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4 **Calcia-Magnesia-Alumino-Silicate (CMAS)-Induced Degradation and Failure of**
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7 **Air Plasma Sprayed Yttria-Stabilized Zirconia Thermal Barrier Coatings**
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Abstract

Thermal barrier coatings (TBCs) used in gas-turbine engines experience severe degradation by calcia-magnesia-alumina-silicate (CMAS) deposits during high-temperature operation. The present study identified and evaluated the chemical and microstructural changes in air plasma-sprayed (APS) 7 wt.% Y_2O_3 stabilized ZrO_2 (7YSZ) TBCs caused by CMAS attack under isothermal conditions at 1340 °C. Additionally, a ‘model’ experimental study was conducted by characterizing 7YSZ ceramic powders immersed in molten CMAS glass at 1300 °C for different exposure times. The combined results from both studies highlight the importance of local CMAS glass composition on the 7YSZ/CMAS interaction. Specifically, low Y-content in the glass, caused by a relatively large glass 'sink,' produces Y-depleted ZrO_2 grains that undergo tetragonal (t) $\rightarrow$ monoclinic (m) phase transformation upon cooling. Alternatively, small pockets of Y-enriched glass induce the formation of t'' - ZrO_2 , a phase characterized by its high stabilizer content. After prolonged high-temperature exposure, solution-precipitation induces the formation of both m - ZrO_2 and t'' - ZrO_2 throughout the APS 7YSZ TBC in accordance with the phase diagram. Using a thermomechanical model it is shown that the strain associated with the martensitic $t \rightarrow m$ phase transformation plays an important role in the delamination failure of TBCs attacked by CMAS.

1. Introduction

Ceramic thermal barrier coatings (TBCs) have become indispensable for protecting and insulating hot-section metallic components in gas-turbine engines used in aerospace and power-generation applications [1-4]. The use of TBCs has allowed higher engine operating temperatures, resulting in enhanced engine performance and efficiency [3, 4]. However, the high operating temperatures result in the melting of any silicates (sand, dust, runway debris, fly ash, volcanic ash, *etc.*) that may be ingested by the engine [5-14]. These molten silicates, commonly referred to as CMAS (calcium-magnesium-alumino-silicate), cause severe degradation of TBCs and premature delamination, exposing the metallic components to dangerously hot gases.

The most commonly used TBC composition is 7 wt.% yttria-stabilized zirconia (7YSZ), which has been optimized based on years of experience [1-4]. The 7YSZ composition crystallizes as the metastable, non-transformable tetragonal phase (t') under ordinary conditions (Fig. 1) [15-17], which has high toughness, both at low and high temperatures, as a result of the reversible ferroelastic toughening [16, 18, 19]. However, prolonged exposure to high temperatures (>1400 °C) results in the destabilization of t' 7YSZ into Y-lean monoclinic (m) and Y-rich tetragonal (t'') ZrO_2 phases (Fig. 1) [20].

The mechanisms involved in the CMAS-induced degradation and failure of 7YSZ TBCs, made by electron-beam physical vapor deposition (EB-PVD) or air plasma spray (APS), have been documented in the literature [5-10, 13, 21-24]. The general features of CMAS attack on 7YSZ TBCs at temperatures <1400 °C include [5, 9, 14, 21, 25]: (i) molten CMAS penetration into the TBC *via* open porosity and cracks, (ii) dissolution of 7YSZ grains in the molten CMAS, (iii) enrichment of Y^{3+} and Zr^{4+} in the CMAS glass, (iv) precipitation of Y-lean ZrO_2 grains, and (v) grain coarsening. The solution-reprecipitation process has been used to describe the formation of Y-lean ZrO_2 grains, where the CMAS wets the TBC surface and dissolves the

grains, introducing Y^{3+} and Zr^{4+} into the glass. The low solubility of Zr^{4+} , compared to Y^{3+} , in CMAS leads to the precipitation of Y-depleted ZrO_2 grains [9, 26]. However, the small amount of Y^{3+} solute available in 7YSZ TBCs (0.08:1::Y:Zr atomic ratio) is not sufficient to alter the composition of the CMAS and its flow behavior significantly, resulting in full TBC penetration by the CMAS. This leads to a significant reduction in the ‘strain-tolerance’ (compliance) of the 7YSZ TBCs during cooling, causing them to fail [14, 27]. Furthermore, CMAS-induced depletion of ZrO_2 grains results in the $t \rightarrow m$ martensitic phase transformation during cooling (Fig. 1), which is associated with a 3-5% volume expansion that can influence the stress state in the CMAS-penetrated TBC [28].

