Fatigue Lifetime Approximation Based On Quantitative Microstructural Analysis For Air Plasma Sprayed Thermal Barrier Coatings

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FATIGUE LIFETIME APPROXIMATION BASED ON QUANTITATIVE MICROSTRUCTURAL ANALYSIS FOR AIR PLASMA SPRAYED THERMAL BARRIER COATINGS

by

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B.S. University of Central Florida, 2010

A thesis submitted in partial fulfillment of the requirements for the degree of Masters of Science in the Department of Mechanical, Materials, and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

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Major Professor: Yong-Ho Sohn
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ABSTRACT

The durability of thermal barrier coatings (TBCs) affects the life of the hot section engine components on which they are applied. Fatigue is the general failure mechanism for such components and is responsible for most unexpected failures; therefore it is desirable to develop lifetime approximation models to ensure reliability and durability.

In this study, we first examined the microstructural degradation of air plasma sprayed ZrO$_2$-8wt.%Y$_2$O$_3$ TBCs with a low-pressure plasma sprayed CoNiCrAlY bond coat on an IN 738LC superalloy substrate. The durability of TBCs were assessed through furnace thermal cyclic tests carried out in air at 1100°C with a 1-, 10-, and 50-hour dwell period, preceded by a 10-minute heat-up and followed by a 10-minute forced-air-quench. Failure mechanisms of the TBCs were thoroughly investigated through materials characterization techniques including: X-Ray Diffraction, Scanning Electron Microscopy, and Energy Dispersive X-Ray Spectroscopy.

Quantitative microstructural analyses were then carried out to document the growth of the thermally grown oxide (TGO) scale, the depletion of the Al-rich β-NiAl phase in the bond coat, and the population and growth of micro-cracks near the YSZ/bond coat interface. Trends in the TGO growth and the β-phase depletion in the bond coat followed those of diffusion-controlled processes—parabolic growth of the TGO and exponential depletion of the β-phase. Formation and propagation of cracks within the YSZ resulted in complete spallation of the YSZ topcoat from the bond-coated superalloy substrate.

Evolution in these microstructural features was correlated to the lifetime of TBCs, which showed cracking within the YSZ to be the cause of failure; thus a lifetime
approximation model was developed, via modification of Paris Law, based on the experimental data. The model predicted the TBC lifetime within 10% of the experimental lifetime.
This work is dedicated to my father, who has always been there to support me.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my advisor, Dr. Yong-Ho Sohn for his support, guidance and patience; and I would also like to extend my thanks to my committee members: Dr. Helge Heinrich and Dr. Linan An. I would like to acknowledge the financial support that funded my MS research from Doosan Heavy Industry. I would also like to express my thanks to all my fellow students at the Laboratory of Materials and Coatings for Extreme Environment (MCEE) and to the engineers, faculty and staff members at the Advanced Materials Processing and Analysis Center (AMPAC) and the MMAE department. Finally, I would like to thank my family and friends for always being there for me.
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1 INTRODUCTION

In gas turbine engines, thermal barrier coatings (TBCs) are employed to provide thermal insulation to metallic hot-section components, increase engine efficiency, and improve component lifetime [1] [2]. TBCs are multilayered structures that consist of a ceramic topcoat, a thermally grown oxide (TGO), and a metallic bond coat, which are applied on a superalloy substrate. Yttria-stabilized zirconia (YSZ) is often used as the topcoat material because of its low thermal conductivity, relatively high thermal expansion coefficient, and excellent mechanical properties. It is typically deposited via air plasma spray (APS) and electron beam physical vapor deposition (EB-PVD). YSZ topcoats applied by APS contain a characteristic intersplat porosity and a network of crack-like voids that provide strain tolerance and lower thermal conductivity [3]. The TGO scale is a layer formed during thermal cycling at the bond coat and YSZ interface, which influences the durability of TBCs [3]. The bond coat is an oxidation-resistant metallic layer that serves as an Al reservoir to facilitate α-alumina TGO formation. The bond coat can greatly influence the structure and morphology of the TGO, and dictate the failure of the TBC [1] [3] [4]. Commonly used bond coats are MCrAlY’s (M= Ni and/or Co), which can be deposited onto the superalloy substrate via vacuum plasma spray (VPS), low-pressure plasma spray (LPPS), and APS methods [5].

Identifying and understanding the failure mechanisms of TBCs is essential to developing life prediction models, and many studies have been carried out to such extent [4] [6] [7] [8] [9] [10] [11] [12] [13] [14] [15] [16]. It has been shown that APS TBC failure occurs by a sequence of nucleation, propagation and coalescence of cracks within the YSZ
that typically lead to the spallation of the YSZ [3] [4] [6] [7] [8]. Equally important is improved accuracy of life prediction models [17] that enable reduced conservatism in part designs, which improves the thermal efficiency for turbine engines. In efforts to develop such models [18] [19] [20] [21] [22], Busso et. al. proposed a damaged-based life prediction methodology based results from parametric unit cell finite element (FE) analyses, [19] [20] while Robin et. al. described the usefulness of combining acoustic emission short-term monitoring with FE modeling to predict the performance of such coatings when subjected to cyclic thermal loads [22]. However, these FE-based models require fundamental and complex materials properties and parameters, of which some are difficult, if not impossible to obtain.

In this study, we first examine the failure mechanisms of APS TBCs via quantitative microstructural analysis. A thorough investigation of the microstructural evolutions in APS TBCs is presented, such as the cracking behavior within the YSZ, TGO formation and depletion of Al-rich β-phase from the bond coat. A simple life prediction model is then derived based on experimental data that utilizes the fatigue-like crack propagation within the APS YSZ.
2 LITERATURE REVIEW

2.1 Thermal Barrier Coatings

Demands for higher turbine operating temperatures were originally met with metallurgical advances in the development of superalloys, but such demands pushed the limits of superalloys [23]. Additional increases in operating temperatures were achieved with the development and evolution of TBCs that are used in gas turbine engines to protect hot section components, including blades and vanes. Developments in different chemistries and processing techniques for TBCs remain the most challenging tasks to further TBC technologies.

There are different types of coatings available for protection from various environmental factors, such as high temperature, high pressure and/or corrosion. TBCs have become the most used materials system for improved efficiency and performance of gas turbine engines because they provide thermal insulation to hot section components and also protect these components from extreme environments [23]. TBCs are multilayered structures that consist of a ceramic topcoat, a thermally grown oxide (TGO) scale, and a metallic bond coat which are deposited on the superalloy substrate [1] [24]. Each of these layers have a specific purpose: the topcoat typically composed of ZrO$_2$ stabilized with 7-8 wt.% Y$_2$O$_3$ (YSZ) provides thermal insulation, the TGO predominantly composed of $\alpha$-alumina protects against oxidation and corrosion, and an aluminum-rich bond coat promotes the formation of the aforementioned protective alumina scale. In Figure 1, the multilayered structure of TBCs can be observed and a schematic spatial temperature distribution is also shown.
Figure 1. Typical cross-sectional micrograph of an APS TBC with a superimposed spatial temperature distribution.

