Response of Molten Silicate Infiltrated $\text{Gd}_2\text{Zr}_2\text{O}_7$ Thermal Barrier Coatings to Temperature Gradients

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ABSTRACT

The delamination tendency for bilayer gadolinium zirconate/yttria-stabilized zirconia (GZO/YSZ) thermal barrier coatings (TBCs) was investigated using a continuous laser-based thermal gradient test and a computational model for the analysis of multilayer structures. TBCs with different architectures were exposed to molten silicate compositions, representative of aero-engine deposits, and subjected to thermal cycles prescribed to impart specified levels of strain energy in the coating. The exposed surface of the intercolumnar gaps in the outer part of the GZO layer was found to rapidly dissolve into the intruding molten silicate and precipitate reaction products that seal the flow paths, limiting the penetration depth and the ensuing stiffening of the TBC. Nevertheless, the stiffened layer magnifies the thermal stresses in the coating upon thermal cycling. The influence of the thermal history and multilayer structure on the driving force for delamination was modeled and compared with the experimental results. The effects that the substrate coefficient of thermal expansion, the temperature gradient, and the TBC thickness have on the driving force for delamination were analyzed and the critical amount of stored elastic strain energy for failure under different scenarios was assessed.

Keywords: thermal barrier coatings, zirconates, silicates, delamination, thermal gradient.

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1. INTRODUCTION

The durability of thermal barrier coatings (TBCs) is strongly dependent on their ability to maintain the porous, compliant structure that enables strain tolerance during operation [1]. Sintering [2,3] and molten silicate (CMAS)[†] penetration [4,5] can markedly reduce compliance by inducing TBC densification. While both mechanisms are exacerbated by increasing temperature, even a brief thermal excursion above the incipient melting temperature of a siliceous deposit can lead to significant penetration that increases the TBC stiffness to a level approaching that of dense zirconia [6].

The degradation of TBCs by CMAS has become increasingly common as the operating temperature of aero-engines increases to improve efficiency [5]. Due to the low viscosity of many CMAS melts above their incipient melting temperature [7-9] and their sluggish intrinsic crystallization kinetics [10-12], the depth of penetration into state-of-the-art TBCs based on 7 wt% yttria stabilized zirconia (7YSZ) is controlled by the interplay between the melt composition/viscosity and the thermal gradient through the TBC. Penetration is limited by the location of the isotherm within the coating wherein rapid crystallization occurs or the viscosity becomes sufficiently high to render the flow rate negligible within the time scale of the process [5,6]. In many cases, however, the TBC surface will be exposed to a temperature sufficiently high for a substantial fraction of the 7YSZ coating to be penetrated [4,13,14].

While infiltrating a 7YSZ TBC, the molten silicate also dissolves the outer surface of the coating and re-precipitates transformable tetragonal zirconia [15]. Under certain conditions, other reaction products have been observed on 7YSZ TBCs, most commonly zircon, calcium zirconate, the garnet-type kimzeyite [16,17], and $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ [18]. However, the formation of these phases is not sufficiently fast to markedly inhibit CMAS infiltration into the TBC.

If yttria or rare earth (RE) oxide stabilizers are added to ZrO_2 in high enough concentrations to form pyrochlore ($\text{Zr}:\text{RE} = 1$) or δ -phase ($\text{Zr}:\text{RE} = 0.75$) zirconates, the reaction with CMAS is found to yield silicates that nucleate and grow much faster than the reaction products observed on 7YSZ [19-21]. Notably, gadolinium zirconate ($\text{Gd}_2\text{Zr}_2\text{O}_7$, GZO) has been shown to limit CMAS penetration to a small fraction of the TBC thickness under isothermal exposure at 1300°C after 4 h, compared with full penetration of 7YSZ in a few minutes at the same temperature [19]. The underlying mechanism involves the formation of an oxi-apatite (Ap) based on

[†] The four primary constituents of the inorganic debris ingested by aero-engines are calcium, magnesium, aluminum, and silicon oxides, leading to the designation CMAS. Iron, and to a lesser extent titanium and nickel oxides plus some alkaline oxides are also present in many cases.

$\text{Ca}_2\text{Gd}_8(\text{SiO}_4)_6\text{O}_2$, and re-precipitated Gd-stabilized fluorite, which fill the intercolumnar gaps of the TBC and block further penetration.

The improved resistance to CMAS penetration of GZO relative to 7YSZ, as well as its lower thermal conductivity and superior phase stability, have motivated the implementation of GZO into aero-engines [5,22]. There are, however, some trade-offs in this exchange. Absent CMAS, the superior durability of 7YSZ under thermal cycling has been ascribed to ferroelastic toughening enabled by its tetragonal structure [23,24]. In contrast, fluorite and rare-earth zirconates (REZ) display cubic structures that have no intrinsic toughening mechanisms and are, in principle, less strain tolerant [25]. Moreover, 7YSZ is thermochemically compatible with the thermally grown oxide (TGO) that provides environmental protection to the metal, whereas GZO is not [26]. These challenges are usually addressed by introducing a bilayer architecture with 7YSZ next to the TGO [27-29], where intrinsic failures often initiate in conventional systems [1].

When CMAS is present, the stiffened TBC promotes delamination by magnifying the stresses present in the TBC, which result from (i) the mismatch in coefficient of thermal expansion (CTE) between the layers in the coating system [30,31], and may be further aggravated by (ii) rapid changes in the surface temperature that induce transient but severe thermal gradients within the TBC [32-34]. While the CMAS stiffened layer is thinner in GZO than in 7YSZ, the benefit in reducing the strain energy driving delamination is counteracted by the lower toughness of GZO. Notwithstanding these limitations, the introduction of GZO into engine technology suggests that the TBC design can be made sufficiently robust to survive in the engine environment.

The goal of this investigation is to assess the response of GZO coatings exposed to CMAS deposits under time-dependent thermal gradients and identify possible conditions that lead to safe operation. The influence of substrate CTE, temperature gradient, and coating thickness were analyzed. The results are interpreted with the aid of models to develop guidelines for durability.