Here we present new insights into the nature of the CMAS/TBC interactions at high temperatures, based on results from experiments on free-standing 7YSZ TBCs and ‘model’ experiments involving 7YSZ powders. Most significantly, we find that the formation of m - ZrO_2 is highly dependent on the Y^{3+} and Zr^{4+} concentrations in the CMAS. We also analyze the influence of the strain arising from the $t \rightarrow m$ martensitic phase transformation on the delamination of a CMAS-penetrated TBC subjected to thermal excursions under a temperature gradient across the TBC.

2. Experimental Procedure

The APS method was used to deposit 7YSZ composition (t' - ZrO_2 phase) TBCs (~300 μm thickness) on aluminum (Al6061) substrates. Hollow-sphere plasma-densified (HOSP) feedstock powder (Metco 204NS, Oerlikon Metco, Westbury, NY) (Fig. 2A) and spray parameters listed in Table 1 were used. APS was performed with an atmospheric DC plasma torch with an 8-mm diameter nozzle and a swirl flow as distribution ring (F4-MB, Oerlikon Metco, Westbury, NY).

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4 The substrates were dissolved in acid to obtain free-standing TBCs, which enabled the use of
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6 high temperatures for isothermal TBC/CMAS interaction studies. Polished cross-sections of as-
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8 sprayed free-standing APS 7YSZ TBCs were thermally etched at 1400 °C for 10 min in a box
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10 furnace to reveal the grain boundaries.
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14 The CMAS powder used here is from previous studies, and the composition (Table 2) is
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16 based on sand from the field [21, 29, 30]. Briefly, a mixture of the oxide constituents in their
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18 stoichiometric amounts were mixed and melted at 1550 °C for 4 h in a platinum crucible, and
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20 then quenched to room temperature in water. The glass was then crushed using a mortar and
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22 pestle, and remelted again to ensure chemical homogeneity. The final CMAS powder was
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24 formed by crushing the glass and then ball-milling it for 72 h in ethanol with ZrO₂ milling media.
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26 (The composition of the CMAS glass was measured after ball-milling using inductively-coupled
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28 plasma atomic-emission spectroscopy (ICP-AES; JY2000, Horiba Jobin Yvon, Edison, NJ), and
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30 the amount of Zr⁴⁺ in the glass was found to be below the detection limit (<0.1 wt.%)). The
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32 CMAS glass frit was mixed in ethanol to form a paste, which was then applied over a small
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34 circular area at the center of top surfaces of the as-sprayed free-standing APS 7YSZ TBCs (30
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36 mg/cm² loading). The isothermal TBC/CMAS interaction studies were performed at 1340 °C for
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38 24 or 72 h in a box furnace, using heating and cooling rates of 10 °C/min. Cross sections from
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40 the center of the interaction regions were cut using a low-speed diamond saw, and then polished
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42 to a 1 μm finish using standard procedures.
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50 As mentioned earlier, the *t'*-ZrO₂ phase in 7YSZ TBCs destabilizes when exposed to high
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52 temperatures for long periods of time without any CMAS [20]. Therefore, control samples of
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54 free-standing APS 7YSZ TBCs were exposed to the same heat treatments as above (1340 °C, 24
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4 or 72 h) but without the CMAS, and they were analyzed to separate the effect of heat-treatment
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6 alone and that due to CMAS attack on the phase transformation in these TBCs.