2.2 Ceramic Topcoat Chemistry

Materials selection for the topcoat is dictated by certain design requirements such as high melting temperature, phase stability through a large temperature range, low thermal conductivity, high thermal expansion coefficient and low sintering rate. Therefore, there is a limited selection of materials that can be used. Zirconia based ceramics have been utilized to satisfy these requirements [1] [2] [3] [25]. Stabilizers including CaO, MgO, Y₂O₃, ScO₃, In₂O₃ and CeO₂ among other oxides are used to avoid the polymorphic phase transformations pure zirconia undergoes as shown in Figure 2 [23] [26]. The crystallographic structure of these phases (cubic, tetragonal and monoclinic) are shown in Figure 3 [27] [28]. However, for high temperature applications, studies showed yttria as the stabilizer of choice for zirconia with a composition of 6-8 wt.% yttria.
Figure 2. Phase diagram of ZrO$_2$-Y$_2$O$_3$ system [27] [28] [29].

Figure 3. Crystal structures of ZrO$_2$ polymorphs: (a) tetragonal, (b) monoclinic and (c) fluorite-cubic ZrO$_2$ [30].
As observed from the ZrO\textsubscript{2}-Y\textsubscript{2}O\textsubscript{3} phase diagram (Figure 2) phase transformations are dependent on the concentration of the stabilizer. A mixture of 2-3 mol.\% Y\textsubscript{2}O\textsubscript{3} with proper heat treatments and cooling yields a metastable tetragonal (t) phase, called the tetragonal zirconia polycrystalline (TZP) phase or the yttria-tetragonal zirconia polycrystalline (Y-TZP) phase, instead of the equilibrium monoclinic and cubic phases [31]. For 4-5 mol.\% Y\textsubscript{2}O\textsubscript{3} a metastable non-transformable tetragonal (t’) phase referred to as partially stabilized zirconia (PSZ or Y-PSZ) forms upon rapid cooling. The formation of the t’ phase helps prevent transformations to room temperature phases like the monoclinic (m) phase, which is accompanied by a 3-5\% volume increase, during cooling, thus helping to prevent failure by delamination and spallation of the topcoat [26].

2.2.1 Air Plasma Sprayed (APS) TBCs

For this processing technique a plasma plume, which is created in a plasma torch, melts the coating feedstock that are in powder form and deposits the molten powders on the working surface (Figure 4) [32] [33]. These coatings are referred to as air or atmospheric plasma sprayed coatings because the process is carried out in open atmosphere. In this method the plasma is generated between the tungsten cathode and anode by electrically exciting the primary and secondary gases, usually a mixture of argon plus hydrogen or hydrogen plus nitrogen. The plasma generates temperatures on the order of 10,000 K to melt the internally or externally fed powders, which are sprayed at a velocity of around 300 m/s onto the work piece at a standoff distance of 75-150 mm.
The desired coating thickness is obtained by spraying multiple passes of the molten particles, which form splats once they hit the substrate yielding the microstructure shown in Figure 5a. The coating adheres to the work piece by mechanical interlocking of the splats to the bond coat, which can also be sprayed by the same method (Figure 5b), and therefore requires a rough bond coat surface. Due to the process of splat formation, porosity is inherent with this technique. However a 10-15% volume porosity is necessary for lower thermal conductivity of the ceramic topcoat. The effect of porosity changes on the thermal cyclic lifetime of TBCs can be observed in Figure 6.
2.2.2 Electron Beam Physical Vapor Deposition (EB-PVD) TBCs

The EB-PVD process (Figure 7) consists of heating ingots of the raw materials (YSZ) with a focused high-energy electron beam, which melts and vaporizes the ingot. The vapor deposits and solidifies on the part and results in a columnar growth of the YSZ [36]. The
YSZ microstructure attained via EB-PVD processing (Figure 8) is chemically bonded to the bond coat by depositing a thin, dense layer of ZrO₂. A smooth bond coat surface is preferred for better adhesion. EB-PVD TBCs have better surface finish and higher durability than APS TBCs, however, they also have higher production costs and process times and higher thermal conductivity than their APS counterparts.

Figure 7. Schematic representation of the EB-PVD process set up [30].

Figure 8. Typical cross-sectional microstructure of an EB-PVD topcoat on a (Ni, Pt)Al bond coat.


### 2.3 Bond Coat Chemistry

Bond coats provide environmental resistance, oxidation and corrosion resistance to the superalloy substrate [37]. The chemical composition of bond coats can contain Ni, Co, Al, Cr, Al, Pt, Ta, Si, Y, Hf, etc. Each of these elements can influence the TBC lifetime and its oxidation/corrosion behavior as shown in Table 1 and Figure 9.

Table 1. Constituents of metallic coatings, functions and effects [24].

<table>
<thead>
<tr>
<th>Element</th>
<th>Role</th>
<th>Disadvantages</th>
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<tr>
<td>Ni</td>
<td>Major constituent in solid solution. Provides strength.</td>
<td>Reacts with sulfur causing degradation of the coating system.</td>
</tr>
<tr>
<td>Co</td>
<td>Major constituent, provides strength</td>
<td>Reacts with sulfur causing degradation of coating system.</td>
</tr>
<tr>
<td>Al</td>
<td>Primary element in providing oxidation resistance.</td>
<td>Large concentrations lowers melting temperature.</td>
</tr>
<tr>
<td>Cr</td>
<td>Contributes to hot corrosion resistance and oxidation resistance up to 816°C.</td>
<td>Lowers creep strength.</td>
</tr>
<tr>
<td>Ta</td>
<td>Enhances hot corrosion and strength.</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>Enhances oxidation and type II (&lt;850°C) hot corrosion.</td>
<td>Increase in silicon concentration leads to formation of brittle phases.</td>
</tr>
<tr>
<td>Hf, Y, and reactive elements</td>
<td>Improves adherence of alumina and chromia scales.</td>
<td>Large amounts are detrimental.</td>
</tr>
<tr>
<td>Pt</td>
<td>Improves oxidation and hot corrosion resistance.</td>
<td></td>
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</table>
2.3.1 Air Plasma Sprayed Bond Coats

The same basic principle, explained earlier, for application of APS topcoats is used for bond coats, however, a different powder, MCrAlYs, are fed to the torch. The resulting bond coat has a relatively high roughness to assist in the mechanical interlocking with the topcoat. APS bond coats also exhibit high oxide content due to the oxidation of molten particles as they are being sprayed onto the superalloy. The cross-sectional microstructure of an APS bond is shown in Figure 10.
2.3.2 Low Pressure Plasma Spray (LPPS) or Vacuum Plasma Spray (VPS) Bond Coats

LPPS/VPS processes are performed to eliminate oxidation during deposition of the metallic coating that occurs with APS coatings. The torch and part are enclosed in a vacuum chamber, which is first evacuated and then back filled with argon to obtain an inert environment [38]. A schematic representation of this system is shown in Figure 11, and the resulting cross-sectional microstructure in Figure 12.

Figure 10. Cross-sectional microstructure of a typical APS bond coat.
2.4 Failure Mechanisms in TBCs

Exposure to extreme environments causes incremental damage in the TBC that accumulates with time and cycles. The TGO growth, as a consequence of oxidation of the bond coat during thermal cycling, is primarily responsible for the spallation failure of TBCs.
Edge and buckle driven delamination have been observed to compete for final failure mechanisms. For final failure to occur, cracks must first initiate whose mechanisms differs between APS and EB-PVD TBCs.