2. EXPERIMENTAL

2.1. Thermal gradient test

The TBC systems in this work were tested in an apparatus especially designed to impose a tunable temperature gradient [5,6]. In this setup, the top coat surface was heated by a 2 kW, 10.6 μm , continuous CO_2 laser while the back surface of the substrate was cooled using an air jet, Fig 1. T_{Surf} , the surface temperature of the TBC was mapped by a far-infrared, (7-10 μm or 8-9.4 μm) imaging pyrometer, e.g. Fig 2(a), from which a single surface temperature was calculated by averaging the temperature in a region of interest covering the majority of the surface of TBC specimen. k-type thermocouples, 250 μm in diameter, were used to measure the temperature on

the back surface, T_{Back} , and within the substrate, at a short distance below the substrate/TGO interface, T_{Sub} . The surface of the TBC was imaged at high temperature using an optical camera, fitted with a 100 mm macro lens, neutral density and 425-495 nm band pass filters, while illuminated with blue LED light assembly (440-460 nm) [35,36]. An image of the TBC surface at 1300°C is presented in Fig 2(b).

The thermal cycle used in this investigation comprised a heating stage, a high-temperature dwell, and a cooling stage. The rate of heating and cooling were controlled by suitably tailoring the rate at which the laser power was increased or decreased. In all cases, the high-temperature dwell was 10 minutes, and the surface temperature of TBC was approximately 1300°C. Guided by the thermo-mechanical model [34] the cooling rate was prescribed to be sufficiently slow such that a linear temperature gradient was maintained in each layer. The measured temperatures, T_{Surf} , T_{Sub} , and T_{Back} , along with the geometrical parameters and the initial cooling rate of each specimen are listed in Table 1. The TBC was subjected to one thermal cycle but in cases in which no damage was observed the test was repeated up to five cycles to assess the robustness of the system.

2.2. Specimen Preparation

The majority of the experiments used TBCs deposited on 3 mm thick superalloy substrate, PW-1484, first coated with a 30-100 μm thick NiCoCrAlY-Hf-Si bond coat at Pratt and Whitney using argon shrouded plasma spray. For the purposes of evaluating the effect of the substrate CTE an additional specimen was deposited on a 3 mm thick FeCrAlY substrate (Goodfellow, Cambridge, UK). The specimens were designed to facilitate the placement of thin thermocouples directly below the TGO and at the back face. For the superalloy specimens a 300 μm diameter hole was created using a plunge EDM in the substrate directly below the TGO, approximately at the boundary between the substrate and the bond coat, and a 300 μm wide trench was cut into bottom surface of the substrate to allow thermocouples to be placed in the specimen. For the FeCrAlY specimen grooves were machined into the top and bottom surfaces of a 3 mm thick disk using electrical discharge machining (EDM). A 100 μm FeCrAlY foil was then diffusion bonded to the top surface.

Prior to topcoat deposition, the substrates were pre-oxidized in a low $p\text{O}_2$ ($\text{Ar}\sim 10^{-13}\text{O}_2$) atmosphere at 1100°C for 4-10 hours to establish a thin, dense layer of $\alpha\text{-Al}_2\text{O}_3$. Sequential deposition of 7YSZ then GZO TBCs via electron-beam physical vapor deposition was performed upon each substrate, either in an in-house dedicated EB-PVD facility or at Pratt and Whitney. The resulting YSZ and GZO layer thickness are listed in Table 1.

2.3. Silicate preparation and deposition

Two silicate compositions characterized in a previous study [12], namely $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ and $\text{C}_{33}\text{F}_{10}\text{A}_{13}\text{S}_{44}$ (hereafter CMAS-1 and CFAS-1), were used in this investigation. Their composition, calculated viscosity at 1300°C [37], glass transition temperature, T_g , and the incipient melting temperature, T_{IM} , measured by differential scanning calorimetry (DSC) are listed in Table 2. The CMAS-1 composition has been used in previous investigations [6,12,15,19] and is a quaternary version of the average intruding melt composition found within airfoil coatings by Borom et al. [4]. CFAS-1 is an analogous composition wherein Mg is replaced by Fe; the latter has been found to have similar viscosity but a somewhat broader melting range and slightly more active intrinsic crystallization behavior by DSC [12]. In the end, no significant differences were observed in the infiltration behaviors of the two silicate compositions so they are treated as equivalent for the purposes of this paper.

The CMAS-1 and CFAS-1 powders were synthesized following the procedures in [12]. The constituent oxides (99.95% CaO, 99.95% MgO, 99.8% SiO_2 and 99.99% Fe_2O_3 from Alfa Aesar, and 99.99% AKP-50 Al_2O_3 from Sumitomo Chemical) were mixed in de-ionized water, ball milled for 4 h, dried, crushed in a mortar and pestle and pre-reacted by heating in air for 24 h at 1200°C for CMAS-1 and at 1000°C for CFAS-1 (because of its lower incipient melting temperature in DSC, Table 2). Both mixtures were then crushed a second time in a mortar and pestle.

The powders were ultrasonically suspended in ethanol at a concentration of 200 mg/ml. The suspensions were deposited drop-wise on the TBC surface to form a thin, uniform layer, and dried under a heat lamp for 30 min to drive off the ethanol, resulting in a C(M/F)AS loading of approximately 5 mg/cm^2 .

2.4. Characterization

Following exposure, the TBC coupons were impregnated with a low viscosity, cold-curing epoxy under vacuum and sectioned with a slow speed diamond wafering blade. The cut samples were polished with diamond suspensions and then analyzed with a scanning electron microscope (SEM). Chemical analysis was performed in the SEM with energy-dispersive X-ray spectroscopy (EDS).

