Furnace Cyclic Behavior of Plasma-Sprayed Zirconia-Yttria and Multi-Component Rare Earth Oxide Doped Thermal Barrier Coatings

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ABSTRACT

Ceramic thermal barrier coatings will play an increasingly important role in advanced gas turbine engines because of their ability to enable further increases in engine temperatures. However, the coating performance and durability become a major concern under the increasingly harsh thermal cycling conditions. Advanced zirconia- and hafnia-based cluster oxide thermal barrier coatings—having lower thermal conductivity and improved thermal stability—are being developed using a high-heat-flux laser-rig based test approach. Although the new composition coatings were not yet optimized for cyclic durability, an initial durability screening of numerous candidate coating materials was carried out using conventional furnace cyclic tests. In this paper, furnace thermal cyclic behavior of the advanced plasma-sprayed zirconia-yttria-based thermal barrier coatings that were co-doped with multi-component rare earth oxides was investigated at 1163 °C using 45 min hot cycles. The ceramic coating failure mechanisms were studied by using scanning electron microscopy combined with X-ray diffraction phase analysis after the furnace tests. The coating cyclic lifetime will be discussed in relation to coating phase structures, total dopant concentrations and other properties.

INTRODUCTION

Ceramic thermal barrier coatings (TBCs) have received increased attention for advanced gas turbine engine applications. The advantages of using TBCs include increased engine efficiency by allowing higher gas temperatures and improved reliability from lower component temperatures. Future TBC systems will be more aggressively designed for the thermal protection of engine hot section components, thus allowing significant increases in engine operating temperatures, fuel efficiency and reliability. However, the increases in engine temperature can raise considerable coating durability issues [1, 2]. The development of next generation lower thermal conductivity
and improved thermal stability TBCs thus becomes a necessity for advancing the ultra-efficient and low emission gas turbine engine technology.

Advanced ZrO₂-Y₂O₃ based thermal barrier coatings, that are co-doped with paired or multi-component rare earth oxides [3], are being developed using a high heat-flux laser-rig based approach at the NASA Glenn Research Center. These novel oxide coatings have been found to have significantly lower thermal conductivity and improved sintering resistance at high temperatures. The effects of the total dopant concentration on coating thermal conductivity and sintering have been evaluated using the laser high heat flux approach [4]. However, the thermal cyclic durability of the new coating systems is yet to be determined. This is because the coating development had initially emphasized compositional modifications to improve conductivity performance, while deferring cyclic life processing optimization to a later date. In fact, in an attempt to partially remove the confounding effects of sample-to-sample porosity variations, the coatings were generally intentionally processed so they were somewhat too dense for optimum cyclic life. Although these coatings were not optimized for cyclic durability in terms of the compositions and processing, the initial screening tests of the large number of coating systems using conventional furnace cyclic testing can still provide insights into the coating failure modes, and help to guide future coating design directions by using more sophisticated compositional modification and processing optimization approaches. The coating thermal conductivity and cyclic performance information will also be used to down-select coatings for comprehensive laser-simulated engine high-heat-flux thermal gradient cyclic testing at higher surface temperatures.

The purpose of this paper is to report the preliminary furnace cyclic performance of the advanced plasma-sprayed zirconia-yttria and multi-component rare earth oxide doped thermal barrier coatings as a function of the dopant concentration and processing variations. The ceramic coating failure mechanisms were investigated by using scanning electron microscopy (SEM) combined with X-ray diffraction phase analysis after the furnace cyclic tests. The coating cyclic lifetime will be discussed in relation to coating phase structures, total dopant concentrations and properties.

EXPERIMENTAL MATERIALS AND METHODS

Plasma-sprayed ZrO₂-Y₂O₃ based thermal barrier coatings that were co-doped with additional multiple rare earth (RE₂O₃) type dopants (oxide cluster coatings) were used for the furnace thermal cycling tests. These multi-component rare earth oxide coatings were found to have significantly lower thermal conductivities and better thermal stability as compared to the conventional ZrO₂-4.55mol%Y₂O₃ (4.55YSZ, or ZrO₂-8wt%Y₂O₃, conventionally known as 8YSZ) coating. Optimum thermal conductivity region was reported in the range of 6-13mol% total dopant concentrations, which was believed to be near the tetragonal/cubic phase boundary region of the zirconia alloys [4]. The coatings for the furnace cyclic study were the ZrO₂ based oxides, also stabilized with the primary yttria dopant and/or paired Group A (such as Nd₂O₃, Gd₂O₃, and Sm₂O₃) and Group B (such as Yb₂O₃, Sc₂O₃) rare earth oxide co-dopants [3, 4]. The total dopant concentrations for the coatings ranged from 4.5 to 52.5mol%.