### 2.4.1 Failure Mechanism in APS TBCs

APS TBCs fail via spallation of the ceramic topcoat; the failure mechanisms observed are: cracking at the YSZ/TGO interface and cracking at the TGO/bond coat interface [9]. The driving force for failure is a combination of cyclic thermal strain due to the thermal expansion coefficient mismatch, TGO growth, and sintering of the YSZ.

Cracking at the YSZ/TGO interface occurs from out-of-plane stresses caused by the TGO growth, along with the thermal expansion mismatch within the topcoat from sintering. The undulating bond coat/topcoat interface causes compressive stresses at the troughs and tensile stresses at the crest which result in the fracture of the TBC at the TGO/topcoat interface at the crests (Figure 13). However, many of these initial cracks are required for large scale buckling to occur.

![Figure 13. Schematic representation of localized separation at the TGO/bond coat interface caused by residual stress across the interface.](image-url)

[14]
The rough bond coat surface, sprayed for initial mechanical interlocking between the topcoat and the bond coat, causes out-of-plane stresses at the vicinity of the topcoat/TGO interface. Tensile stresses in the crest and compressive stresses in the troughs lead to cracking at the TGO/bond coat interface (Figure 14) due to prolonged thermal exposure and TGO growth.

![Figure 14. Schematic representation of crack initiation/propagation within the topcoat at the TGO/bond coat interface due to the CTE mismatch and out-of-plane tensile stresses in the TGO.](image)

### 2.4.2 Failure Mechanism in EB-PVD TBCs

Due to the columnar structure of EB-PVD TBCs, these coatings have a higher strain tolerance than APS TBCs and therefore their life-limiting factor is the strain that develops within the TGO. Failure occurs either at the TGO/topcoat interface or at the bond coat/TGO interface (Figure 15). Failure at the TGO/topcoat interface may occur due to various mechanisms, including roughening of the TGO because of bond coat creep during cooling, phase transformations within the YSZ and TGO along with sintering of the YSZ, and/or formation of brittle Ni/Co rich oxides at the TGO/YSZ interface [3]. Failure at the bond coat/TGO interface is similar to APS TBCs. However, crests in EB-PVD TBCs are surface...
irregularities or undulations. Void formation and internal oxidation, which occurs after the Al-rich β-phase is depleted from the bond coat, are the primary reasons for degradation of the TGO/bond coat interface.

Figure 15. Schematic representation illustrating the two common failure mechanisms of EB-PVD TBCs.
3 EXPERIMENTAL

3.1 Specimen Description of Thermal Barrier Coatings

Disc-shaped (25.4 mm in diameter and 8.0 mm in height) TBC specimens, schematically illustrated in Figure 16, were prepared by an industrial partner by LPPS deposition of CoNiCrAlY powders to obtain 100 μm-thick bond coat, and APS deposition of YSZ powders to obtain a dense 200 μm-thick topcoat on an IN 738-LC superalloy substrate (Figure 17). After deposition, the YSZ surface was ground to obtain a flat and even topcoat. Chemical compositions of the TBC constituents are presented in Table 2.

Figure 16. Schematic depicting the specimen geometry for TBCs employed in this study.
Table 2. Chemical composition of the thermal barrier coating system employed in this study.

<table>
<thead>
<tr>
<th>TBC Constituent</th>
<th>Elemental Composition in wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>APS YSZ Topcoat</td>
<td>ZrO₂  Y₂O₃</td>
</tr>
<tr>
<td></td>
<td>bal-  8</td>
</tr>
<tr>
<td>LPPS CoNiCrAlY Bond Coat</td>
<td>Co  Ni  Cr  Al  Y</td>
</tr>
<tr>
<td></td>
<td>bal-  32  22  10  0.3</td>
</tr>
<tr>
<td>IN 738-LC Superalloy Substrate</td>
<td>Ni  Cr  Co  Ti  Al  W  Mo  Ta  Nb  C  Zr  B</td>
</tr>
<tr>
<td></td>
<td>bal-  16  8.5  3.5  3.5  2.5  1.7  1.7  0.8  0.9  0.0  0.0  1</td>
</tr>
</tbody>
</table>

3.2 Furnace Thermal Cycling

Thermal cyclic lifetimes for TBCs were evaluated using a CM™ Rapid High Temperature furnace with automated vertical cycling capabilities (Figure 18 and Figure 19). Each cycle consisted of a 10-minute heat-up to 1100°C, 1-, 10- or 50-hour hold at 1100°C, and a 10-minute forced-air quench. Computer controls ensured the TBCs reached the desired temperatures within the 10-minute heating and cooling periods. TBC specimens were rotated in between thermal cycles to assure uniformity in temperature
exposure. Thermal cycling was carried out until failure, defined by complete spallation of the YSZ topcoat, using up to 5 TBC specimens per 1-, 10-, or 50-hour series. Then, additional cyclic tests were carried out as a function of thermal cycling lifetime using the matrix given in Table 3.

Figure 18. CM™ Rapid High Temperature furnace with automated vertical cycling capabilities.

Figure 19. CM™ Rapid High Temperature furnace schematic diagram during high temperature oxidation and cooling.
Table 3. Matrix of the thermal cyclic tests for TBCs.

<table>
<thead>
<tr>
<th>Type of Test</th>
<th>Microstructural Analysis (% Lifetime)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.A.</td>
<td>0</td>
</tr>
<tr>
<td>1 hour</td>
<td>5, 10, 30, 40, 50, 65, 80 and Failure (5 specimens)</td>
</tr>
<tr>
<td>10 hour</td>
<td>10, 20, 30, 40, 50, 80 and Failure (5 specimens)</td>
</tr>
<tr>
<td>50 hour</td>
<td>10, 20, 30, 40, 50, 65 and Failure (3 specimens)</td>
</tr>
</tbody>
</table>

### 3.3 Microstructural Characterization

TBC specimens were used for the microstructural and failure analysis as presented in Table 3. Microstructural evolution and phase constituents of the TBC were examined as a function of thermal cycles by optical microscopy (OM), scanning electron microscopy (SEM) equipped with X-ray energy dispersive spectroscopy (XEDS), and X-ray diffraction (XRD). Specimens used for microstructural characterization were mounted using Buehler® cold mount epoxy and then sectioned using Allied™ TechCut4 low speed saw to minimize damages associated with mechanical sectioning. Cross-sectional samples were then ground and polished down to 0.25 μm using diamond paste on a Struers™ RotoPol11 polishing machine. Thin gold palladium coatings (10 nm) were applied to the sample surface prior to examination via SEM for conduction purposes using an Emitech K550 sputter coating system.