3. OBSERVATIONS FROM LASER GRADIENT TESTS

Experimental observations of the GZO/7YSZ bilayer TBCs exposed to C(M/F)AS melts in the laser gradient test are described in this section, followed by the thermo-mechanical analysis in section 4. The thermal history parameters for each TBC specimen are listed in Table 1. In

each test, the surface temperature was approximately 1300°C , chosen to simulate the service environment during which molten silicate infiltration might take place. The temperature gradient, coating thickness and substrate were varied to impose a range of strain energy in the coating. The TBCs were cooled at rates between $25\text{--}200^\circ\text{C}/\text{min}$, sufficiently slow such that an approximately linear temperature gradient would be maintained through each layer of the multilayer TBC system. The temperature drops across the bilayer were significantly different in all cases, ranging from 184°C for P-1 to 375°C for P-2, but because of the different topcoat thickness the average gradients were relatively close, in the range of 0.98 to $1.13\text{ K}/\mu\text{m}$ for all but the P-2 sample, which was designed to have a significantly larger gradient of $\sim 1.4\text{ K}/\mu\text{m}$ (Table 1).

Low magnification cross-sectional SEM images of all specimens after laser exposure are presented in Fig. 3. The average silicate penetration for all specimens was typically $25\pm 10\text{ }\mu\text{m}$ but could vary at some locations over a range as broad as $5\text{--}50\text{ }\mu\text{m}$ depending on the width of the intercolumnar gaps. This level of penetration was similar to that observed in isothermal experiments with the same surface temperature [19], suggesting that the thermal gradient has no significant effect in the intrinsic mitigation reaction under the conditions explored here. While all TBCs remained adherent to the substrate following one thermal cycle, cracks were observed within the GZO layer for the P-1 and P-3 specimens, Figs. 3(b,d),-but not after the tests on F-1, P-2 and P-4, Figs. 3(a,c,e). (Samples P-2 and P-4 were subjected to a total of 5 cycles after no damage was observed in the first cycle.) Notably, multiple cracks approximately parallel to the substrate are present in the middle of the GZO layer for the P-1 coating, Fig. 3(b). Cracks within the uninfiltrated region can be highly tortuous with steps at the inter-columnar gaps, as shown in Fig. 4(c), except in the vicinity of the YSZ/GZO interface.[‡] Steps in the crack path occur at intercolumnar gaps, with a typical step width of 1 to 3 columns. In contrast, cracks within the infiltrated layer are much flatter locally, although they can exhibit bifurcation/branching, Fig. 4(b). A similar crack within the infiltrated region on P-3, Fig. 3(d), had minimal branching and allowed the reacted portion of the coating to buckle away from the TBC. Cracks grow near interface but do not usually deflect into the YSZ. No large cracks were found within the GZO coating on the edge of the samples that were not penetrated by C(M/F)AS.

The cross-sectional SEM micrograph in Fig 4(a) shows the morphology of the GZO TBC following interaction with CMAS-1. A dark contrast layer surrounding each TBC column was analyzed by SEM/EDS and found to contain acicular crystals of apatite, nominally $\text{Ca}_2\text{Gd}_8(\text{SiO}_4)_6\text{O}_2$, and globular crystals of Gd+Ca stabilized zirconia (fluorite), consistent with prior

[‡] The YSZ/GZO interface itself is not a preferential crack path as GZO grows epitaxially on the YSZ columns. Instead, cracks extend through GZO, which is significantly less tough than YSZ [42].

reports on isothermal experiments at similar temperatures [19]. This reaction product fills the top of each intercolumnar gap, arresting the penetration of the molten silicate.

The morphology of the GZO-TBC following reaction with CFAS-1, Fig 5(a), is similar to the TBC exposed to CMAS-1 in 4(b); a reaction product covers the TBC column tips and blocks the intercolumnar gaps. The similarity in the features of the reaction layer is expected as the two melts have similar Ca:Si ratios and relatively low viscosities of approximately 5 Pa·s at 1300°C [12]. A higher magnification image of the reaction zone shows a dense layer, approximately 5 µm in thickness, on the TBC surface with acicular grains of apatite extending into the residual melt. A small pocket of glass entrapped in the intercolumnar gap by the growth of the precipitated phases can be observed in Fig 5(b).

Unlike the GZO exposed to CMAS-1, dendritic crystallites are found on the surface of the TBC and within the residual CFAS-1 melt, Fig. 5(a) [12]. EDS analysis suggests that these crystalline phases have the approximate composition, (Ca_{0.83}Gd_{0.17})₃(Fe_{0.81}Zr_{0.19})₂(Si_{0.8}Al_{0.2})₃O₁₂, consistent with garnets of the form A₃B₂C₃O₁₂ observed in other studies [21], where the A, B, and C sites have 8, 6 and 4 fold coordination by oxygen, respectively. (Some intermixing between sites is feasible, as Si strongly prefers the tetrahedral site but some Al may fit in both tetrahedral and octahedral sites, and Fe may exhibit mixed oxidation states. Mg can also be found in the mix, but the absence of garnet with CMAS and its presence with CFAS indicate the Fe is promoting its formation, as suggested by Braue et al [17]. The dendritic morphology and their presence within the residual melt suggest that the garnet grows primarily during cooling, as shown in other studies [21] and therefore is unlikely to play a role in the arrest of the melt flow into the column gaps. Therefore, the reactions that lead to the arrest of the flow within the gaps are similar for both silicate melts.

4. THERMO-MECHANICAL EFFECTS

The experiments above were broadly intended to explore the dependence of the propensity for TBC cracking and delamination on (i) the thermal expansion mismatch between coating and substrate (F-1 vs. P-1), (ii) the thermal gradient through the top coat (P-1 vs. P-2), (iii) the overall coating thickness (P-1 vs. P-4) and (iv) the relative ratios of GZO vs. YSZ at the same coating thickness (P-1 vs. P-3). A recently developed thermo-mechanical model [34] will be employed to assess these trends and the calculations will be compared with the results of the tests.