The thermal barrier coating systems consisted of a 120 μm thick NiCoCrAlY or NiCrAlY bond coat and a 180–250 μm thick ceramic top coat which were plasma-sprayed on to the 25.4 mm diameter and 3.2 mm thick nickel base superalloy René N5 disk substrates. The bond coat was processed using the typical low-pressure-plasma-spray technique. The ceramic top coats with various designed compositions were air plasma-sprayed using pre-alloyed powders. The ceramic powders were first spray-dried, and then plasma-reacted and spheroidized (two passes) in order to
ensure the appropriate phase homogeneity and particle size distributions. Several batches of powders from different vendors were used in the tests. The plasma-spraying parameters and conditions for processing the oxide cluster top-coats were the same as those for the standard baseline 4.55YSZ coating. Some processing variations, including removing very fine particles (<37 \(\mu\text{m}\) in size), and plasma-spraying duplex layer ceramic coatings that consisted of a 50 \(\mu\text{m}\) first-layer 4.55YSZ near the bond coat interface and a regular thickness (180–250 \(\mu\text{m}\)) cluster oxide coating, were also used to investigate the effects of processing and coating structure on the cyclic lifetime.

Furnace cyclic tests were carried out at 1163 °C (2125 °F) using either a tube or a box furnace in air with 45 min hot time cycles. The cooling times were 15 minutes for the tube furnace test and 3 hours for the box furnace, and the specimens were cooled to ~120 °C after each cooling cycle. The specimens were inspected in 10 or 20 cycle intervals. The coating cycle lifetime was determined by the cycle numbers when the coating failure occurred, using a failure criterion of observed delamination or spallation region being equal or larger than 20% of the total coating area. The spalled coating specimens were examined using X-ray diffraction for phase analysis, and SEM for detailed failure morphology analysis.

RESULTS AND DISCUSSION

Furnace Cyclic Life

Figure 1 shows the furnace cyclic test results for the plasma-sprayed multi-component oxide cluster coatings, and the baseline 4.55YSZ and yttria-stabilized-zirconia (YSZ) binary coatings. The variation of coating cyclic lifetime from batch to batch is obvious. In addition, the cyclic life of the oxide coatings generally decreased with increasing total dopant concentration. The low yttria-dopant 4.55YSZ coating generally had good furnace cyclic durability. The multi-component cluster oxide coatings showed evidence to have better durability than yttria-doped zirconia binary coatings at given dopant concentrations, especially in the 6–13mol% higher dopant concentration range where the coatings have the optimum low thermal conductivity.

The batch 1 coatings had the shortest cyclic lifetime, ranging from 10 to 50 cycles for the cluster oxide coatings. The two baseline 4.55YSZ coating specimens in this batch failed at 60 and 110 cycles, respectively. The early failure of the coating systems was attributed to the dense top coat, and also probably the non-optimized NiCoCrAlY bond coat in this batch. Both factors can result in large thermal- and oxidation-induced stresses in the ceramic coating, thus significantly weakening the ceramic/bond coat interface region due to extensive cracking during thermal cycling.

The cyclic durability of the initial batch 1 oxide cluster coatings was considerably improved (life increased by 2–3 times) using some processing modifications. Less dense oxide cluster coatings were processed by removing the fine particles (with the particle sizes below the –325 mesh or 37 \(\mu\text{m}\)) from the plasma-spraying powders; improved interface adhesion and thermal shock resistance of the low conductivity oxide coatings were also attempted by adding a thin layer of 4.55YSZ coating (~50 \(\mu\text{m}\)) between the NiCoCrAlY bond coat and the cluster oxide top coatings. The two processing approaches demonstrated the effectiveness in improving the coating life for the present furnace cyclic tests.

