Reaction, transformation and delamination of samarium zirconate thermal barrier coatings

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The rare earth zirconates have attracted interest for thermal barrier coatings (TBCs) because they have very low intrinsic thermal conductivities, are stable above 1200 °C and are more resistant to sintering than yttria-stabilized zirconia (YSZ). Samarium zirconate (SZO) has the lowest thermal conductivity of the rare earth zirconates and its pyrochlore structure is stable to 2200 °C but little is known about its response to thermal cycling. Here, columnar morphology SZO coatings have been deposited on bond coated superalloy substrates using a directed vapor deposition method that facilitated the incorporation of pore volume fractions of 25 to 45%. The as-deposited coatings had a fluorite structure which transformed to the pyrochlore phase upon thermal cycling between 100 and 1100 °C. This cycling eventually led to delamination of the coatings, with failure occurring at the interface between the TGO and a “mixed zone” that formed between the thermally grown alumina oxide (TGO) and the SZO. While the delamination lifetime increased with coating porosity (reduction in coating modulus), it was significantly less than that of similar YSZ coatings applied to the same substrates. The reduced life resulted from a reaction between the rare earth zirconate and the alumina-rich bond coat TGO, leading to the formation of a mixed zone consisting of SZO and SmAlO3. Thermal strain energy calculations show that the delamination driving force increases with TGO and mixed layer thicknesses and with coating modulus. The placement of a 10 μm thick YSZ layer between the TGO and SZO layers eliminated the mixed zone and restored the thermal cyclic life to that of YSZ structures.

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1. Introduction

Thermal barrier coating (TBC) systems are an enabling materials technology for the gas turbine engines used in modern aerospace applications [1]. Current TBC systems consist of a 100–300 μm thick thermally protective ceramic layer, a much thinner (up to 5–10 μm thick) thermally grown oxide (TGO) that protects superalloy turbine airfoils against rapid oxidation, and a relatively thick (50–100 μm) metallic “bond coat” applied to the turbine airfoil alloy to slow the kinetics of oxidation and promote TGO adherence. The bond coat has a high aluminum concentration to promote slow (parabolic) growth of a protective alumina-rich TGO layer [2,3]. The thermal protection part of the coating system traditionally consisted of 7 wt.% yttria stabilized zirconia (7YSZ) which has a desirable combination of low thermal conductivity ($-2.1 \text{ W m}^{-1} \text{ K}^{-1}$ at $1000 \leq T \leq 1200 \text{ °C}$ [4,5]), excellent thermochemical compatibility with the TGO layer [6,7], and good durability to thermal cycling [8] because of its high and well-matched thermal expansion coefficient and low in-plane elastic stiffness (especially when through thickness voids are incorporated in the coating). This material is relatively easily applied by a variety of thermal spray [1] and physical vapor deposition methods [9].

As the temperature within gas turbine engines increases, the continued use of 7YSZ has become problematic. The primary concerns arise from: (i) accelerated sintering kinetics of porous 7YSZ (which decreases the pore content of the TBC and thus its in-plane compliance and thermal resistance) [9–12]; (ii) de-stabilization of the desirable non-transformable $t$-phase [6,13–16] that is responsible for the intrinsic toughness of 7YSZ [17,18]; and (iii) an increased propensity for penetration of the coating by molten deposits of calcium-magnesium-alumino-silicates (CMAS) which dissolve the coating and accelerate YSZ destabilization. Upon solidification, these deposits degrade the strain tolerance of the coating and lead to premature failure [19–21]. These concerns, coupled with the potential design benefits of further reductions of the thermal conductivity relative to 7YSZ [22–24], have motivated a far-reaching search for alternate thermal barrier oxides [6,25–27].