4.1. Thermo-mechanical model

The TBC is modeled as a stack of semi-infinite, isotropic layers[§] with prescribed properties listed in Table 3. The coordinate system is defined in Fig. 1 with the origin at the backside of the substrate and the distance through the stack corresponding to the y coordinate. For convenience, the locations of the interfaces are defined as $y_{S/B}$ (substrate/bond-coat), $y_{B/T}$ (bond coat/TGO), $y_{T/Y}$ (TGO/YSZ), $y_{Y/G}$ (YSZ/GZO), $y_{G/A}$ (GZO/GZO+Apatite), and $y_{A/C}$ (GZO+Apatite/CMAS overlayer). Distances may often be referred to a specific interface of interest, rather than to the origin, e.g. $\Delta y_{Y/G}$ would be the distance in the positive y direction from the YSZ/GZO interface. The total coating thickness appearing on Table 1, is $\Delta y_{T/Y} = H_{TBC}$. In subsequent calculations the thickness of the TBC stiffened by CMAS is set to be 25 μm . While a range of penetration depth exists, as described in section 3, the effect of the minor thickness variation on the energy release rate is small compared to the other parameters being varied [6]. This assumption was applied to facilitate analysis of the effect that single parameters have on the overall response.

The temperature profile through the coating during the high temperature dwell is determined using the data collected in the laser experiment as boundary conditions and then solving Fourier's law for 1-D heat conduction. In the mechanical analysis, it is assumed that (i) the stress-free state defining the reference temperature for thermal strains is the initial steady-state temperature distribution through the TBC held during the high-temperature dwell, (ii) the materials behave as linear-elastic during cooling, (iii) all multilayers, either the original complete TBC or sub-sections created by an interface crack, experience a linear strain distribution, consistent with Bernoulli-Euler bending, and (iv) there are no externally applied loads or constraints that resist elongation or bending [33]. This approach is a rigorous generalization of the bilayer results described in reference [38]; complete details of the generalization are given in [34,39] for systems with an arbitrary number of layers.^{**} Stresses and crack driving forces are calculated when the multilayer has cooled to a uniform temperature of 25°C throughout the system.

4.2. Effect of substrate CTE

Owing to the comparatively large thickness and stiffness of the substrate the total strain through a multilayer TBC is largely dictated by the contraction of the substrate during cooling. Two alloy substrates were used to assess this effect, PW-1484 ($\alpha_{\square\square} = 15 \text{ ppm}\cdot\text{K}^{-1}$) and FeCrAlY ($\alpha_{\square\square} = 13 \text{ ppm}\cdot\text{K}^{-1}$). While the difference appears to be modest, the mismatch with the topcoat is twice as large for PW-1484 ($\Delta\alpha \approx 4 \text{ ppm}\cdot\text{K}^{-1}$) than for FeCrAlY ($\Delta\alpha \approx 2 \text{ ppm}\cdot\text{K}^{-1}$).

[§] An EB-PVD topcoat is clearly anisotropic but because of the segmented geometry the difference in the out-of-plane modulus has only a small effect on the behavior of the system.

^{**} Codes to perform this type of calculations are freely available online.
<<http://www.engineering.ucsb.edu/~begley/LayerSlayer.html>>

The calculated biaxial stress distributions through the coatings upon cooling to 25°C, based on the conditions from Table 1, are depicted in Fig 6(a). For the same thermal history, the compressive stresses in the TBC on F-1 were calculated to be much lower in magnitude than those in the P-1 specimen, by about a factor of 2 as expected from the smaller CTE mismatch of the former. (While the cooling rate of the F-1 specimen is significantly higher, as shown in Table 1, the comparison in Fig. 6 is after cooling down to ambient, independent of the cooling rate as long as damage is suppressed.) The energy release rate available for delamination, G , was calculated as a function of location in the coating and is depicted in Fig. 6(b). The value of G at the Y/G interface for the P-1 coating is about an order of magnitude larger than for the F-1 coating, i.e. 126 J·m⁻² vs. 13 J·m⁻²—note that the topcoat is significantly thicker in F-1 but T_{sub} is appreciably lower (Table 1). Moreover, G in Fig. 6(b) is considerably higher at all locations in P-1 relative to F-1, even at the bottom of the stiffened layer (82 J·m⁻² vs. ~13 J·m⁻² at $y_{G/A}$) which is of the same thickness in both cases. These estimates are consistent with the extensive cracking in the P-1 coating and its absence in F-1 after one cycle, shown in Fig 2.

The dependence of the driving force for delamination on the substrate CTE is examined in more detail in Fig. 7(a), wherein G is plotted for three critical locations in a model system, i.e. at $y_{T/Y}$, $y_{Y/G}$ and $y_{G/A}$ interfaces. In the model system the topcoat comprises a 50 μm YSZ layer, 125 μm of GZO, 25 μm of dense GZO + apatite, and 10 μm of residual CMAS. The temperature gradient through the multilayer is prescribed such that $T_{surf} = 1300^\circ\text{C}$, $T_{sub} = 1085^\circ\text{C}$ and $T_{back} = 900^\circ\text{C}$. Because delamination cracks in all these cases propagate through the topcoat, rather than at the bond coat/TGO interface, the highest driving force is at the TGO/YSZ interface. However, the lower toughness of the GZO relative to YSZ makes the relevant G that within the GZO layer, which is maximum at the YSZ/GZO interface. The magnitude of G is minimum at $\alpha_{\square\square\square} = 11.3 \text{ ppm}\cdot\text{K}^{-1}$ and increases approximately quadratically for a given ΔT with increasing the CTE of the substrate according to $G \propto (\Delta\alpha\Delta T)^2$ [38]. Hence, the maximum driving force for delamination would be about a factor of 5 larger for PW-1484 than for FeCrAlY, and significantly greater for alloys with larger CTE such as IN718 [40] or certain cobalt-based superalloys [41].

Markers, the vertical span of which represent the range of energy release rates for delamination throughout the GZO layer in the actual F-1 and P-1 specimens, i.e. with the thickness and temperature distribution in Table 1, are overlaid on the Fig 7(a). Delamination cracks were observed throughout the GZO layer of P-1 while the F-1 specimen remained intact, Fig 3. From these two experiments, the toughness of the GZO EB-PVD layer, Γ_{GZO} , can be inferred to be between 13 and 82 J·m⁻². (The lower end of the range is selected for P-1 because

cracks form above the YSZ/GZO interface.) This range of toughness values will be narrowed with analysis of the results in sections 4.3 and 4.4.