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9 To complement these studies of high-temperature interactions between free-standing
10 7YSZ TBCs and CMAS, a set of ‘model’ experiments, as described elsewhere, [26] were
11 performed by immersing 7YSZ powder particles in reservoir of molten CMAS glass. Fused and
12 crushed (F&C) 7YSZ powder particles (Oerlikon Metco, Westbury, NY) were used in these
13 experiments because they are fully dense and polycrystalline, and they have uniform
14 morphologies (Fig. 2B) as compared to the HOSP powder (Fig. 2A) used in the APS process. A
15 simplified ‘model’ CMAS composition from previous studies, which contains only the major
16 four components, was used (Table 2) [26, 31]. The ‘model’ CMAS glass powder was prepared
17 using the same method as the regular CMAS glass powder mentioned earlier. Small platinum
18 crucibles (5 mm diameter, 5 mm height) were filled with the ‘model’ CMAS powder and then
19 heat treated at 1350 °C for 4 h, before quenching to room temperature in air. This heat-treatment
20 was repeated to remove any air bubbles and to produce a homogeneous CMAS glass reservoir at
21 the bottom of the crucible. The F&C 7YSZ powder particles (13 wt.% 7YSZ in the
22 CMAS/powder mixture) were placed on the surface of the CMAS glass in the crucible, and then
23 heated to 1300 °C (10 °C/min) and held for either 1 or 4 h, before being quenched in air to room
24 temperature. (The 13 wt.% 7YSZ in CMAS amount is well above the ‘solubility’ limit
25 determined as 7-8 wt% 7YSZ in CMAS in related experiments. In those experiments, various
26 amounts of the F&C 7YSZ powder were mixed with the CMAS powder, and the mixtures heat-
27 treated at 1300 °C for 24 h and characterized using X-ray diffraction.) The platinum crucibles
28 were cut in half using a low-speed diamond saw, and the cross-sections were polished to a 1 µm
29 finish using standard procedures.
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The powder particles and the cross-sections were characterized using a scanning electron microscope (SEM; LEO 1530VP, Carl Zeiss, Munich, Germany), equipped with an energy dispersive spectrometer (EDS). Transmission electron microscopy (TEM; 2100F, JEOL, Peabody, MA or CM20, FEI, Hillsboro, OR), operated at 200 keV accelerating voltage and also equipped with EDS, was used to characterize the cross-sections as well. TEM samples were extracted from specific locations by *in situ* lift-out techniques using a focused ion beam (FIB; Helios 600, FEI, Hillsboro, OR). Selected area electron diffraction patterns (SAEDPs) were collected for various grains and indexed using standard procedures. In the case of the cross-sections from the ‘model’ experiments, the chemical compositions were measured using an electron-probe microanalysis (EPMA; SX-100, Cameca Instruments Inc., Gennevilliers, France) system in the wavelength dispersive spectroscopy (WDS) mode, operated at 15 keV accelerating voltage.

X-ray diffraction (XRD) was performed using a high-resolution diffractometer (D8 Advance Bruker AXS, Karlsruhe, Germany) with $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). XRD patterns were collected from the surface of the TBCs after heat treatment, both with and without CMAS. Detailed analysis of these XRD patterns was performed by the Rietveld method using the standard protocol of refinement [32, 33], employing FullProf integrated into the WinPlotr software package [34].

A confocal Raman spectroscope (Alpha 300, WITec Ulm, Germany), with a He:Ne 633 nm laser source, was used to characterize the cross-sections. In the case of TBC cross-sections, Raman signals were collected using line-scans, where each line-scan is the average of 21 or 11 spectra collected along a 100 or 50 μm line, respectively. The distance between the adjacent line-

scans is 5 μm . In the case of ‘model’ experiment cross-sections, single spectra were collected to identify the crystal structure of various grains.

Results

As-Sprayed TBCs

Figure 3A is a SEM image of the as-sprayed free-standing 7YSZ TBC (thermally etched). Long, interlamellar separations, intralamellar cracks, and large voids are visible throughout the coating thickness. In Fig. 3B, the high magnification SEM image reveals a diversity of the grain structures. Splats with vertical columnar grains ($\sim 0.5 \mu\text{m}$ wide), which are characteristic of APS microstructures, together with regions with equiaxed grains, are visible. EDS measurements were used to confirm that the TBC has no significant chemical gradient across its thickness.