The batch 2 and 3 coatings, which used more favorable spray particle size distributions and a NASA in-house NiCrAlY bond coat, showed better cyclic durability than the batch 1 coatings. As
can be seen from Fig. 1, even the single layered cluster oxide coatings generally achieved better cyclic life than the duplex 4.55YSZ+oxide cluster two-layered coatings in batch 1. The cyclic life improvement was more pronounced for the lower dopant (6mol% total dopant) concentration coatings. The oxide cluster coating life reached as high as 150 cycles for the 13.5mol% dopant coating, and 300 cycles for the 6mol% total dopant coating. The multi-component cluster oxide coatings showed a better cyclic life than the yttria-zirconia binary oxide coatings (solid squares) at the equivalent dopant concentrations.

The batch 4 coatings, which also used the NiCrAlY bond coat, showed excellent cyclic resistance probably due to more optimum coating processing conditions and resulting coating microstructures. It can be seen from Fig. 1 that, even for some medium high dopant concentration (13.5mol% and 15.8mol% total dopant) coatings, the coating cyclic life reached near 450–500 cycles. Under the same furnace cyclic tests, the baseline 4.55YSZ coatings (solid circles) in the batches 2 to 4 had the furnace cyclic life ranging from 140 to 420 cycles. The higher dopant yttria–zirconia binary coatings (ZrO2-10mol%Y2O3, ZrO2-12mol% Y2O3, and ZrO2-30mol%Y2O3 ) showed poor cyclic resistance. The life of these binary ZrO2-Y2O3 coatings seemed less dependent on the processing conditions. The failure morphologies and mechanisms for the coating will be further discussed later in this paper.

It should be mentioned that in this study, both tube furnace and box furnace tests generally showed good agreement in the coating life results. The slightly longer coating life observed in the box furnace tests may be due to the much slower cooling rate (3 hours cooling for box furnace and 15 minutes cooling for the tube furnace) which can reduce some of the thermal shock effect for the very low conductivity and slightly higher thermal expansion cluster oxide coatings. The thermal conductivity values and thermal expansion coefficients of the multi-component oxide cluster coating are listed in Table 1.

Table 1. Thermal conductivity values and thermal expansion coefficients of oxide cluster coatings

<table>
<thead>
<tr>
<th></th>
<th>Thermal conductivity (W/m-K)</th>
<th>Coefficient of thermal expansion (m/m-K)</th>
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<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>after 20 hours testing at 1316 °C</td>
</tr>
<tr>
<td>Baseline 4.55YSZ</td>
<td>1.0</td>
<td>1.3−1.5</td>
</tr>
<tr>
<td>Cluster oxide coating</td>
<td>0.5−0.7</td>
<td>0.6−1.1</td>
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The strong processing and composition dependence of the coating cyclic life observed in this study offers considerable challenges, but also great opportunities, for the development of the advanced, high performance thermal barrier coatings. The preliminary test data demonstrate the importance of the coating processing and composition optimizations. The beneficial effects of the added rare earth cluster oxides also showed great promise in significantly improving coating cyclic durability.

Failure Morphologies and Mechanisms

Figure 2 shows typical SEM micrographs of spalled coating surface morphologies and cross-sections for several coating systems after the furnace cyclic testing. It can be seen that the oxide coatings generally failed in a mixed mode, i.e., the coatings were spalled under thermal cycling by a combined mechanism where the coating delaminations occurred within the ceramic top coat near the ceramic/metal bond coat interface (ceramic failure), and through the thermally grown alumina scales at the interface (oxide scale failure). The oxide scale related failure was generally involved
with the separation of the ceramic/alumina scale interface, as well as the cracking/delamination within the oxide scales. However, the failure was also sometimes observed to occur at the scale/bond coat interface where the bare metal surface was exposed after the coating spallation.

Fig. 1  Furnace cyclic test results showing the coating cycles to failure as a function of total dopant concentration for plasma-sprayed advanced cluster oxide coatings, containing \( \text{ZrO}_2-\text{Y}_2\text{O}_3 \) and the paired \( \text{Nd}_2\text{O}_3(\text{Gd}_2\text{O}_3,\text{Sm}_2\text{O}_3)-\text{Yb}_2\text{O}_3(\text{Sc}_2\text{O}_3) \) co-dopants, processed in various batches. As a comparison, the cyclic performance of the baseline 4.55YSZ and other \( \text{ZrO}_2-\text{Y}_2\text{O}_3 \) binary coatings that are processed under the same conditions, is also plotted. The coating cyclic life generally decreases with increasing total dopant concentration. The multi-component rare earth cluster oxide coatings showed evidence to have better cyclic durability than yttria-zirconia binary coatings at given dopant concentrations. The strong processing and composition dependence of the coating cyclic life demonstrates the importance of coating processing and composition optimizations.