4.3. *Effect of thermal gradient*

The driving force for delamination is also influenced by the temperature gradient through the TBC [5,31]. During the high temperature dwell, the lower CTE topcoat is at a higher average temperature than the higher CTE substrate. As a result, the difference in thermal contraction between each layer upon cooling decreases as the temperature gradient increases.^{††} The concept is illustrated first by comparing the stresses and energy release rates for the P-1 and P-2 specimens, shown in Fig. 6. The surface temperature T_{Surf} , is essentially constant for both cases, and the gradient is increased in practice by reducing the backside temperature, T_{Back} , through more active cooling. In addition, P-2 has a thicker coating (similar to F-1) which coupled with the enhanced cooling results in a significantly lower T_{Sub} , i.e. 1086°C for P-1 and 910°C, for P-2. (The thickness effect is further explored in section 4.4.) The stresses in Fig. 6(a) are lower for P-2 than the values for P-1 and closer to those in F-1. Concomitantly, the driving force for delamination in P-2 is higher than that in F-1 but still significantly lower than that for P-1, as shown in Fig. 6(b).

In an effort to decouple the thickness contribution, the effect of the temperature gradient through the TBC on the energy release rate is examined in Fig 7(b) using the model coating with the same dimensions as in section 4.2. G was calculated for cracks propagating at the $y_{T/Y}$, $y_{Y/G}$, and $y_{G/A}$ interfaces by fixing $T_{Surf}=1300^{\circ}\text{C}$ and varying T_{Sub} from 900°C to 1300°C (with a concomitant variation in T_{Back}). Over this interval G increases by a factor of 20 at $y_{Y/G}$. The vertical markers in Fig. 7(b) represent the range of energy release rates for delamination within the GZO, given the experimental conditions of the P-1 and P-2 specimens. The maximum values of G , corresponding to the YSZ/GZO interface, change from $126 \text{ J}\cdot\text{m}^{-2}$ for P-1 to $54 \text{ J}\cdot\text{m}^{-2}$ for P-2. The energy release rate of the P-2 specimen, which remained intact after the test, gives a higher lower bound for the toughness of $\Gamma_{GZO}=54 \text{ J}\cdot\text{m}^{-2}$ relative to that estimated from F-1 in Fig. 7(a). Similarly, the lower upper bound for Γ_{GZO} is the same as that depicted in Fig. 7(a), $\sim 82 \text{ J}\cdot\text{m}^{-2}$, for the reasons stated in section 4.2.

It is worth noting that increasing the temperature gradient by increasing T_{Sub} can also decrease G , as illustrated in Fig. 8. The solid line represents the scenario when the backside temperature is kept constant at 900°C and T_{Sub} increases by increasing T_{Surf} . G is maximum for

^{††} If the temperature gradient is sufficiently large the TBC will transition from compressive to tensile strain upon cooling, after which further increase in the temperature gradient will increase the magnitude of strain and stress in the coating.

the initially isothermal system and decreases with increasing T_{Sub} —and concomitantly the gradient across the TBC—reaching $T_{Sub}=1100^\circ\text{C}$ when $T_{Surf} = 1300^\circ\text{C}$. The scenario depicted in Fig. 7(b) corresponds to the dashed line in Fig. 8, along which T_{Surf} remains constant and T_{Sub} is adjusted by modifying T_{Back} . At the upper end the system is isothermal at 1300°C and gives rise to the maximum G when it cools down to ambient. As the gradient increases with decreasing T_{Sub} , G decreases and reaches the value marked by the circle when T_{Sub} is 1100°C , approximating the experiment P-1. The minimum in both curves arguably corresponds to extreme scenarios not typical of engine operation.

4.4. Effect of TBC thickness

Increasing the coating thickness can either raise or lower the driving force for delamination depending on the thermal environment and multilayer properties. In the absence of a temperature gradient, the stored elastic strain energy upon cooling increases proportionally with the coating thickness, making thicker coatings more prone to delamination [38]. However, the magnitude of the stress in a layered coating system with fixed thermal expansion coefficients is, to a first approximation, proportional to the difference between the average temperatures of the substrate and coating. If the bounding temperatures T_{Surf} and T_{Back} are fixed, increasing the TBC thickness reduces the bond coat temperature, T_{Sub} , and therefore the thermal excursion of the substrate as it cools to ambient. The net effect of increasing TBC thickness is then is a reduction in the stress on the coating, and because G is proportional to the square of the thermal strain, a reduction in the driving force for delamination.

The energy release rate at the critical T/Y, Y/G and G/A interfaces is plotted in Fig 7(c). Following the examples in Figs. 7(a,b) the thickness of the YSZ layer is $50\text{ }\mu\text{m}$ and that of the GZO+Ap layer is $25\text{ }\mu\text{m}$ while the thickness of the GZO is varied from $25\text{ }\mu\text{m}$ to $225\text{ }\mu\text{m}$. In these calculations, the TBC surface temperature is 1300°C and the backside is 900°C . As the total TBC thickness increases, T_{Sub} decreases from 1169°C to 1043°C and G the ERR decreases monotonically with coating thickness at each of the interfaces considered, as shown in Fig. 7(c).

The consequences of varying the coating thickness are evident when comparing P-1 and P-4, which have substantially different thickness but essentially the same ratio of YSZ to GZO layer thickness. The surface temperatures are similar (1270°C and 1280°C , respectively), and the average gradients are reasonably close, but the bond coat interface temperatures are markedly different (1086°C vs. 940°C), and the T_{Back} is also smaller (840°C v. 780°C). The thermal excursion experienced by the substrate upon cooling to ambient is then smaller for the thicker coating, and since the substrate controls the overall expansion/contraction of the system the magnitude of the stress on the coating and G are considerably reduced. The ranges across the

entire GZO are marked by symbols in Fig. 7(c). The results are consistent with the experiments, in which cracks are formed in P-1 but not in P-4. (Note that if the experiments had been done under isothermal furnace cycling, the results would have been different.).