Quantitative analysis was carried out by image processing via IQ Materials™ image analysis software. Thickness measurements of the TGO and the β + γ region in the bond coat to quantify the TGO growth and the bond coat degradation (i.e., β-phase depletion), respectively, were taken at 50 random locations on the cross-sectional specimens. The
lengths of in-plane cracks within the YSZ (e.g., up to 300 per specimen) were systematically measured. Inter-splat boundaries and other defects were distinguishable from the in-plane cracks since the YSZ had a relatively dense microstructure (i.e., less than 5% porosity as opposed to the 15-20% porosity found in conventional APS YSZ coatings for TBC applications). Crack-like features less than 30 μm in length were defined as inter-splat boundaries. To account for the large number of cracks parallel to the TGO interface and ambiguity due to the “edge-effect” that is attributed to the sample geometry, a statistical “75th percentile approach” [39] was employed to determine the average crack length (Figure 20). It was assumed that cracks of maximum length fell within the top 25% of those measured, which allows for an average to be taken without the inclusion of the unrepresentative edge-cracks (i.e., outliers). The crack length measurements obtained using the aforementioned approach will be referred to herein as the effective maximum crack length. The crack propagation data was then used to derive a lifetime approximation model using a modified Paris Law for fatigue crack growth.
Figure 20. 75th percentile approach used for quantifying crack length depicting the effective maximum crack length.
4 RESULTS

4.1 Characterization of As-Received Specimens

As-received specimens had a dense YSZ microstructure (Figure 21a) along with characteristic volume defects typical to APS processing such as pores, interconnected cracks and intersplat boundaries (Figure 21b). The as-processed microstructure of the LPPS CoNiCrAlY bond coat consisted of solid solutioned β-NiAl and γ (Ni solid solution) phases (Figure 21d). Phase constituents were verified via XEDS (Figure 22). The presence of a continuous α-Al₂O₃ TGO layer was also observed at the YSZ/bond coat interface (Figure 21c).
Figure 21. Cross-sectional backscattered electron micrographs of the as-received TBC specimen showing the respective microstructure of each layer.
Figure 22. XEDS spectra of the β and the γ phases of the LPPS CoNiCrAlY bond coat, the TGO scale and the APS YSZ topcoat.

XRD patterns of the YSZ surface from the as-received APS TBCs demonstrated the presence of metastable tetragonal (t') ZrO2 as the primary constituent of the YSZ coating (Figure 23). There was no evidence of detrimental monoclinic (m) or fluorite-cubic (f) ZrO2 phases. Polishing marks on the YSZ surface were observed (Figure 24), which resulted from the post-processing step of TBC fabrication.

Figure 23. XRD pattern from the YSZ surface of the as-received TBC specimen.
4.2 Furnace Thermal Cyclic Lifetime

TBC lifetime was determined by carrying out thermal cyclic tests at 1100°C with 1-, 10-, and 50-hour dwell periods until failure by complete spallation of the YSZ topcoat using up to 5 TBC specimens per series. TBCs demonstrated an average lifetime of 295 cycles for 5 specimens with 1-hour dwell periods, 50 cycles for 5 specimens with 10-hour dwell periods, and 15 cycles for 3 specimens with 50-hour dwell periods as reported in Table 4 and Figure 25. The total hot temperature dwell time before failure obtained from the TBC cyclic lifetime of the 3 testing periods is also presented in Figure 26.

Table 4. Thermal cyclic lifetime for TBCs with 1-, 10-, and 50-hour dwell periods.

<table>
<thead>
<tr>
<th>Cyclic Testing Type</th>
<th>Number of TBC Specimens</th>
<th>Average Lifetime (cycles)</th>
<th>Standard Deviation (cycles)</th>
<th>Average Hot Time (hrs)</th>
<th>Standard Deviation (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>5</td>
<td>295</td>
<td>10</td>
<td>295</td>
<td>10</td>
</tr>
<tr>
<td>10 hour</td>
<td>5</td>
<td>50</td>
<td>5</td>
<td>500</td>
<td>45</td>
</tr>
<tr>
<td>50 hour</td>
<td>3</td>
<td>15</td>
<td>2</td>
<td>767</td>
<td>75</td>
</tr>
</tbody>
</table>
Figure 25. Furnace cyclic lifetime for TBCs tested at 1100°C using 1-, 10-, and 50-hour dwell periods.

Figure 26. Dwell time life during thermal cycling for TBCs tested at 1100°C using 1-, 10-, and 50-hour dwell periods.
4.3 Failure Assessment of TBC Specimens using 1-hour Thermal Cycling

After evaluating the durability of TBCs cycled at 1100°C using 1-hr dwell time, the failed samples were visually inspected and then characterized using XRD, SEM and XEDS.

4.3.1 Visual Observation

Failure occurred by complete spallation of the YSZ topcoat from the bond coated superalloy substrate (Figure 27). The spalled YSZ coating was cracked after failure. The fracture surface shows that failure occurred at the topcoat/bond coat interface. The failed YSZ topcoat and the bare bond coat fracture surfaces were examined via XRD and SEM after visual observation.

![Digital macrograph of a failed TBC specimen after 1-hour thermal cyclic tests at 1100°C.](image)

4.3.2 Phase Identification

The failed topcoat surface revealed no significant phase transformation and remained primarily composed of the metastable t’ ZrO₂ phase (Figure 28). Surface cracks on the spalled YSZ were also observed (Figure 29).
The bare bond coat surface after YSZ spallation had a significant amount of YSZ (Figure 30a), which indicated that the TBC failure occurred mainly through cracking within the YSZ. The presence of alumina and detrimental spinel oxides [(Ni, Co) (Cr, Al)\(_2\)O\(_4\)] were also observed at the failure interface and confirmed by XEDS (Figure 31b-c) and XRD (Figure 32a). The bottom surface of the YSZ topcoat had small amounts of α-Al\(_2\)O\(_3\) (Figure 30b), which further supports predominant failure within the YSZ but close to the TGO due to the localized presence of the TGO on the spalled YSZ surface as confirmed by XEDS (Figure 31a-b) and XRD (Figure 32b).
Figure 30. Backscatter electron micrographs of (a) the top surface of the bare bond coat after YSZ spallation and (b) the bottom surface of the spalled YSZ of a failed TBCs after 1-hour thermal cycle tests at 1100°C.

Figure 31. XEDS spectra of the (a) YSZ, (b) TGO, and (c) Spinel Oxide corresponding to the fracture surfaces of failed TBCs after 1-hour thermal cycle tests at 1100°C.
Figure 32. XRD patterns from (a) the top surface of the bare bond coat after YSZ spallation and (b) the bottom surface of the spalled YSZ of failed TBCs after 1-hour thermal cycle tests at 1100°C.

4.3.3 Microstructural Characterization

Failed cross-sectional TBC specimens examined by SEM (Figure 33) showed that the YSZ topcoat failed very close to the YSZ/TGO interface. Cracks normal to the TGO within the spalled YSZ were also observed. The CoNiCrAlY bond coat, which initially had a two-phase microstructure (β + γ), was found to be entirely composed of single-phase γ (Figure 33b) in failed specimens. YSZ remains still attached to the TGO enabled the observation of a 5.82 μm thick TGO scale composed of α-Al₂O₃. Localized spinel formation at the topcoat/bond coat interface along the TGO interface was also noted.
4.4 Quantitative Microstructural Analysis of TBC Specimens using 1-hr Dwell Time as a Function of Thermal Cycles

TBC specimens thermally cycled to various intervals of the 1-hr lifetime were characterized via cross-sectional backscatter electron microscopy (Figure 34). The growth of the thermally grown oxide (TGO) scale, the depletion of the Al-rich $\beta$-NiAl phase in the bond coat, and the population and growth of micro-cracks near the YSZ/bond coat interface were further analyzed and results are shown in Table 5.
Figure 34. Cross-sectional backscattered electron micrographs of TBC specimens thermally cycled at 1100°C using 1-hour dwell periods after: (a) 15 cycles, (b) 30 cycles, (c) 89 cycles, (d) 118 cycles, (e) 147 cycles, (f) 192 cycles, and (g) 236 cycles.