For those ceramic coatings thermally sprayed using more optimized processing to control coating porosity, longer cyclic life was often observed. This is because the properly processed ceramic coatings possessed a more optimum porosity, which can have a more elastically compliant microstructure but still retain adequate coating strength. The coatings can thus have reduced thermal cyclic stresses, originating either from the thermal expansion mismatch between the ceramic and metal substrate or from the bond coat oxidation during the cycling, without significantly deteriorating the coating mechanical properties. In addition to the coating processing effect, the relatively low yttrium dopant 4.55YSZ coating and certain multi-component cluster dopant coatings exhibited excellent thermal cycling resistance, implying also a strong compositional effect on coating cyclic performance. Since the high cyclic stress region is primarily located near the ceramic/bond coat interface (the observed ceramic failure is usually within about 10–20 \( \mu \text{m} \) above the interface), applying a thin layer of a more cyclic resistant coating such as
4.55YSZ to the interface and forming a duplex coating system would greatly improve the overall coatings furnace cycling performance.

The longer-life coatings, due to either from improved processing or modified multi-component rare earth dopant compositions, typically showed a more predominant interface scale failure, as indicated by the increasing area fraction of the interface scale failure region after furnace cyclic testing. Low magnification SEM images of the spalled surface morphologies for two distinctively different performance coatings, i.e., a low toughness, poor cyclic resistance $\text{ZrO}_2$-30mol%$\text{Y}_2\text{O}_3$ (cyclic life 10–20 cycles), and a long cyclic life $\text{ZrO}_2$-13.5mol% (Y,Gd,Yb)$_2\text{O}_3$ coating (cyclic life 430 cycles), are shown in Fig. 3 to illustrate the failure mechanisms.
Fig. 2 SEM images of the spalled coating surface morphologies and cross-sections showing a mixed failure mode involving both the ceramic failure and scale interface failure after furnace thermal cyclic testing. (a) 4.55YSZ; (b) ZrO$_2$-30mol\%Y$_2$O$_3$; (c) ZrO$_2$-6mol\%(Y,Nd,Yb,Sc)$_2$O$_3$; (d) ZrO$_2$-16mol\%(Y,Sm,Yb)$_2$O$_3$; (e) Cross-section of 4.55YSZ; (f) Cross-section of ZrO$_2$-6mol\% (Y,Gd,Yb)$_2$O$_3$.

Fig. 3 SEM micrographs showing the spalled thermal barrier coatings on the substrates after the furnace thermal cyclic testing (dark and bright regions are exposed alumina scales, and the remaining attached ceramic top coats, respectively). (a) Low toughness ZrO$_2$-30mol\%Y$_2$O$_3$, cyclic life 20 cycles, showing the predominant ceramic failure; (b) ZrO$_2$-13.5mol\% (Y,Nd,Yb)$_2$O$_3$ coating, cyclic life 430 cycles, showing a more predominant interface scale failure.
As previously mentioned, the coatings with lower dopant concentrations generally exhibited a better cyclic resistance, suggesting a possibly more toughened phase structure in the lower concentration region. The X-ray diffraction results in Fig. 4 shows the phase structure changes as a function of the dopant concentration for several oxide thermal barrier coatings. It can be seen that the ZrO$_2$-4.55mol%Y$_2$O$_3$ (4.55YSZ) and ZrO$_2$-6mol%(Y,RE)$_2$O$_3$ (6(YNdYb)SZ and 6(YNdSc)SZ) possessed the predominant tetragonal phase structure. The ZrO$_2$-10mol%(Y,RE)$_2$O$_3$ dopant coatings (10YSZ and 10(YNdYb)SZ) had mostly the cubic structure, because the tetragonal peak split of t(400) and t(004) observed for lower concentration coatings started to disappear in this composition. The higher dopant concentration coatings, such as ZrO$_2$-16mol%(Y, Re)$_2$O$_3$ and ZrO$_2$-30mol%Y$_2$O$_3$ (16(YNdYb)SZ and 30YSZ), had a fully cubic phase structure. The fact that the coating cyclic life typically decreases with dopant concentration may suggest that the tetragonal phase has a better cyclic resistance and thus possibly higher fracture toughness; and the observed coating life decreases, corresponding to the tetragonal phase fraction decrease, with increasing the dopant concentrations.