Comparison of P-1 and P-3 is insightful because both coatings have the same total thickness but the relative proportions of YSZ and GZO are markedly different, by a factor of ~ 3 in the GZO:YSZ thickness ratio. Both coatings have the same bond coat interface temperature, T_{Sub} , but because of the reduced amount of the GZO the composite thermal conductivity is higher in P-3, and so is the backside temperature (Table 1). This results in higher values of G for P-3, as illustrated by the overlapping symbols in Fig. 7(c). Cracks would be expected to form in both cases, as shown by the experiment, but the overall morphology is different, for reasons discussed in the following section. Finally, it is worth noting that the bounds on the toughness deduced from the previous tests are not modified by the G values estimated from the tests on P-3 and P-4.

4.5. Multiple Cracking in the TBC

Specimens P-1 and P-3 were the only ones experiencing significant cracking in this series of tests, albeit with intriguing differences in their behavior. In P-3 there is a dominant crack that propagates in a planar fashion along the G/A interface, followed by buckling of the detached layer, Fig. 3(c). In contrast, P-1 shows multiple cracking both through the stiffened and compliant GZO layers, with long cleavage segments at shallow angles within the former and tortuous, stepped paths within the latter. The evolution of the crack is relatively clear in P-3 but not in P-1, which exhibits branching and some connectivity among the regions between cracks.

Analysis of the dynamics of the branched cracks is beyond the scope of this paper, but insight into the difference in behavior can be gained from the mechanics model described above. The working assumption is that the crack(s) within the stiffened region evolve first^{††}, and the issue is whether there is sufficient energy remaining in the stack after the first delamination to drive a secondary crack within the more compliant GZO layer. Fig. 9 shows the energy release rate for a second crack as a function of distance from the Y/G interface, $\Delta y_{\text{Y/G}}$, for different locations of the first crack within the stiffened layer, $\Delta y_{\text{G/A}}$. The abscissa in this figure covers the range of compliant GZO thickness for specimen P-1. The calculated curve for P-3, which has a thinner GZO layer, is given only for $\Delta y_{\text{G/A}} = 0$ and falls below the corresponding curve for P-1. The shaded area corresponds to the condition for cracking based on the lower bound for the toughness of the EB-PVD GZO layer ($\sim 54 \text{ J}\cdot\text{m}^{-2}$) estimated from Fig. 7.

^{††} It is also possible to analyze these scenarios assuming that the crack in the GZO layer evolves first, but in reality there may be cracks propagating from multiple initiation sites in P-1. The assumption used here is based on the observation that only one crack evolves in P-3 and that is in the upper section of the stack, at the G/A interface, so one can compare the two behaviors on the same basis.

When a single crack propagates at the G/A interface the estimated G across the entire GZO layer, given by in Fig. 9, is below the cracking condition for both P-1 and P-3, consistent with the behavior in P-3. However, the upper crack(s) in P-1 propagate above $y_{\text{G/A}}$ at shallow angle(s) to the substrate plane, with some waviness and apparent branching. In consequence, the cracked dense layer is likely to retain some connectivity and attachment to the underlying GZO. An approximation of the ensuing scenario is to assume the effect is similar to that having a thin layer of remaining stiffened layer attached to the GZO. These calculations correspond to the curves for different values of $\Delta y_{\text{G/A}}$ in Fig. 9. It is evident that it takes a relatively modest residual layer to generate enough energy to drive a crack not only at the Y/G interface, where G is largest, but also within the GZO layer, with the affected thickness increasing as $\Delta y_{\text{G/A}}$ increases. The inference is that the first crack in P-1 could still allow the propagation of secondary cracks within the bulk GZO, whereas the requisite conditions do not arise in P-3 partly because of the clean removal of the dense layer and partly because of the thinner GZO. The reasons for the cracks in the top layer to evolve in such different patterns remain to be elucidated by future work.

5. IMPLICATIONS FOR TBCs

Examination of the results and analyses in the sections above provides insight not only on the failure mechanisms but, more importantly, on the conditions that allow a coating to survive similar excursions. The interplay between those factors that influence the substrate temperature (coating thickness, thermal conductivity, imposed gradient) and the driving force for delamination is evident. There are, however, additional helpful lessons regarding the layers that do not fail in spite of the significant elastic energy available.

The energy release rate for delamination at each interface within each multilayer coating tested is plotted in Fig 10. (To facilitate comparison the abscissa is normalized so each layer appears to be the same thickness in all systems, so the comparison is focused on the magnitude of G rather than on its variation with distance.) The shaded areas denote the conditions wherein significant delamination was observed. The threshold values are estimated from the toughness ranges inferred in Fig. 7. The observations that P-1 and P-3 crack at or above the $y_{\text{G/A}}$ interface, but the other specimens do not, sets the lower bound for the toughness of the GZO + Apatite layer at $\sim 30 \text{ J}\cdot\text{m}^{-2}$. Concomitantly, the observation that P-1 cracks at various depths but P-2 and P-4 do not suggests the effective toughness of the GZO layer should be in the range $\sim 54 \text{ J}\cdot\text{m}^{-2}$ to $82 \text{ J}\cdot\text{m}^{-2}$. This is substantially higher than the toughness of dense GZO measured by microindentation, of order $\sim 10 \text{ J}\cdot\text{m}^{-2}$ [42]. The rationale for this enhancement is discussed below.

The case of P-3 merits special consideration because the sample delaminates first at the G/A interface and there is no subsequent cracking of the GZO. Fig. 9 suggests there would have been sufficient driving force to crack the GZO if the densified layer had not delaminated first, but once that happens the remaining driving force does not exceed the lower bound of the toughness at any point within the GZO layer, as illustrated by the dashed line labeled P-3* in Fig. 10. P-1 will also lower its driving force as suggested by Fig. 9, but it is likely to still overlap the shaded area between 54 and 82 $\text{J}\cdot\text{m}^{-2}$ as inferred from the fact that there is ample cracking through the GZO in this specimen, albeit not usually at the Y/G interface. This is probably associated with origin of the crack closer to the surface and its branching as it propagates.