Table 5. Results of quantitative microstructural analyses as a function of thermal cycling using 1-hr thermal cycling.

<table>
<thead>
<tr>
<th>TBC Specimen</th>
<th>Thermal Cycles (N)</th>
<th>Avg. TGO Thickness (μm)</th>
<th>Fraction of β-phase (%)</th>
<th>Eff. Max. Crack Length (μm)</th>
<th>Number of Cracks Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Received</td>
<td>0</td>
<td>0.556 ± 0.10</td>
<td>86.2 ± 6.2</td>
<td>30</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-hour dwell period</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% of Lifetime</td>
<td>15</td>
<td>1.61 ± 0.29</td>
<td>76.5 ± 4.2</td>
<td>37.6 ± 6.2</td>
<td>259</td>
</tr>
<tr>
<td>10% of Lifetime</td>
<td>30</td>
<td>2.02 ± 0.36</td>
<td>59.0 ± 6.4</td>
<td>91.2 ± 20.4</td>
<td>157</td>
</tr>
<tr>
<td>30% of Lifetime</td>
<td>89</td>
<td>3.11 ± 0.52</td>
<td>5.2 ± 4.3</td>
<td>125.7 ± 31.0</td>
<td>170</td>
</tr>
<tr>
<td>40% of Lifetime</td>
<td>118</td>
<td>3.29 ± 0.44</td>
<td>0</td>
<td>165.4 ± 100.5</td>
<td>96</td>
</tr>
<tr>
<td>50% of Lifetime</td>
<td>147</td>
<td>4.17 ± 0.89</td>
<td>0</td>
<td>212.9 ± 154.9</td>
<td>165</td>
</tr>
<tr>
<td>65% of Lifetime</td>
<td>192</td>
<td>3.65 ± 0.61</td>
<td>0</td>
<td>544.6 ± 138.1</td>
<td>107</td>
</tr>
<tr>
<td>80% of Lifetime</td>
<td>236</td>
<td>4.37 ± 0.70</td>
<td>0</td>
<td>901.7 ± 416.5</td>
<td>100</td>
</tr>
<tr>
<td>5 Failed Specimens</td>
<td>295 ± 10</td>
<td>5.82 ± 0.66</td>
<td>0</td>
<td>25400</td>
<td>N.A.</td>
</tr>
</tbody>
</table>
4.4.1 Beta Depletion

The CoNiCrAlY bond coat, which initially had a two-phase microstructure ($\beta + \gamma$), was found to be entirely composed of single-phase $\gamma$ (Figure 34c) as soon as 118 1-hour cycles. Depletion of the Al-rich $\beta$-phase of the CoNiCrAlY bond coat is also observed via inward diffusion of Al into the superalloy substrate and outward diffusion of Al to form the TGO during elevated temperatures (Figure 34). The measured values of the average thickness of the $\beta + \gamma$ region as a function of thermal cycles demonstrated an exponential depletion of the $\beta$-phase in the bond coat (Figure 35). The depletion of the $\beta$-phase with thermal cycling, based on image analysis, is also reported in Table 5.

![Figure 35. $\beta$-depletion as a function of thermal cycling of the LPPS CoNiCrAlY bond coat at 1100°C using 1-hour dwell period.](image-url)
4.4.2 TGO Growth

The TGO growth kinetics were examined for TBC specimens tested at various intervals of the average lifetime including failure. The TGO was observed to be primarily composed of Al₂O₃, however, the detrimental spinel oxides were also observed within the YSZ but close to the YSZ/TGO interface. Measured values of the average TGO thickness are reported in Table 5. The measured thickness as a function of the square root of high-temperature dwell time (hours) revealed the parabolic growth of the TGO (Figure 36) with an estimated growth constant (kₚ) of 0.253 μm/h₁/₂ at 1100°C.

![Figure 36. Thickness of the TGO scale in APS TBCs as a function of the square root of high temperature dwell time at 1100°C using 1-hour dwell period.](image)

4.4.3 Crack Propagation and Growth

The systematic examination of in-plane cracks within the YSZ topcoat by measurement of crack length via “75th percentile” statistical approach yielded values of the effective maximum crack length reported in Table 5. The overall crack density along the TBC sample decreased as thermal cycling increased, which can be attributed to the
propagation and link-up of cracks. The evolution of the effective maximum crack length as a function of thermal cycles (Figure 37) is best described by the exponential function:

\[
\bar{a} = 36.56 \exp[0.0135 \times N]
\]  

(Equation 1)

where \( \bar{a} \) is the effective maximum crack length and \( N \) is the number of thermal cycles for the 1-hour dwell period cycling.

Figure 37. Effective maximum crack length as a function of thermal cycles for APS TBCs thermally cycled at 1100°C using 1-hour dwell period.

4.5 Failure Assessment of TBC Specimens using 10-hr Thermal Cycling

TBCs cycled at 1100°C using 10-hr dwell time exhibited a lifetime of 50 cycles. After this average lifetime was determined the failed samples were visually inspected and characterized using XRD, SEM and XEDS.
4.5.1 Visual Observation

TBC failure, after an average of 50 cycles, was observed as spallation of the YSZ coating as a whole from the substrate (Figure 38); this is similar to the failure mode observed for the 1-hour thermal cyclic tests at 1100°C. The failed YSZ topcoat and the bare bond coat fracture surfaces were examined via SEM and XRD after visual observation.

Figure 38. Digital macrograph of a failed TBC specimen after 10-hour thermal cyclic tests at 1100°C.

4.5.2 Phase Identification

The XRD pattern obtained from the failed topcoat surface (Figure 39) revealed no significant phase transformation, and the YSZ primarily consisted of the metastable t’-ZrO₂ phase. Surface cracks on the spalled YSZ were also observed (Figure 40), which is similar to those observed in the 1-hr failed samples.
Figure 39. XRD pattern from the YSZ surface of a failed TBC specimen after 10-hour thermal cyclic tests at 1100°C.

Figure 40. Backscatter electron micrograph showing the YSZ surface cracks on failed TBCs after 10-hour thermal cyclic tests at 1100°C.

Large amount of the YSZ was found on the bare bond coat surface after the YSZ spallation (Figure 41a). This indicates that the TBC failure occurred through cracking within YSZ, which is the similar to the observed failure characteristics from 1-hour thermal cyclic test. Alumina and detrimental spinel oxides, (Ni,Co)(Cr,Al)₂O₄ were found, and confirmed by the XEDS (Figure 42b-c) and XRD (Figure 43a), at the failure interface. To further support failure occurring within the YSZ but close to the TGO, the bottom surface of the YSZ topcoat had small amounts of α-Al₂O₃ from the TGO (Figure 41b), which was confirmed by XEDS (Figure 42b) and XRD (Figure 43b).
Figure 41. Backscatter electron micrographs of (a) the top surface of the bare bond coat after YSZ spallation and (b) the bottom surface of the spalled YSZ of a failed TBCs after 10-hour thermal cycle tests at 1100°C.