The equiatomic rare earth zirconates (REZ’s) $M_2Zr_2O_7$ ($M=\text{La} \rightarrow \text{Gd}$), with an ordered pyrochlore structure, have attracted significant attention because of their lower thermal conductivity ($-1.2–1.6 \text{ W m}^{-1} \text{ K}^{-1}$ at $1000 \leq T \leq 1200 \text{ °C}$ [23,28–31]). In addition, these materials are phase-
stable at temperatures relevant to future gas turbine operation (turbine inlet temperatures, \(T \leq 1500\ °C\)) [32]. They also appear more resistant to morphological evolution of the pore structure (sintering) than 7YSZ [31,33,34]; furthermore, one of the rare earth zirconates (\(Gd_2Zr_2O_7\)) has shown potential for inhibiting CMAS penetration by inducing crystallization of the melt [35]. However, the REZ’s suffer two fundamental disadvantages relative to 7YSZ. Firstly, \(Gd_2Zr_2O_7\) is susceptible to reaction with the alumina TGO [6,36], resulting in the formation of aluminate interphases by diffusional reactions [37,38]. The other REZ’s are also predicted to be susceptible to similar reactions with alumina TGOs. Secondly, as with the cubic \(ZrO_2\)-based phases, the REZ’s exhibit a substantially lower toughness than the tetragonal \(t’\) phase of 7YSZ [2,17,39,40]. This has deleterious consequences for both their erosion resistance and other failure mechanisms that involve crack propagation through the TBC [2,41]. To alleviate the aluminate reaction problem, gadolinium zirconate TBCs are typically deposited on a TGO-compatible 7YSZ underlayer [6,23,37,42]. However, little is known about the factors governing the delamination resistance of these bi-layer coatings upon thermal cycling at temperatures of relevance in gas turbine engines.

Samarium zirconate, \(Sm_2Zr_2O_7\) (SZO), coatings have recently been deposited on MCrAlY bond coated Hastelloy-X substrates using a directed vapor deposition (DVD) method [34]. By varying the deposition temperature and rotation conditions, it was possible to vary the pore volume fraction in the SZO coating from 20 to 45%. The lowest density coatings had a very low thermal conductivity (0.5 W/mK), resulting from the low intrinsic solid material’s conductivity and the high void volume fraction. Inasmuch as the elastic modulus decreases with increasing pore fraction [43], these columnar coatings also have low in-plane elastic stiffness and might be anticipated to have good thermal delamination resistance.

Here, we deposit a series of SZO coatings with widely varying pore volume fractions upon the same bond coat substrate system used for an earlier study of thermocyclic delamination of 7YSZ coatings [43]. We then investigate its response to thermal cycling, and identify the mechanism of failure and its relationship to the thermochemical stability of the SZO-TGO interface. An aluminate phase is indeed formed at this interface, and an elastic thermal strain analysis of the multilayer system shows a significant delamination driving force at both the TGO-mixed zone and mixed zone-SZO interfaces, which results in a shortened thermocyclic lifetime. We then show that a 7YSZ/SZO bi-layer TBC system can restore the cyclic life (and return the failure mode) to that of the 7YSZ system, and examine the factors that govern the stored strain energy that drives eventual failure at the bond coat/TGO interface.

2. Experimental methods

The SZO coatings were grown by the DVD method using a deposition temperature of 1000 °C at various substrate rotation rates [44,45]. A detailed description of the fabrication is presented elsewhere [45]. Bi-layer (7YSZ/SZO) coatings were also deposited using the same technique. In the bi-layer case a two-source-rod crucible that held 12.7 mm diameter 7YSZ and SZO rods was used, Fig. 1. The substrates were heated to 1000 °C, and a 10 \(\mu\)m thick 7YSZ coating was deposited. This was then followed by deposition of an 80 \(\mu\)m thick SZO layer by translating the electron beam to the second source rod without cooling or breaking the vacuum system. The substrates were rotated at 6 rpm during both of these depositions.

A 10:1 helium/oxygen mixture was used to form a transonic gas jet which entrained and directed the vapor to the substrates. The jet was created by gas expansion through a nozzle using an upstream pressure of 140 Pa and a downstream (chamber) pressure of 16 Pa. These process conditions resulted in a deposition rate of 4 ± 1 \(\mu\)m/min for both 7YSZ and SZO. The SZO and 7YSZ/SZO coated samples were then thermally cycled between ambient and 1100 °C under identical conditions to those used for a study of the thermocyclic response of 7YSZ coatings grown by a similar method on the identical bond coat/substrate system [43]. The coatings were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis and transmission electron microscopy (TEM).