The better thermal cyclic resistance (thus the expected higher fracture toughness) of the tetragonal phase structure, as compared to the cubic phase structure, may be attributed to its long-term small grain structure and even further continuous grain size refinement due to the progressive phase transformations (tetragonal to monoclinic and/or tetragonal to monoclinic+cubic) during the thermal cycling. The refined grain sizes of the tetragonal phase can enhance the coating crack healing, which would improve the coating toughness. The martensitic phase transformation of the tetragonal phase to monoclinic phase, even at small volume fractions, may significantly toughen the ceramic coatings during the thermal cycling, because of the crack arrest by the formation of the monoclinic phase. The martensitic phase transformation accompanying a favorable micro-crack network produced in the coating, may also contribute to the overall coating toughening [5].
Fig. 5 shows the microstructure of several coating systems after furnace cyclic testing. As can be seen from Fig. 5(a), the 4.55YSZ coating containing the partially stabilized tetragonal phase, still maintained relatively small grain sizes after the extended high temperature thermal cycling testing (160 cycles). The coating also failed by a tougher mechanism, which involved the severe scale interface delamination and non-brittle type ceramic coating fracture, showing evidence of certain coating deformations. However, as shown in Figs. 5(b) and 5(c), the higher yttria dopant content binary alloy, ZrO$_2$-10mol%Y$_2$O$_3$ and ZrO$_2$-30mol%Y$_2$O$_3$ coatings that possessed the cubic phase structure, experienced significant grain growth, and thus resulting in very low toughness structures. Brittle coating fracture was observed in these extensive grain growth regions after very short thermal cycles (10–30 hours).

The oxide cluster coatings showed a different grain growth behavior as compared to the binary coatings under the thermal cyclic condition. As can be seen in Fig. 5 (d) and (e) of the spalled coating interface regions of the ZrO$_2$-6mol%(Y,Nd,Yb,Sc)$_2$O$_3$ (failed at 140 cycles) and ZrO$_2$-16mol%(Y,Sm,Yb)$_2$O$_3$ (failed at 470 cycles), extremely fine grains were observed after the long-term cyclic tests. It should be mentioned that the ZrO$_2$-6mol%(Y,Nd,Yb,Sc)$_2$O$_3$ and ZrO$_2$-16mol%(Y,Sm,Yb)$_2$O$_3$ coatings had a partially stabilized tetragonal structure and a fully stabilized cubic structure, respectively. The cluster dopant coatings had little grain growth even for a high dopant concentration cubic phase system.

The observed grain growth as a function of the dopant concentration for the ZrO$_2$-Y$_2$O$_3$ binary and multi-component cluster oxide coatings is plotted in Fig. 6. The data show the grain growth generally increases with increasing the total dopant concentrations. Significant grain growth (up to 2–5µm in size) was observed for the higher yttria concentration, cubic phase structured zirconia coatings after furnace cyclic testing. However, the multi-component cluster oxide coatings showed much smaller grain sizes (typically less than 1 µm) at given dopant concentrations. This experimental evidence strongly suggests the added rare earth dopants to the ZrO$_2$-Y$_2$O$_3$ binary coating systems can significantly suppress the grain growth at high temperatures, and thus potentially can greatly improve the coating toughness and thermal cycling resistance.

Fig. 7 is a high resolution SEM image of a cross-section from a plasma-sprayed 4.55YSZ coating, showing further grain refinements and toughening by a small amount of monoclinic phase transformations (tetragonal to monoclinic and/or tetragonal to monoclinic+cubic) during the thermal cyclic testing. The grain refinements and phase transformation toughening can greatly contribute to the good cyclic life performance of the 4.55YSZ and other lower dopant coatings containing some transformable tetragonal phase. The monoclinic phase content of the plasma-sprayed 4.55YSZ coating as a function of cycle time at 1163 ºC, derived from the X-ray diffraction analysis and using the approach described in literature [6], is shown in Fig. 8. It can be seen that the monoclinic phase progressively increases with the cycle time which can help to continuously toughen the coating structure and thus provide the excellent cyclic performance.

