composition of the TGO. Therefore, TGO thickness and composition of thermally cycled buttons up to failure were compared with TBC coated combustion hardware received from the field after 30,000-40,000 hours of operation in this study to evaluate the validity of basing part lifetime prediction on thermal cycling test results.

Experimental
The coating system used consists of a Ni superalloy base with a NiCrAlY bond coat and an air plasma sprayed (APS) YSZ TBC. The nominal coating composition of the starting materials is shown below in Table I.

Table I. Bond coat and TBC starting compositions according to Solar specifications.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Elemental Composition</th>
<th>Weight %</th>
</tr>
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<tbody>
<tr>
<td>Bond Coat</td>
<td>Nickel</td>
<td>Balance</td>
</tr>
<tr>
<td></td>
<td>Chromium</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Aluminum</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Yttrium</td>
<td>1</td>
</tr>
<tr>
<td>TBC</td>
<td>Zirconia</td>
<td>Balance</td>
</tr>
<tr>
<td></td>
<td>Yttria</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>4 max.</td>
</tr>
</tbody>
</table>

For thermal cycling tests, 1" diameter buttons were cycled in an open air CM Furnaces bottom loading box furnace from room temperature to 1150°C, held for 10 hours then forced air cooled for 1.5 hours; the heating and cooling rates were approximately 20°C/minute. Specimens were removed from the furnace at intervals of 2, 25, 50, 76, and 94 cycles; the coating failed at 94 cycles. Failure of the TBC was specified as the number of cycles that caused complete spallation of the coating from the substrate/bond coat.

Coated parts received from the field and buttons from thermal cycling were sectioned, mounted in epoxy, and polished in preparation for microstructural investigation. Specimens were examined using optical microscopy on an Olympus GX51 then coated with a thin layer of
Carbon using an Electron Microscopy Sciences EMS150R ES sputter coater to prepare the surface for scanning electron microscopy (SEM) imaging. A Jeol JSM-6460LV SEM was used, and the composition of the coatings were found using EDAX Genesis Energy Dispersive Spectroscopy (EDS). Compositional spectra were obtained using a dead time between 20-30% at 15 keV accelerating voltage, and elemental weight percentages are reported with carbon omitted.

Results and Discussion

Figure 1 shows the as processed microstructure of the NiCrAlY bond coat (thickness ~150 µm) and APS YSZ TBC (thickness ~300 µm). EDS of different regions in the bond coat and TBC show weight percentages that are within Solar specifications with small amounts of Si being the main contaminant species (~1 wt. %).

![Figure 1. As received APS TBC on NiCrAlY bond coat.](image)

In comparing TGO growth in thermally cycled buttons to engine hardware, tracking the compositional changes of the bond coat is important in understanding how the composition and morphology of the TGO will evolve. As the Al in the bond coat is depleted, mixed oxides begin to form in addition to alumina. The most prevalent being Ni(Cr,Al)2O4, which is most detrimental to the integrity of the coating in thermal cycling due to the associated volume expansion in its formation as well as a higher coefficient of thermal expansion mismatch3. The bond coats of the thermally cycled buttons and the engine hardware were evaluated at areas near the TBC interface as well as near the superalloy metal interface, as illustrated below (Figure 2). Areas with extensive internal oxidation were avoided to give a more representative compositional analysis of the bond coat.
Figure 2. EDS area analysis performed near the bond coat-metal interface and the bond coat-topcoat (TGO) interface (bond coat after 94 furnace cycles pictured).

Thermal Cycling Tests
Figure 3 shows the microstructures of the thermally cycled buttons at several intervals from 2-94 cycles. A uniform TGO containing aluminum and oxygen, assumed to be alumina, was present even as early as two cycles, which grows uniformly with increased cycles. Formation of a mixed oxide, assumed to be spinel, was evident above the alumina layer in the SEM images as the light gray phase in the TGO. There were also small, light colored particles found in the TGO, which were found to be nickel oxide precipitates. Internal oxidation of the bond coat was present in addition to TGO growth. EDS of the internal oxides showed a mix of Al, Y, Cr, and Si oxides. Formation of internal oxides containing Al could be an additional means for aluminum depletion in the bond coat, which could contribute to spinel formation in the TGO.
Figure 3. Optical (a) and SEM images (b-e) of the thermally grown oxide after thermal cycling. TGO ranges from approximately 3 to 20 µm at failure. In the SEM images, the light color layer above the dark layer in the TGO is a mixed oxide consisting mainly of Ni, Cr, Al, and O, which was assumed to be a spinel. The dark layer in the TGO is aluminum oxide. The backscatter contrast is present because of the different densities of the two materials. The cracking present above the TGO in b-d is likely the initiation of delamination cracks intensified by the cutting and polishing process.
Figure 4. Bond coat aluminum depletion with increased number of cycles. Showing both the areas in the bond coat near the topcoat and metal interfaces (I/F).