Two additional insights can be derived from Fig. 10. There was no evidence of any delamination occurring at the bond coat/TGO interface (leftmost points in the figure). The implication is that this interface has a minimum toughness of $\sim 130 \text{ J}\cdot\text{m}^{-2}$, which is the maximum energy available for P-3 after cracking occurs at the G/A interface. (Arguably the toughness could be as high as $\sim 180 \text{ J}\cdot\text{m}^{-2}$ which is the value achieved by P-1 upon cooling to ambient, but since cracking within the GZO layers is likely to have occurred before the end of cooling the maximum energy buildup was probably lower than that.) These values would be consistent with reports that the toughness of this interface can be as high as $400 \text{ J}\cdot\text{m}^{-2}$ in mode II [43]. There are, however, substantially lower estimates [44,45] as measurement of this interfacial toughness has been an elusive problem.

A second insight arises from the absence of failures within the YSZ or the TGO/YSZ interface, where the energy release rate could reach values as high as ~ 80 to $150 \text{ J}\cdot\text{m}^{-2}$ (based on similar arguments as those articulated above). This is well above the toughness measured by microindentation on dense 7YSZ, $\sim 40 \pm 5 \text{ J}\cdot\text{m}^{-2}$ [24,46,47]. It has been shown, however, that microstructural features can significantly elevate the effective toughness of a TBC, notably in the case of dense, vertically cracked (DVC) 7YSZ where R-curve behavior led to steady state values of order $350 \pm 50 \text{ J}\cdot\text{m}^{-2}$. The higher toughness was ascribed to extensive tortuosity in the crack and frictional dissipation upon crack opening [48], through a mechanism reminiscent of fiber pull-out in ceramic matrix composites [49,50]. While the effective toughness of EB-PVD TBCs has not been rigorously measured, tortuous cracks can develop by interplay with the column boundaries, as illustrated for GZO in Fig. 4(c), where the opening of the crack can be envisaged to involve frictional dissipation at the surfaces normal to the average crack plane. This could justify not only the higher toughness of 7YSZ needed to withstand the G values generated in these tests, but also the enhanced toughness inferred for the GZO layer.

The lessons from this fracture analysis to the design and assessment of TBC durability is an extension of the delamination maps presented by Evans and Hutchinson [31] where delamination

safe regions were mapped in terms of thermal history. They point to strategies to manipulate the thermal profile through control of the overall topcoat thickness, the relative proportions of the ceramic layers and the imposed heating and cooling conditions at the bounding surfaces to minimize the driving force for delamination. It also provides insight into the robustness of the GZO as a topcoat layer, wherein the penetrated layer may delaminate but the CMAS mitigation mechanism can continue to operate on the newly exposed GZO surface.

6. CONCLUSIONS

This investigation has shown that bilayer YSZ/GZO TBCs can be designed to explore different regimes of response to CMAS infiltration and thermal cycles with an imposed temperature gradient using a laser-based test facility and appropriate mechanics models. Notable findings are the insight into conditions that avoid or induce damage in the GZO layer, and the determination of an effective toughness range for the columnar GZO microstructure produced by EB-PVD. Absent CMAS penetration, the GZO layer exhibits an effective toughness in the range of ~ 54 to $\sim 82 \text{ J}\cdot\text{m}^{-2}$, whereas when stiffened by CMAS leading to a mixed layer of apatite, fluorite and residual GZO the effective toughness is lower than $30 \text{ J}\cdot\text{m}^{-2}$. The former could be justified on the basis of the observed tortuosity in the crack propagation that may introduce frictional dissipation effects in the fracture process. It was also shown that 7YSZ did not fail in spite of G values of at least $80 \text{ J}\cdot\text{m}^{-2}$, much higher than the usually accepted toughness of dense t' -7YSZ, presumably for reasons similar to the toughness enhancement of the GZO.

The driving force for delamination in the GZO was increased by a seemingly modest ($\sim 15\%$) increase in the CTE of the substrate, as this results in doubling the mismatch with the topcoat CTE. More importantly, the driving force can be decreased significantly by decreasing the overall temperature of the substrate for the same coating surface temperature, either by increasing the thickness of the topcoat or by enhancing the backside cooling on the metal. It was also shown that coatings with similar thickness but different ratios of YSZ:GZO can exhibit significantly different cracking patterns when subjected to the same thermal excursion.

Finally, no significant effect of the thermal gradient on the extent of CMAS penetration was apparent when compared with previously reported isothermal exposures at the same temperature [19], suggesting that the associated changes in the width of the column gaps are not sufficiently significant to modify the rate of the mitigation mechanism.

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Figure 1. Schematic illustration of the GZO/YSZ bilayer TBC in the laser gradient testing apparatus. The co-ordinate system used in the mechanical analysis is overlaid.

Figure 2. (a) Plan-view image, constructed from temperature data measured by the pyrometer, of the TBC surface held in the specimen fixture. (b) Plan-view photograph imaged using blue-light illumination, of the TBC surface during the high-temperature dwell segment of the thermal cycle.

Figure 3. Cross-sectional SEM images of F-1 (a) P-1 (b) P-2 (c) P-3 (d), and P-4 (e) following laser gradient testing. (The hair line crack in (c) is ascribed damage induced during preparation of the cross sectioned specimen.)

Figure 4. Cross-sectional SEM images of the P-1 following a thermal cycle. (a) The intercolumnar gaps and TBC column tips have reacted with CMAS creating a reaction zone, darker contrast, composed of apatite and fluorite. (b) Cracks running near the GZO/GZO+Ap interface. (c) Cracks running through the un-infiltrated GZO columns showing the stepped crack surface.