![Fig. 1. The vapor deposition approach used to deposit yttria stabilized zirconia and samarium zirconate coatings. The coatings were deposited on 25.4 mm diameter, 3.2 mm thick Hastelloy-X substrate with a smooth (polished) NiCoCrAlY bond coat at a temperature of 1000 °C.](image-url)
The TEM cross section samples were prepared by a “lift-out” technique using a FEI Quanta 3D dual-beam SEM/FIB microscope [46]. A 20 μm × 10 μm, 1.5 μm thick slice was prepared that included the bond coat and SZO layer using the focused ion beam (FIB). This was lifted out and placed on a 3 mm copper grid. Further thinning of the sample was then performed with the sample on the grid (using a modest ion beam current to minimize FIB damage) until the specimen was electron transparent. This corresponded to a final foil thickness of 110–130 nm.

The TEM samples were examined in a Zeiss Libra 200 keV FEG transmission electron microscope with an in-column “omega” filter. The microscope is equipped with a STEM detector and a Thermo Noran XEDS system running Noran System Seven (NSS) software. The analyzer on this XEDS system is capable of handling quite high X-ray counts, making the instrument suitable for elemental mapping in reasonable times. The mapping was performed using a 37 μm condenser aperture with a spot size of 10 nm for 15 min. The instruments drift compensator was activated to compensate for possible drift during X-ray data acquisition.

3. Thermally cycled SZO coatings

The as-deposited SZO coatings had a columnar structure with faceted column tips, Fig. 2(a). The tips had a well-defined 4-sided pyramidal shape typical of vapor-deposited fluorite-derivative structures. A detailed analysis of the columnar structure has been described in an earlier paper [45]. The coatings exhibited a compositional variation across the thickness of up to ±12% SmO1.5, resulting from the difference in vapor pressure of the constituent oxides and their scattering rates in the vapor phase. Sm2O3 was most highly enriched near the first deposited SZO due to its much higher vapor pressure at typical melt temperatures. A ~0.4 μm thick TGO layer, Fig. 2(d), was formed as the samples were heated prior to and during deposition.

The SZO coated test coupons were thermally cycled to 1100 °C in air (with a 1 h hold at peak temperature), and their microstructural changes examined. Representative micrographs of their outer surfaces and cross-sections are shown in Fig. 2. After 50 thermal cycles, the sharp edges of the column tips and growth steps on the facets had become

![Fig. 2. The surface (a) and cross-section (d) of the as deposited SZO coating. (b) and (e), (c) and (f) show the coating after 50 and 300 cycles, respectively. The delamination occurs at the SZO/TGO interface for the spalled samples. The coatings were thermally cycled between 1100 °C and ambient temperature.](image-url)
rounded, Fig. 2(b), indicative of appreciable surface diffusion. Increasing the number of thermal cycles to 300, Fig. 2(c), caused more substantial surface reconstruction.

Examination of cross-section views Fig. 2(d)–(f) shows a rapid increase in TGO thickness with thermal exposure, as expected. The thin (~0.4 μm thick) TGO layer formed during deposition of the SZO layer increased with high temperature exposure time and Y-Al oxide “pegs” developed in the TGO and protruded into the bond coat, Fig. 2(e) and (f). At ~300 cycles, the TGO thickness had increased to ~4 μm and the coating spalled at the SZO/TGO interface. Close examination of Fig. 2(e) and (f), reveals the presence of a ~0.4 μm thick mixed zone above the TGO layer in both thermally cycled samples. In Fig. 2(f) major failure at the mixed zone-TG interface can be observed. It appears that the factors governing delamination (strain energy release rates and interface toughness’s) are similar for the two interfaces and the eventual failure path jumps between them.

A sample that had been exposed to ~300 thermal cycles with the SZO coating partially attached was examined by XRD. The result in Fig. 3(a) corresponds to diffraction from the top surface of the SZO layer. Compared to the equivalent XRD pattern of the as-deposited coating, which corresponded to diffraction from a “disordered” cubic fluorite structure, small additional peaks are present in the thermally cycled coating. These peaks have been indexed and arise from the ordered pyrochlore structure. This indicates that the fluorite structure of as-deposited SZO coating had transformed from fluorite to the ordered pyrochlore structure after exposure to high temperature for 300 h.