Figure 42. XEDS spectra of the (a) YSZ, (b) TGO, and (c) Spinel Oxide corresponding to the fracture surfaces of failed TBCs after 10-hour thermal cycle tests at 1100°C.
Figure 43. XRD patterns from (a) the top surface of the bare bond coat after YSZ spallation and (b) the bottom surface of the spalled YSZ of failed TBCs after 1-hour thermal cycle tests at 1100°C.

4.5.3 Microstructural Characterization

The YSZ topcoat failed very close to the topcoat/TGO interface due to progressive cracking within the YSZ as shown by the failed cross-sectional TBC specimens examined via SEM (Figure 44). This is similar to the failure of the 1-hour thermally cycled TBCs. A 6.08 μm thick TGO composed of α-Al₂O₃ was observed and confirmed by XEDS; while complete beta depletion in CoNiCrAlY bond coat was also observed at failure (Figure 44b). The spalled YSZ had vertical cracks throughout its cross-section (Figure 44a) and localized spinel formation at the topcoat/bond coat interface along the TGO was observed.
4.6 Quantitative Microstructural Analysis of TBC Specimens using 10-hr Dwell Time as a Function of Thermal Cycles

TBC samples thermally cycled to various intervals of the 10-hour average lifetime were characterized to observe their microstructural evolution via cross-sectional backscatter SEM analysis (Figure 45). The growth of the thermally grown oxide (TGO) scale, the depletion of the Al-rich β-NiAl phase in the bond coat, and the population and growth of micro-cracks near the YSZ/bond coat interface were further analyzed and results are shown in Table 6.
Figure 45. Cross-sectional backscattered electron micrographs of TBC specimens thermally cycled at 1100°C using 10-hour dwell periods after: (a) 5 cycles, (b) 10 cycles, (c) 15 cycles, (d) 20 cycles, (e) 40 cycles.
Table 6. Results of quantitative microstructural analyses as a function of thermal cycling using 10-hr thermal cycling.

<table>
<thead>
<tr>
<th>TBC Specimen</th>
<th>Thermal Cycles (N)</th>
<th>Avg. TGO Thickness (μm)</th>
<th>Fraction of β-phase (%)</th>
<th>Eff. Max. Crack Length (μm)</th>
<th>Number of Cracks Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Received</td>
<td>0</td>
<td>0.556 ± 0.10</td>
<td>86.2 ± 6.2</td>
<td>30</td>
<td>N.A.</td>
</tr>
<tr>
<td>10% of Lifetime</td>
<td>5</td>
<td>2.48 ± 0.89</td>
<td>38.8 ± 7.2</td>
<td>65.7 ± 5.7</td>
<td>127</td>
</tr>
<tr>
<td>20% of Lifetime</td>
<td>10</td>
<td>2.88 ± 0.60</td>
<td>0.1% ± 0.05</td>
<td>74.9 ± 15.9</td>
<td>132</td>
</tr>
<tr>
<td>30% of Lifetime</td>
<td>15</td>
<td>4.34 ± 1.33</td>
<td>0</td>
<td>125.6 ± 30.2</td>
<td>103</td>
</tr>
<tr>
<td>40% of Lifetime</td>
<td>20</td>
<td>4.41 ± 0.77</td>
<td>0</td>
<td>101.0 ± 23.7</td>
<td>130</td>
</tr>
<tr>
<td>80% of Lifetime</td>
<td>40</td>
<td>5.88 ± 1.69</td>
<td>0</td>
<td>1748.9 ± 973.7</td>
<td>7</td>
</tr>
<tr>
<td>5 Failed Specimens</td>
<td>50 ± 5</td>
<td>6.08 ± 1.82</td>
<td>0</td>
<td>25400</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

4.6.1 Beta Depletion

The CoNiCrAlY bond coat was nearly depleted of the Al-rich β phase by 10 10-hour cycles (Figure 45b). The measured values of the average thickness of the β + γ region as a function of thermal cycles demonstrated an exponential depletion of the β-phase in the bond coat (Figure 46), a similar trend to that of the beta depletion in the 1-hour TBCs. The depletion of the β-phase with thermal cycling, based on image analysis, is also reported in Table 6.
4.6.2 TGO Growth

The TGO growth kinetics were examined for TBC specimens tested at various intervals of the average lifetime including failure. The TGO was observed to be primarily composed of Al₂O₃, however, the detrimental spinel oxides were also observed within the YSZ but close to the YSZ/TGO interface; also similar to the 1-hour TBCs. Measured values of the average TGO thickness are reported in Table 6. The measured thickness as a function of the square root of high-temperature dwell time (hours) revealed the parabolic growth of the TGO (Figure 47) with an estimated growth constant (kₚ) of 0.254 μm/h¹/₂ at 1100°C.
4.6.3 Crack Propagation and Growth

The measured values of the effective maximum crack length as a function of thermal cycles are reported in Table 6 and illustrated in Figure 48; whose evolution is best described by the exponential function:

\[ \bar{a} = 29.18 \exp[0.0953 \times N] \]  \hspace{1cm} (Equation 2)

where \( \bar{a} \) is the effective maximum crack length and \( N \) is the number of thermal cycles for the 10-hour dwell period cycling.
4.7 Failure Assessment of TBC Specimens using 50-hour Thermal Cycling

After evaluating the durability of TBCs cycled at 1100°C using 50-hour dwell time, which yielded an average lifetime of 15 cycles, the failed samples were visually inspected and then characterized using XRD, SEM and XEDS.

4.7.1 Visual Observation

Similar to the 1-hour and 10-hour failure modes, failure for the 50-hour thermally cycled TBCs occurred by complete spallation of the YSZ topcoat from the bond coated superalloy substrate (Figure 49) after an average of 15 cycles. The fracture surface shows that failure occurred at the topcoat/bond coat interface. The failed YSZ topcoat and the bare bond coat fracture surfaces were examined via XRD and SEM after visual observation.
4.7.2 Phase Identification

The XRD pattern obtained from the failed topcoat surface (Figure 50) revealed no significant phase transformation, and the YSZ primarily consisted of the metastable $t'$-$\text{ZrO}_2$ phase. Surface cracks on the spalled YSZ were also observed (Figure 51), which is similar to those observed in the 1-hour and 10-hour failed samples.
Figure 51. Micrograph showing the YSZ surface cracks on failed TBCs after 50-hour thermal cyclic tests at 1100°C.

As observed with the other cyclic tests, the bare bond coat surface had YSZ remnants after spallation (Figure 52), indicating failure occurred through cracking within the YSZ. Alumina was also found and confirmed by XEDS (Figure 53) at the failure interface. The bottom surface of the YSZ topcoat also had $\alpha$-Al$_2$O$_3$ remnants from the TGO, which supports the failure mode stated above.