Bond coat composition analysis found small amounts of Si and Fe in the bond coat, with Si being less than 3 wt. % and Fe being less than 2 wt. %. Both contaminants showed an increasing trend with number of cycles. The change in aluminum composition of the NiCrAlY bond coats in the thermally cycled buttons is shown in Figure 4. The amount of Al decreased significantly with number of cycles and from the metal interface to the topcoat interface. Aluminum depletion near the topcoat interface is due to the formation of the TGO. As long as there is still Al in the bond coat, there will be formation of the TGO layer, consisting of aluminum oxide and mixed oxides. In the 94 cycles button, the amount of Al in the bond coat decreased from the initial 11 wt. % to less than 2 wt. %. A significant difference in this sample was that the Al depletion was throughout the entire bond coat thickness. In other samples, the Al percentage at the topcoat interface was low, but there was still ~10 wt. % Al near the metal interface region of the bond coat.

Engine Run Combustion Hardware
To compare the thermally cycled buttons to TGO formation found in engine run hardware, combustor liners were investigated with engine operating times between 30,000-40,000 hours. An inner combustor liner with 32,000 hours and two outer combustor liners with 31,000 and 41,000 hours run time were investigated. Figure 5 shows representative microstructures of the topcoat and bond coat for the inner liner (left) and outer liners (right). Table II shows approximate bond coat and topcoat thicknesses for the engine hardware. The TGO layer was minimal, and there were clusters of oxides present at the bond coat-topcoat interface; these are especially prevalent on the outer liners.
Figure 5. Representative microstructures of an inner liner with 32,000 hours run time (left) and outer liner with run time around 41,000 hours (right).

Table II. Bond coat and TBC thicknesses for engine run hardware.

<table>
<thead>
<tr>
<th>Approximate Thickness</th>
<th>Inner Liner 32,000 hrs.</th>
<th>Outer Liner 31,000 hrs.</th>
<th>Outer Liner 41,000 hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Coat</td>
<td>160 µm</td>
<td>100 µm</td>
<td>180 µm</td>
</tr>
<tr>
<td>TBC</td>
<td>650 µm</td>
<td>550 µm</td>
<td>600 µm</td>
</tr>
</tbody>
</table>

Figure 6 shows the thermally grown oxide layers present on the engine run hardware. TGO thickness was ~1 micron for the 31,000 (outer) and 32,000 hour (inner) liner, and ~3 microns for 41,000 hour outer liner. The TGO was mainly alumina, but had regions of mixed oxide spinel present, as seen in Figure 6b (light gray region). In addition, there were large oxide clusters present in some areas along the TGO of the outer liners, as pictured in Figure 6d. EDS results of the different phases in the oxide clusters showed four main oxide phases were present. They were aluminum oxide, Ni(Al,Cr)₂O₄ spinel, nickel oxide, and yttrium aluminum oxide. There were also small amounts of Si found in these oxide clusters. Bond coat internal oxidation was present with mainly Al, Ni, Cr, and Y oxides that contain small amounts of Si. Some areas of oxidation at the metal interface were also present containing mainly Ni, Cr, and Al oxides, with small amounts of Si and Fe. The Si found in these oxides likely came from the YSZ TBC, which contained ~1 wt. % silicon in the as processed coating.

EDS results for Al concentration in the bond coat regions near the topcoat and metal interfaces are shown in Figure 7 for the engine hardware. Aluminum depletion in the bond coat was greatest near the topcoat interface region, but remained close to the starting percentage near the metal interface. This indicates the material still has sufficient amounts of Al left in the bond coat to continue alumina TGO formation.
Figure 6. SEM images of the TGOs in engine hardware run from ~30,000-40,000 hours (a-c) and of an oxide cluster found in some regions along the TGO of the outer liners (d, 41,000 hrs. pictured).

Figure 7. Bond coat Al composition change in engine hardware run from ~30,000-40,000 hours.
Conclusion

Microstructural investigation and EDS results of thermally cycled buttons were compared to engine run combustion hardware with ~30,000-40,000 operating hours. The largest TGO layer thickness found in the engine hardware was minimal at ~3 µm. As compared to TGO thickness at failure of thermally cycled buttons, which was 15-20 µm, engine run hardware TBCs have seen well under half their estimated lifetime. However, the TGO microstructure and composition differed between the thermally cycled buttons and engine hardware making that direct comparison uncertain. There were thick, even TGO layers present in thermally cycled buttons that consisted of alumina with a layer of mixed oxide spinel above the alumina layer. The uniform spinel layer would cause increased strain in the system that would contribute to coating failure. The engine hardware, on the other hand, had very thin, uneven TGO growth that was mainly alumina with sparse areas of mixed oxide spinel formation. There were also large clusters of oxides found along the TGO, however. It is presently unclear how these oxide clusters will affect TGO growth and the critical TGO thickness to failure in engine hardware. Further work to determine the source of the oxide clusters and their impact on coating life is recommended.

References