The diffraction pattern from the TGO side of the substrate exposed by the delamination for this sample is shown in Fig. 3(b). Fig. 2(f) suggests this pattern is from the “mixed” zone. Diffraction peaks from the SZO coating are present in the pattern, which indicates that in some regions the SZO coating remained attached to the TGO after coating delamination. The distinct peaks (the solid circles) for the pyrochlore SZO phase are evident in the pattern. In addition to the peaks from the SZO phase, new peaks have appeared in the XRD data. Most of them are consistent with SmAlO3 reflections, which imply that SZO and Al2O3 have reacted to form this new phase.

STEM images of the delamination region of a thermally cycled SZO sample are shown in Fig. 4(a). It can be seen that in this region of the sample, the crack propagated at the interface of the mixed zone and the alumina rich TGO. Elemental mapping was performed on the corresponding region, Fig. 4(b) and (c). The TGO layer beneath the crack is Al-rich, while the mixed zone contains Al, Sm and Zr. Fig. 4(b) shows that Sm had diffused into the TGO layer and reacted with alumina to form samarium aluminate.

A TEM image of a thermally cycled SZO sample is shown in Fig. 5(a). The polycrystalline electron diffraction pattern was obtained in the mixed zone, Fig. 5(b), and was indexed as shown in Table 1, indicating...
that these rings originate from the SZO coating and the reaction product, SmAlO3.

The dependence of the cyclic lifetime upon rotation rate for the SZO coatings is shown in Fig. 6(a). Like 7YSZ coatings applied to the identical bond coat, the SZO coating delamination life decreases with the rotation rate used to deposit the coating (from ~350 to ~150 cycles). The growth in TGO thickness with thermal exposure time (number of 1-h holds at 1100 °C) is shown in Fig. 6(b). The data have been fitted to a parabolic TGO growth law: 
\[
(x - x_0)^2 = k_p t
\]
where \(x_0\) is the 'as-deposited' TGO thickness, \(x\) the thickness after accumulating a time \(t\) at 1100 °C. The best fit to the parabolic rate constant, \(k_p\), was 0.035 μm²/h.

In order to compare the response of the SZO coatings with that of 7YSZ coatings deposited on the same bond coat/substrate system under the same deposition conditions, the TGO thickness versus number of thermal cycles has been plotted for both coatings in Fig. 7(a). The SZO coatings have a higher TGO growth rate than YSZ whose parabolic constant was 0.014 μm²/h; less than a half that of the SZO system. YSZ coatings also had much longer thermocyclic lifetimes than SZO coatings, Fig. 7(b). Since increases in rotation rate increase the density of the SZO and YSZ coatings, the lifetime of both coatings decreased as the coating density was increased.

4. SZO coating failure mechanism

The SZO coatings on NiCoCrAlY bond coats clearly have very short cyclic lifetimes, as much as a factor of four less than identically deposited YSZ coatings on the same bond coats [43]. The bond coat surface condition initially governs the spallation failure mechanism. Rough (grit blasted) bond coats of the composition used here are susceptible to a "rumpling" failure mechanism with delamination occurring at the TGO-YSZ interface [43]. For the smooth bond coats used here, rumpling was suppressed and failure occurred at the bond coat-TGO interface underneath a YSZ coating. Failure was initiated at small cracks at local TGO thickness heterogeneities. Complete delamination finally occurred at the bond coat/TGO interface when the strain energy release rate was greater than the toughness of bond coat/TGO interface.

Several experiments have shown that rare earth zirconates react with alumina in the TGO layer. Leckie et al. found that Gd2O3 reacts with Al2O3 when exposed at high temperature [37]. In their case, GdAlO3 appeared to greatly lower the interface toughness of the TBC/TGO. It was thus anticipated that SmO1.5 would react with Al2O3 to form SmAlO3;

![Fig. 5.](image)

![Fig. 6.](image)