The test results demonstrate that the design of optimum composition and micro-structured thermal barrier coatings can lead to excellent cyclic performance. The ceramic coatings using improved cluster oxide compositions can achieve a better toughness and cyclic life, even in a composition region which contains a fully cubic phase because of their ability to maintain long-term fine grain structures and sintering resistance due to the formation of low mobility oxide defect clusters [4]. Because the tetragonal to monoclinic phase transformation can further refine the grain structures and toughen the coating systems, by utilizing compositional and structural heterogeneity design approaches, a small amount of tetragonal phase transformation can be incorporated into the coating systems during thermal cycling which can significantly improve the coating delamination and spallation resistance.
Fig. 5 Scanning electron micrographs showing the ceramic coating spalling/fracture morphologies near the ceramic/bond coat interface region after furnace thermal cyclic testing. (a) 4.55YSZ, 160 cycles; (b) ZrO₂-10mol%Y₂O₃, 30 cycles; (c) ZrO₂-30mol%Y₂O₃, 10 cycles; (d) ZrO₂-6mol%(Y,Nd,Yb,Sc)₂O₃, 140 cycles; (e) ZrO₂-16mol%(Y,Sm,Yb)₂O₃, 470 cycles.
Fig. 6  Ceramic coating grain growth after the furnace cyclic testing for the multi-component cluster oxide coating systems and the yttria-zirconia binary coating systems. The shadowed areas in the plot show the approximate grain size distribution bands observed in many noticeable coating grain growth regions.

Fig. 7  High resolution scanning electron micrograph showing the overall fine grain structures of ZrO$_2$-4.55mol%Y$_2$O$_3$. Further grain refinements and toughening by a small amount of monoclinic phase transformations (tetragonal to monoclinic and/or tetragonal to monoclinic+cubic) during the thermal cyclic testing can contribute to the excellent cyclic life performance of the 4.55YSZ and other lower dopant coatings containing some transformable tetragonal phase. The arrows in this micrograph indicate the possible crack arrests and the ceramic toughening by the formation of the monoclinic phase (seen as rippled needle-like structure).
Fig. 8 The monoclinic phase content of the plasma-sprayed 4.55YSZ coating as a function of cycle time at 1163 °C, derived from the X-ray diffraction analysis. Insert is the X-ray diffraction patterns for 4.55YSZ coating specimens under conditions of as-processed, and after testing for 50 and 100 cycles at 1163 °C in a tube furnace, respectively, showing the monoclinic phase increases progressively with the cycle time.

CONCLUDING REMARKS

The durability of plasma-sprayed ZrO$_2$-Y$_2$O$_3$ binary coatings and advanced low conductivity multi-component cluster oxide coatings was evaluated using conventional cyclic furnace tests at 1163 °C. The results have shown that the cluster oxide coatings have the potential to achieve significantly better cyclic performance than the binary ZrO$_2$-Y$_2$O$_3$ coatings because of their improved high temperature stability, reduced grain growth, and thus increased toughness structures.

The ceramic coating cyclic life generally decreases as the dopant concentration increases presumably due to the reduced fraction of tetragonal phase and the increased fraction of the cubic phase. The cubic phase usually shows an enhanced grain growth behavior, and also lacks the further grain-refining and toughening mechanisms by the tetragonal to monoclinic phase transformation present in a partially stabilized tetragonal phase. Therefore, very low toughness coating structures were often observed in high-dopant-concentration coatings, and especially for the ZrO$_2$-Y$_2$O$_3$ binary coatings.

Although the advanced cluster oxide coatings followed a similar trend as the ZrO$_2$-Y$_2$O$_3$ binary coating systems in the furnace cyclic behavior (where the coating cyclic life decreases with
increasing the total dopant concentration), the cluster oxide coatings showed promise for achieving better cyclic life than the binary ZrO$_2$-Y$_2$O$_3$ coatings with equivalent dopant concentrations. Cyclic life comparable to (or better than) that of the low dopant 4.55YSZ coating has been observed for some intermediate-dopant-concentration, low-conductivity coating systems. Advanced processing and composition optimization will be used to further improve the durability of the high performance ceramic thermal barrier coating systems.

REFERENCES

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