Figure 52. Backscatter electron micrographs of (a) the top surface of the bare bond coat after YSZ spallation and (b) the bottom surface of the spalled YSZ of a failed TBCs after 50-hour thermal cycle tests at 1100°C.
4.7.3 Microstructural Characterization

As observed with the failed 1-hour and 10-hour thermally cycled TBCs, the YSZ topcoat failed close to the topcoat/TGO interface (Figure 54). A 6.63 μm thick TGO composed of α-Al₂O₃ was observed and confirmed by XEDS; while complete beta depletion in CoNiCrAlY bond coat was also observed at failure (Figure 54b). Vertical cracks were observed throughout the spalled YSZ cross-section (Figure 54a) as well as localized spinel formation.

Figure 53. XEDS spectra of the (a) YSZ and (b) TGO corresponding to the fracture surfaces of failed TBCs after 50-hour thermal cycle tests at 1100°C.

Figure 54. Cross-sectional backscattered electron micrograph of a failed TBC specimen after 15 cycles of 50-hour thermal cycling at 1100°C.
4.8 Quantitative Microstructural Analysis of TBC Specimens using 50-hour Dwell Time as a Function of Thermal Cycling

TBC samples thermally cycled to various intervals of the 50-hour average lifetime were characterized to observe their microstructural evolution via cross-sectional backscatter SEM analysis (Figure 55). The growth of the thermally grown oxide (TGO) scale, the depletion of the Al-rich $\beta$-NiAl phase in the bond coat, and the population and growth of micro-cracks near the YSZ/bond coat interface were further analyzed and results are shown in Table 7.
Figure 55. Cross-sectional backscattered electron micrographs of TBC specimens thermally cycled at 1100°C using 50-hour dwell periods after: (a) 2 cycles, (b) 3 cycles, (c) 5 cycles, (d) 6 cycles, (e) 10 cycles.
Table 7. Results of quantitative microstructural analyses as a function of thermal cycling using 50-hr thermal cycling.

<table>
<thead>
<tr>
<th>TBC Specimen</th>
<th>Thermal Cycles (N)</th>
<th>Avg. TGO Thickness (μm)</th>
<th>Fraction of β-phase (%)</th>
<th>Eff. Max. Crack Length (μm)</th>
<th>Number of Cracks Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Received</td>
<td>0</td>
<td>0.556 ± 0.10</td>
<td>86.2 ± 6.2</td>
<td>30</td>
<td>N.A.</td>
</tr>
<tr>
<td>50-hour dwell period</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% of Lifetime</td>
<td>2</td>
<td>2.91 ± 0.36</td>
<td>26.2 ± 3.7</td>
<td>80.8 ± 10.5</td>
<td>301</td>
</tr>
<tr>
<td>20% of Lifetime</td>
<td>3</td>
<td>2.97 ± 0.70</td>
<td>0</td>
<td>68.0 ± 16.1</td>
<td>126</td>
</tr>
<tr>
<td>30% of Lifetime</td>
<td>5</td>
<td>3.88 ± 0.61</td>
<td>0</td>
<td>75.6 ± 21.0</td>
<td>65</td>
</tr>
<tr>
<td>40% of Lifetime</td>
<td>6</td>
<td>5.02 ± 0.85</td>
<td>0</td>
<td>86.2 ± 19.4</td>
<td>103</td>
</tr>
<tr>
<td>65% of Lifetime</td>
<td>10</td>
<td>5.89 ± 0.70</td>
<td>0</td>
<td>322.3 ± 127.8</td>
<td>77</td>
</tr>
<tr>
<td>3 Failed Specimens</td>
<td>15 ± 2</td>
<td>6.63 ± 1.18</td>
<td>0</td>
<td>25400</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

4.8.1 Beta Depletion

The CoNiCrAlY bond coat, which initially had a two-phase microstructure (β + γ), was found to be entirely composed of single-phase γ (Figure 55b) after 3 50-hour cycles, or 150 hours of dwell time comparable to the 1- and 10-hour TBCs. The measured values of the average thickness of the β + γ region as a function of thermal cycles demonstrated an exponential depletion of the β-phase in the bond coat (Figure 56), a similar trend to the beta depletion in the 1-hour TBCs. The depletion of the β-phase with thermal cycling, based on image analysis, is also reported in Table 7.
Figure 56. \( \beta \)-depletion as a function of thermal cycling of the LPPS CoNiCrAlY bond coat at 1100°C using 50-hour dwell period.

4.8.2 TGO Growth

Similar to the 1- and 10-hour TBCs, the TGO for the 50-hour thermal cyclic tests was observed to be primarily composed of Al\(_2\)O\(_3\), however, detrimental oxides were also observed within the YSZ but close to the YSZ/TGO interface. Measured values of the average TGO thickness are reported in Table 7. The measured thickness as a function of the square root of high-temperature dwell time (hours) revealed the parabolic growth of the TGO (Figure 57) with an estimated growth constant \((k_p)\) of 0.231 \(\mu\)m/h\(^{1/2}\) at 1100°C.
Figure 57. Thickness of the TGO scale in APS TBCs as a function of the square root of high temperature dwell time at 1100°C using 50-hour dwell period.

4.8.3 Crack Propagation and Growth

The measured values of the effective maximum crack length as a function of thermal cycles are reported in Table 7 and illustrated in Figure 58; whose evolution is best described by the exponential function:

\[ \bar{a} = 34.83 \exp(0.2026 \times N) \]  

(Equation 3)

where \( \bar{a} \) is the effective maximum crack length and \( N \) is the number of thermal cycles for the 50-hour dwell period cycling.
Figure 58. Effective maximum crack length as a function of thermal cycles for APS TBCs thermally cycled at 1100°C using 50-hour dwell period.

4.9 Life Approximation Model

The crack growth behavior observed for the 1-, 10-, and 50-hour thermally cycled TBCs with an exponential increase is similar to fatigue crack growth; thus, a model for steady-state growth of in-plane cracks within the YSZ was devised by modifying the Paris Law. The relation similar to Paris Law of log (dā/dN) vs. log (ā) can be employed to approximate TBC lifetime.

The linear relationship between crack growth rate (dā/dN) and the effective maximum crack length (ā) can be expressed by:

\[
\frac{d\bar{a}}{dN} = B \times a^m
\]

(Equation 4)
where $B$ and $m$ are empirical constants. The values of $B$ and $m$ were determined by a linear-fit of the steady state crack growth (Figure 59) as $B = 1.24 \times 10^{-3}$ and $m = 1.49$.

Equation 4 for this particular system using a 1-hour dwell period can be rewritten as:

$$\frac{d\bar{a}}{dN} = 1.24 \times 10^{-3} \times (\bar{a})^{1.49}$$

(Equation 5)

In the same manner, values of $B$ and $m$ were determined for the 10- and 50-hour dwell periods as $B = 1.91 \times 10^{-2}$, $m = 1.33$ and $B = 1.84 \times 10^{-2}$, $m = 1.55$, respectively. Therefore Equation 4 can be rewritten for the 10-hour dwell period as:

$$\frac{d\bar{a}}{dN} = 1.91 \times 10^{-2} \times (\bar{a})^{1.33}$$

(Equation 6).