**Table 1**

<table>
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<tr>
<th>Ring</th>
<th>d(Å)</th>
<th>Diffraction planes</th>
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<tbody>
<tr>
<td>1</td>
<td>3.35</td>
<td>(111) SmAlO3</td>
</tr>
<tr>
<td>2</td>
<td>3.05</td>
<td>(222) SZO</td>
</tr>
<tr>
<td>3</td>
<td>2.69</td>
<td>(200) SmAlO3/(400)SZO</td>
</tr>
<tr>
<td>4</td>
<td>2.17</td>
<td>(202) SmAlO3</td>
</tr>
<tr>
<td>5</td>
<td>2.05</td>
<td>(511) SZO</td>
</tr>
<tr>
<td>6</td>
<td>1.87</td>
<td>(440) SZO</td>
</tr>
</tbody>
</table>
The thermo-mechanical properties of the mixed layer can be estimated by taking an average of the values of these two compounds. These and the properties of the other layers are summarized in Table 2, and an energy release rate calculation performed for the system, Fig. 8(b). The mixed layer has a very high modulus compared to the SZO and significant misfit strains with the substrate, which implies significant stored elastic energy in this layer when it is adhered to the substrate. When debonding occurs at the TGO/mixed layer interface, the significant stored elastic energy in the mixed layer is released. This is completely analogous to the role of the TGO in YSZ systems.

Fig. 8(b) shows the energy release rates for various interfaces in the system as a function of either TGO or mixed layer thickness. Results are shown for three debonding scenarios and three values of SZO modulus, spanning the range of the experiments. The dashed lines correspond to debonding beneath the TGO, without a mixed layer present; hence the abscissa in this case is the TGO thickness. The solid lines correspond to debonding at the TGO/mixed layer interface; the abscissa in this case is the mixed layer thickness. The dot-dashed lines represent the energy release rate for just the SZO layer. The third scenario neglects the presence of the mixed layer and predicts the driving force for a delamination crack between the TGO and SZO. Since strain energy is only released in the SZO, this driving force is equivalent to that of SZO debonding from a mixed layer that stays attached to the substrate (provided the mixed zone has not significantly altered the total thickness of the SZO).

In all debonding scenarios, the energy release rate increases with increasing SZO modulus. For example, the SZO layers with lowest modulus (highest pore volume fractions) have the lowest elastic strain energy when released by a crack at the bond coat/TGO interface (brown dotted lines). Lower values of SZO modulus imply less strain energy in the adhered state, and consequently less strain released by cracking, and lower energy release rates.

Broadly speaking, the energy release rate will scale with the thickness of any highly stressed layer that is released by cracking. For example, when debonding occurs at the bond coat/TGO interface (dashed lines in Fig. 8b), the energy release rate scales with the TGO thickness, as debonding relieves the high TGO stresses present in the adhered state. When debonding occurs just beneath the SZO layer (dot-dashed lines in Fig. 8b), the energy release rate for debonding is constant with respect to oxide layer thickness (or mixed layer thickness) because the highly stressed layers remain adhered during debonding, and hence, do not release additional strain energy. In Fig. 2(f), the debonding occurred at the interface of the TGO with the mixed layer, the high stresses in this layer in the adhered state being relieved by debonding. The energy release rate for debonding at the TGO/mixed layer interface is roughly equal to the average of the other two cases (underneath the TGO and above the mixed layer), because the properties of the mixed layer are roughly equal to the average of the TGO and SZO. That is, the energy release rate is highest for the interface
underneath the TGO because the misfit strains are greatest in the TGO; the energy release rate for the interface under the mixed layer is smaller, because the misfit strains for the mixed layer are smaller than those of the TGO.

The experimental results show that as the TGO and mixed zone thicknesses increase, debond failure occurred at a combined thickness of just under 5 μm, with a mixed layer thickness of about 0.8 μm. The micrographs in Figs. 2, 4 and 5 suggest that the crack path alternates between the TGO/mixed layer interface, and the mixed layer/SZO interface. This observation, when coupled with the predictions in Fig. 8, implies that the interface toughness of these two interfaces is similar and much lower than that of the bond coat/TGO. For example, for a mixed layer thickness of 1 μm, the driving force at the mixed layer/SZO interface is inferred to be ~65–90 J/m² (noting that the TGO/SZO prediction depends only on the SZO thickness, and hence, is the same as that of the mixed layer/SZO interface), while that at the TGO/mixed layer interface is ~70–100 J/m². The fact that the driving forces are close to one another (and possibly overlap, depending on local values of modulus and mixed layer thickness) supports the observation that the crack is likely to oscillate between these two interfaces.