Figure 5. Cross-sectional SEM images of the P-3 following 5 thermal cycles showing: (a) the presence of the apatite reaction product filling the intercolumnar gaps and consuming the TBC tips is labeled 'Ap' (b) the morphology of reaction product and a region of glass silicate occluded by the apatite growth. Fe-rich garnet 'Gn' dendrites are present within the residual glass 'g' above the TBC (c) A crack running through the GZO/GZO+Ap interface results in a large displacement of infiltrated region of the GZO TBC.

Figure 6. (a) Biaxial stress profile, σ , and (b) energy release rate, G , as a function of position through the F-1, P-1, and P-2 coatings following the steady-state cooling cycle. The TGO/TBC interface is positioned at $\Delta y_{T/Y}=0$ and normalized by the total thickness of the coating (TGO+TBC+CMAS), H_{TBC} .

Figure 7. The energy release rate of an edge delamination at the TGO/YSZ, YSZ/GZO, and GZO/GZO+Ap interfaces following cooling to ambient as a function of (a) substrate CTE, (b) T_{Sub} , and (c) total TBC thickness H_{TBC} . In all calculations the multilayer coating consists of 50 μm YSZ TBC, 25 μm GZO+Ap layer, and 10 μm of CMAS. In (a) and (b) the GZO layer is 125 μm thick while in (c), the GZO thickness is varied from 0-250 μm . The initial temperature gradient for the calculations in (a) and (c) is prescribed by $T_{Surf} = 1300^\circ\text{C}$ and $T_{Back} = 900^\circ\text{C}$ while in (b) $T_{Surf} = 1300^\circ\text{C}$ and T_{Back} is varied. G for delamination throughout the GZO layer of the F-1, P 1-4 specimens are overlaid. The inferred toughness of the GZO TBC is also overlaid.

Figure 8. Comparison of the energy release rate at the YSZ/GZO interface developed upon cooling for two scenarios of increasing the initial thermal gradient through the TBC. In one case (solid blue line) the system is isothermal at 900°C and T_{Surf} increases gradually to yield the T_{Sub} plotted in the abscissa while keeping T_{Back} constant. In the other case (dashed red line) the system is isothermal at 1300°C and T_{Back} is decreased gradually to yield the T_{Sub} on the abscissa while keeping T_{Surf} constant.

Figure 9. Driving force available to propagate a second crack through the GZO layer after formation of a first crack within the stiffened GZO+Apatite layer, as a function of the distance from the YSZ/GZO interface ($\Delta y_{Y/G}$) and the location of the first crack above the GZO/GZO+Ap interface ($\Delta y_{G/A}$).

Figure 10. The energy release rate, G , at the TGO/YSZ/GZO/GZO+Ap/CMAS interfaces following cooling to ambient. Open circles are used to denote regions where delamination was observed. The inferred range of GZO toughness is marked in the grey cross-hatched region. The green dashed line denoted, $P-3^*$, corresponds to the energy release rate throughout the P-3 specimen following exfoliation at $y_{G/A}$.

Table 1. Laser gradient test data.

Table 2. Composition and attributes of silicates investigated. [12]

Table 3. Thermal barrier system properties

Figure(s)

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ID	F-1	P-1	P-2	P-3	P-4
Substrate	FeCrAlY	PW-1484	PW-1484	PW-1484	PW-1484
Bond coat	FeCrAlY	NiCoCrAlY	NiCoCrAlY	NiCoCrAlY	NiCoCrAlY
Silicate deposit	CMAS	CMAS	CFAS	CFAS	CFAS
YSZ thickness (μm)	60	35	60	80	55
GZO thickness (μm)	190	150	210	105	245
Bilayer thickness, H_{TBC} (μm)	250	185	270	185	300
CMAS penetration depth (μm)	27.1	33	29.1	22.9	21.4
Initial T_{Surf} ($^{\circ}\text{C}$)	1281	1270	1285	1300	1280
Initial T_{Back} ($^{\circ}\text{C}$)	922	840	765	980	780
Initial T_{Sub} ($^{\circ}\text{C}$)	1036	1086	910	1100	940
Initial ΔT_{TBC} ($^{\circ}\text{C}$)	245	184	375	200	340
Ave. Grad. TBC ($^{\circ}\text{C}/\mu\text{m}$)	0.98	0.99	1.39	1.08	1.13
k_{ave} (W/mK)	1.13	1.12	1.12	1.23	1.10
ΔT GZO+Ap ($^{\circ}\text{C}$)	18.4	18.6	25.9	22.2	20.7
ΔT GZO ($^{\circ}\text{C}$)	182.4	139.4	287.1	106.7	273.7
ΔT YSZ ($^{\circ}\text{C}$)	44.2	26.0	62.1	71.1	45.6
Grad GZO+Ap ($^{\circ}\text{C}/\mu\text{m}$)	0.74	0.74	1.03	0.89	0.83
Grad GZO ($^{\circ}\text{C}/\mu\text{m}$)	1.11	1.12	1.55	1.33	1.24
Grad YSZ ($^{\circ}\text{C}/\mu\text{m}$)	0.74	0.74	1.03	0.89	0.83
Cooling rate ($^{\circ}\text{C}/\text{min}$)	-140	-25	-100	-200	-100

Table(s)

Deposit	CaO (at. %)	MgO (at. %)	AlO _{1.5} (at. %)	FeO _x (at. %)	SiO ₂ (at. %)	T _g (°C)	T _{IM} (°C)	η ₁₃₀₀ (Pa•s ⁻¹)
CMAS-1	33	9	13	0	45	996	1234	5.3
CFAS-1	33	0	13	10	44	994	1144	3.2

Table(s)

Layer	Thickness h (μm)	Elastic modulus E (GPa)	Poisson's ratio ν	CTE α (10 ⁻⁶ K ⁻¹)	Thermal conductivity k (W•m ⁻¹ K ⁻¹)
FeCrAlY	3000	200	0.3	13	20
Superalloy	3000	200	0.3	15	20
Bond coat	50	180	0.3	15	20
TGO	2	400	0.25	8	20
YSZ	50	40	0.2	11	1.5
GZO	50-200	40	0.2	11	1
GZO+Ap	25	200	0.2	10	1.5
CMAS	10	70	0.2	7	3