And for the 50-hour dwell period as:

$$\frac{d\bar{a}}{dN} = 1.84 \times 10^{-2} \times (\bar{a})^{1.55}$$

(Equation 7).
Figure 59. Crack growth behavior where the steady-state crack growth region (squares) can be observed for TBCs thermally cycled at 1100°C using (a) 1-hour, (b) 10-hour and (c) 50-hour dwell period.
5 DISCUSSION

Thermal cyclic tests at 1100°C demonstrated the durability of these dense APS TBCs to be comparable to the current generation of commercially processed APS TBCs [6,13]. TBC failure, regardless of the dwell time, was observed to result from a complete spallation of the YSZ topcoat. This failure is the characteristic failure mode for APS TBCs [3] [4] [6] [9] [10] [15] [16] [19], however, it is also similar to that observed in dense-vertically-cracked TBCs [7].

To clearly understand the mechanisms leading up to YSZ spallation of these TBCs, additional specimens were thermally cycled up to different intervals of the measured average lifetime as listed in Tables 4-6. Microstructural changes as a function of thermal cycles were quantified. Depletion of the Al-rich β phase in the bond coat has frequently been reported as a critical life-limiting event because of Al depletion of the bond coat gives rise to the formation of deleterious oxides in the TGO scale [3] [4] [10] [11]. While the depletion of the Al-rich phase followed a classical diffusion controlled process (Figure 60), the CoNiCrAlY bond coat examined was found to be solely composed of γ-Ni solid solution after only 40% of the 1-hour dwell lifetime and after 20% of the 10- and 50-hour dwell lifetime, as reported in Table 5, Table 6 and Table 7, all corresponding to ~100 hour dwell at 1100°C. Therefore, in this study TBC failure did not coincide or relate to the β-depletion.
Figure 60. β-depletion as a function of thermal cycling of the LPPS CoNiCrAlY bond coat at 1100°C using 1-, 10- and 50-hour dwell period.

The TGO growth was observed to follow a parabolic trend of a characteristic diffusion-controlled process (Figure 61), which is in good agreement with earlier reported studies [2] [3] [7] [9] [11]. TBC failure has been reported to occur once a critical TGO thickness has been reached [2] [6] [9]. In this study, the TGO thickness at failure was measured to be 5.82 ± 0.66 μm, 6.08 ± 1.82 μm, and 6.63 ± 1.18 μm for the 1-, 10- and 50-hour dwell periods, respectively with the parabolic growth constant of 0.238 μm/h^{1/2}. This compares well with the parabolic rate constants reported by others [3] [7].
Figure 61. Thickness of the TGO scale in APS TBCs as a function of the square root of high temperature dwell time at 1100°C using 1-, 10- and 50-hour dwell period.

In the past, others have studied fatigue behavior in TBCs under thermal cyclic loading [14] [15] [18] [22]; there are three distinct regions to fatigue behavior: an incubation period with negligible crack growth, a period of steady state crack growth, and an unstable crack growth period. Others have examined the steady-state crack growth during thermal cycling [20], where crack growth was correlated to the growth of the TGO scale [16] [21]. In this study the exponential growth in crack length (Figure 62) was used to determine the crack growth rate from which the constants $B$ and $m$ in Equation 4 were calculated from the steady-state region. Based on Paris Law, $B$ and $m$ could be dependent on the testing conditions and materials, respectively. These constants along with the initial ($\bar{a}_i$) and final ($\bar{a}_f$) values of the effective maximum crack length determined in this study, reported in Tables 4-6, can be employed to estimate the lifetime to failure, $N_f$: 
\[ N_f = \frac{1}{B \times \bar{a}^{m-1} (m-1)} \bar{a}_i \]  

(Equation 8)

The initial value of the effective maximum crack length (\(\bar{a}_i\)) was determined as 30 \(\mu\)m from the microstructural evaluation of the as-received TBCs, and the final value of the effective maximum crack length (\(\bar{a}_f\)) was determined as 25400 \(\mu\)m because failure occurred by complete spallation of the entire TBC topcoat which corresponds to a crack length equal to the sample diameter. The model predicted the TBC lifetime to be 306 cycles at 1100°C using a 1-hour dwell period, where the experimental lifetime was determined to be 295 cycles. This discrepancy may be due to the presence of large edge-cracks attributed to the geometry of the specimens used in this study, which can have a profound influence on TBC lifetime. The predicted lifetimes for the 10- and 50-hour dwell periods were 45 cycles and 15 cycles, while the experimental lifetimes were 50 cycles and 15 cycles, respectively. Therefore, the model’s accuracy was at most 10% off from the experimental lifetime.
Figure 62. Effective maximum crack length as a function of thermal cycles for APS TBCs thermally cycled at 1100°C using 1-, 10- and 50-hour dwell period.
6 CONCLUSION

APS TBCs have been subjected to 1-, 10- and 50-hour thermal cycling at 1100°C in order to gain a better understanding of failure. Durability of the TBCs resulted in an average lifetime of 295, 50 and 15 cycles for the 1-, 10- and 50-hour dwell thermal cyclic tests, respectively. Quantitative microstructural analyses were performed to document the parabolic TGO growth with a growth constant of 0.238 μm/h$^{1/2}$, depletion of the Al-rich β-phase from the bond coat, which occurred only after 40% of the 1-hour dwell TBC lifetime and 20% of the 10- and 50-hour dwell TBC lifetime, and the exponential growth of in-plane cracks within the YSZ topcoat. Failure occurred for all cyclic tests by complete spallation of the YSZ topcoat resulting from crack propagation within the topcoat but close to the YSZ/bond coat interface.

A model for lifetime prediction of APS YSZ TBCs with relatively dense microstructure has been proposed based on a modified Paris Law given by Equation 4. Empirical constants $B$ and $m$ were determined based on measurements of in-plane cracks by extensive quantitative microstructural analysis as $B = 1.24 \times 10^{-3}$ and $m = 1.49$, $B = 1.91 \times 10^{-2}$, $m = 1.33$ and $B = 1.84 \times 10^{-2}$, $m = 1.55$ for this particular system using a 1-, 10- and 50-hour dwell period, respectively. The predicted lifetime deviated at most by 10% from the average experimental lifetime.
APPENDIX: LIST OF PRESENTATIONS


• C. Bargraser, P. Mohan, H.J. Choi, S. Mukherjee, Y.H. Sohn, “Failure Assessment of Dense Vertically Cracked Thermal Barrier Coatings by Quantitative Microstructural Analysis,” Presented at 34th International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, Florida, USA

LIST OF REFERENCES


[16] O Trunova, T Beck, R Herzog, R W Steinbrech, and L Singheiser, "Damage mechanisms and lifetime behavior of plasma sprayed thermal barrier coating systems for gas


[34] T J Patterson, "Effects of internal oxidation on thermo-mechanical properties of atmospheric plasma sprayed CoNiCrAlY coatings," University of Central Florida, MS


[40] B Jayaraj, "Correlating the microstructural development and failure mechanism to photo stimulated luminescence & electrochemical impedance spectroscopy in thermal barrier coatings," University of Central Florida, PhD. Dissertation 2011.