Table 2

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>Modulus (GPa)</th>
<th>Poisson's ratio</th>
<th>CTE (ppm/°C)</th>
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<tr>
<td>Substrate</td>
<td>5000</td>
<td>200</td>
<td>0.3</td>
</tr>
<tr>
<td>Bond coat</td>
<td>175</td>
<td>90</td>
<td>0.3</td>
</tr>
<tr>
<td>TGO</td>
<td>Variable</td>
<td>380</td>
<td>0.2</td>
</tr>
<tr>
<td>Mixed layer</td>
<td>Variable</td>
<td>200</td>
<td>0.2</td>
</tr>
<tr>
<td>SZO</td>
<td>90-mixed thick</td>
<td>30, 36, 42</td>
<td>0.2</td>
</tr>
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</table>

5. Thermally cycled 7YSZ/SZO bi-layer

5.1. As-deposited bi-layer

The microstructure of an as-deposited bi-layer coating is shown in Fig. 9. The individual SZO and 7YSZ layers are apparent. The surface morphology was typical of SZO coatings deposited on polished NiCoCrAlY bond coats [45]. The thickness of the samarium zirconate was ~80 μm, while the 7YSZ was ~10 μm thick. A thin, ~0.3 μm, layer of TGO had formed at the 7YSZ/bond coat interface during deposition.

A polished cross section of the 7YSZ/SZO bi-layer is shown in Fig. 10. The transition from 7YSZ to SZO occurred with little disruption of the feathery columnar structure. The continuity of the pre-existing 7YSZ columnar growth pattern in the subsequent SZO coating is apparent at all relevant length scales, from the intercolumnar gaps to the intracolumnar feathers shown in Fig. 10, indicating that the as-deposited 7YSZ/SZO interface is inferred to be ~65–90 J/m² (noting that the TGO/SZO prediction depends only on the SZO thickness, and hence, is the same as that of the mixed layer/SZO interface), while that at the TGO/mixed layer interface is ~70–100 J/m². The fact that the driving forces are close to one another (and possibly overlap, depending on local values of modulus and mixed layer thickness) supports the observation that the crack is likely to oscillate between these two interfaces.
The bi-layer coating retained a strain-tolerant inter-columnar void structure. The relatively small lattice misfit between\textsuperscript{t}-YSZ ($a=0.5111$ nm and $c=0.5169$ nm) \[49\] and the as-deposited cubic fluorite SZO ($a=0.5295$ nm)\[50\] may have contributed to this continuous growth morphology into the SZO layer.

We have measured the chemical composition at five positions along lines parallel to the SZO/7YSZ interface. The line in the 7YSZ layer was ~0.5 μm from the interface while that in the SZO was 0.7 μm from the interface. The average of the five composition measurements along each line is shown in Table 3. It is evident that Sm is present in the YSZ coating but Y is not detectable in the SZO coating, indicating Sm diffusion into the YSZ coating during deposition, probably along the intercolumnar gaps. However, Sm signals are not detected close to the 7YSZ/TGO interface, indicating that this 7YSZ layer acted as a diffusion barrier.

5.2. 50 cycle response

After the bi-layer was thermally cycled between 1100 °C and ambient temperature for 50 cycles, the TGO layer behaved in a similar manner to a single 7YSZ coating on a NiCoCrAlY bond coat. The TGO layer thickened to ~1.5 μm and oxide precipitates appeared in the BEI image of the TGO layer, in Fig. 11(a). EDS analysis indicates that the precipitates contain comparable amounts of Y and Al, which are probably yttrium aluminum garnet, $Y_3A_5O_{12}$ (YAG). There is no evidence of localized interface separations between the 7YSZ and SZO layers. After 50 cycles, the feathery structure on the 7YSZ columnar surfaces had disappeared. The Sm,Zr$_2$O$_7$ feathery structure appears to have suffered a slower evolution, similar to that observed in a 7YSZ/Gd$_2$Zr$_2$O$_7$ bi-layer coating\[40\]. In addition, a mixed zone including YSZ and alumina is also observed at the 7YSZ/TGO interface. The formation of a mixed zone is thought to result from dissolution of the first deposited YSZ in metastable (gamma and theta) alumina oxides and this then precipitates as the metastable alumina transforms to alpha alumina\[2,51\].

The 7YSZ/SZO interface is of particular interest in Fig. 11(d). Although the top SZO coating is intact and attached to the 7YSZ, there is a dense region at the interface within the SZO coating. A similar region has been observed in thermal cycled single layers of SZO and is consistent with Sm enrichment of the SZO coating\[45\]. A line scan analysis (Fig. 12a) was conducted to investigate the diffusion of Sm in the SZO layer and indicated that while Sm had diffused into the YSZ coating, it had not yet reached the YSZ/TGO interface.

5.3. 350 cycle response

At 350 cycles, small voids occur locally at the bond coat/TGO interface, Fig. 11(b). However, the bi-layer coating remained attached to the TGO. The TGO thickness had also increased to ~3.5 μm. Once again, no detachment of SZO occurred at the 7YSZ/SZO interface, Fig. 11(e), even though some spheroidal porosity had formed at this interface. The more prolonged 350-hour thermal exposure also increased the penetration of Sm into the YSZ coating. EDS measurements detected a low concentration of Sm (~1 at.%) near the TGO. A line scan analysis is also shown in Fig. 12(b). The Sm signal is detectable throughout the YSZ coating, consistent with the EDS analysis of the YSZ/TGO interface.

Although the diffusion coefficient of Sm in YSZ at 1100 °C is not available, it can be estimated from the observed diffusion distance ($2\sqrt{Dt}$) of ~15 μm after a diffusion time $\tau=350$ h, Fig. 12(b). This estimated diffusivity ($D$) is $10^{-17}$–$10^{-16}$ m$^2$/s and is comparable to the reported diffusivity of $10^{-16}$ m$^2$/s for Y in YSZ\[52\]. We note that the effective diffusivity may have been accelerated by the unusual microstructure of these coatings. They contain many inter- and intra-columnar pores which increase the opportunities for Sm to migrate along void surface paths with potentially lower barriers to thermally activated diffusion.

5.4. Spallation

Upon further cycling, the bi-layer samples eventually undergo delamination between 1000 and 1150 cycles with the delamination

<table>
<thead>
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<th>Table 3</th>
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<td>EDS analysis for lines 1 and 2.</td>
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<td>Position</td>
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<tr>
<td>Line 1</td>
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<td>Line 2</td>
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Fig. 9. (a) Cross-section view of the as-grown SZO/YSZ bi-layer coating. (b) A high magnification image of the BC/TGO/7YSZ interface.

Fig. 10. The polished cross-section of SZO coating on 7YSZ coating. Small colored circles represent locations where EDS measurements were recorded.
fracture path located at the bond coat/TGO interface (Fig. 11c). The TGO thickness at delamination was ~5.9 μm and wide inter-columnar gaps, probably due to sintering, had deeply penetrated from the surface into the SZO coating, Fig. 11(c). A mixed zone was still evident at the TGO/YSZ interface (Fig. 11c). The two ceramic materials in the bi-layer coating have very similar thermo-mechanical properties and appear to have remained compatible with each other. Fig. 11(f) provides a qualitative comparison of the sintering rate differences between the SZO and YSZ components of the coating. The SZO still retained a columnar structure while the columns of YSZ coating had almost disappeared consistent with the view that SZO has a better resistance to sintering than YSZ.

The effect of thermal cycling time upon the TGO layer thickness is summarized in Fig. 13. The parabolic rate constant that best fits the data has a value of ~0.016 μm²/h, very slightly higher than that of a single 7YSZ coating. A comparison of the delamination lifetimes for 7YSZ, SZO and 7YSZ/SZO bi-layer coatings is shown in Table 4. All the samples experienced the same cycling history, i.e. they were heated at 1100 °C for an hour and followed by 10-min forced air cooling to about 100 °C. Both 7YSZ and the bi-layer coating have comparable failure lifetimes, much longer than that of SZO. The use of the bi-layer coating architecture has therefore enabled exploitation of the lower SZO thermal conductivity without incurring the deleterious reaction between SZO and the alumina rich TGO.

6. Bi-layer failure mechanism

The high temperature cycling results indicate that 7YSZ is a successful diffusion barrier to samarium from SZO even in the presence of the wide inter-column void gaps needed for strain tolerance. The YSZ/SZO bi-layer TBC spalled at the bond coat/TGO interface after a similar number of thermal cycles and by a similar mode to that of a single layer YSZ on the same polished NiCoCrAlY bond coat. This arises because SZO and YSZ have similar thermo-mechanical properties, and so the strain energy release rate calculations summarized in Fig. 8 can be used to deduce the YSZ, SZO and bi-layer driving forces for fracture.

Delamination at the bond coat/TGO interface releases the stored strain energy of both the TGO and thermal barrier coating layers and therefore results in a very large strain energy release which increases with both TGO thickness and thermal barrier coating modulus, Fig. 8. As

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**Fig. 11.** Evolution of the bi-layer SZO/YSZ coatings deposited at 1000 °C on polished substrates. The bilayer coatings were thermally cycled between 1100 °C and ambient temperature. Note that the delamination occurs at the TGO/bond coat interface.
the TGO thickness approached a thickness of 6 μm (the thickness at which delamination fracture was observed to occur), the predicted strain energy release rate reached 160–180 J m$^{-2}$ (depending upon thermal barrier coating modulus). This can be compared to recent experimental estimates of an interfacial toughness of 110 J m$^{-2}$ for β-NiAl related systems [53]. We note that the delamination crack extension at the two-phase bond coat/TGO interface of the system investigated here might exhibit a higher initial toughness than that of the intermetallic NiAl system. However, the growth of the TGO was also accompanied by the gradual appearance of short voids at the bond coat/TGO interface which may have gradually reduced the toughness of the interface over time. Sulfur diffusion to this interface has also been reported [54] and this may also have contributed to a time dependent reduction in toughness. Macroscopic delamination would then have occurred at the time (and TGO thickness) where the drop in toughness crosses over the increase in stored energy with TGO thickness.

These insights indicate that concepts which delay the rate of TGO growth are likely to significantly extend the life of a thermal barrier coating. The use (and maintenance during high temperature exposure) of a low in-plane modulus coating material/coating pore morphology is also advantageous. Bi-layer and even tri-layer coating concepts may open up a wider range of material opportunities. Bond coats or thermal barrier coatings that provide opportunities for plastic dissipation (as opposed to elastic storage) of the thermal expansion mismatch strains are also likely to extend the life of TBC systems. The emergence of flexible coating deposition technologies may enable expanded explorations of these possibilities.

7. Conclusions

Both SZO and SZO/YSZ bi-layer coatings have been deposited on polished NiCoCrAlY bond-coated Hastelloy-X substrates using an electron beam, directed vapor deposition method and their cycling response has been investigated. We find that:

1. The lifetime of SZO coatings is increased by increasing the coatings compliance (by incorporating voids) but is significantly less than that of similar compliance YSZ coatings deposited on the same bond coat. The reduced life resulted from a chemical reaction between the rare earth zirconate and the alumina-rich TGO leading to the formation of SmAlO$_3$ and a reduced toughness interface.

2. The placement of a 10 μm thick YSZ layer between the TGO and SZO layers eliminated the TGO/mixed zone failure mechanisms and significantly improved the coating lifetime to that of YSZ coatings.

3. The YSZ layer successfully acted as a diffusion barrier layer to the migration of samaria to the TGO, inhibiting the chemical reaction between SZO and TGO and slowing the TGO growth rate, and thus increasing the delamination lifetime of bi-layer coatings.

4. Eventual delamination of the 7YSZ/SZO bi-layer occurred at the bond coat/TGO interface. Delamination of this interface releases an estimated 160–180 J m$^{-2}$ of stored strain energy in the coating system. This strain energy increased with TGO layer thickness and coating modulus. For the coatings studied here, final failure occurred by the linking of an array of thin voids at the bond coat/TGO interface and may have been associated with segregation of sulfur to the failure interface.

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References