High-Temperature TBC/CMAS Interactions

SEM micrographs in Figs. 4A and 5A show cross-sections of free-standing 7YSZ TBCs after CMAS attack at 1340 $^{\circ}\text{C}$ for 24 and 72 h, respectively. Elemental-Ca maps (Figs. 4B and 5B collected by EDS and WDS, respectively) confirm that the CMAS has penetrated the TBCs completely. Higher magnification SEM images in Fig. 6 show the differences in the microstructure between the top and bottom of the TBCs after CMAS-attack for 24 h and 72 h (1340 $^{\circ}\text{C}$). After 24 h, large pockets of glass surrounded by long, thin grains are observed at the TBC surface. A wider distribution of grain sizes is found at the bottom of the TBC. After 72 h, both the surface and the bottom of the TBC show a similar bimodal distribution of grain size. However, the morphology of the large grains ($>3 \mu\text{m}$ in diameter) changes with penetration depth, where the grains at the bottom appear more globular. Table 3 lists the elemental

compositions (EDS) of several large grains at the surface (Z1 in Fig. 6B) and at the bottom (Z2 and Z3 in Fig. 6D). The large, globular ZrO_2 grains contain high stabilizer content (Ca^{2+} and Y^{3+}).

X-ray Diffraction and Raman Spectroscopy

Figure 7 shows the XRD pattern for the free-standing 7YSZ TBCs after 24 and 72 h at 1340 °C, with and without CMAS. The TBCs without CMAS show low-intensity $m\text{-ZrO}_2$ peaks after both heat treatments. These peaks could indicate the presence of local heterogeneities in the as-received TBC or destabilization from high temperature exposure. However, the peaks are insignificant compared to the $m\text{-ZrO}_2$ peaks observed in the TBCs exposed to CMAS attack, indicating that the CMAS attack induces the $t' \rightarrow t \rightarrow m$ phase transformation. Also, a noticeable increase in the $m\text{-ZrO}_2$ to $t'\text{-ZrO}_2$ peak intensity ratio is observed after longer exposure time (72 h). Rietveld analysis revealed that the surface of the TBC after 24 h heat-treatment contains 54 vol.% $m\text{-ZrO}_2$ – 46 vol.% $t'\text{-ZrO}_2$, whereas after 72 h heat-treatment it contains 68 vol.% $m\text{-ZrO}_2$ – 32 vol.% $t'\text{-ZrO}_2$.

Figures 4C and 5C show Raman spectra (line-scans) from cross-section of 7YSZ TBCs after interaction with the CMAS for 24 h and 72 h at 1340 °C, respectively. In the case of 24 h heat-treatment, the top ~45 μm of the TBC is found to contain $m\text{-ZrO}_2$. However, in the lower part of the TBC only a few scattered spectra show low intensity $m\text{-ZrO}_2$ peaks. In contrast, significant amount of $m\text{-ZrO}_2$ is found throughout the entire TBC thickness (Fig. 5C) in the case of 72 h heat-treatment with CMAS.

Transmission Electron Microscopy

Figures 8A-8C show bright-field TEM images of specimens retrieved from the specified regions (dashed rectangles) in Fig. 4A (1340 °C for 24 h). The surface of the TBC contains a significant amount of CMAS glass (light gray), with small round (*e.g.* Z4 in Fig. 8A) and oblong ZrO₂ (*e.g.* Z5 in Fig. 8A) grains. Figure 9A is a higher-magnification TEM image of the region imaged in Fig. 8A. The contrast in Fig. 9A indicates that most of the ZrO₂ grains at the surface are twinned, which is characteristic of the martensitic $t \rightarrow m$ phase transformation in ZrO₂. SAEDP from those grains (Fig. 9B) is used to identify them as *m*-ZrO₂, and EDS indicates YO_{1.5} <3 mol.% in those grains. Figure 9C shows a high resolution TEM image of a twin boundary in a *m*-ZrO₂ grain. Note that not all grains at or near the top surface are Y-depleted ZrO₂. For example the ZrO₂ grain Z4 in Fig. 8A has 7.0 mol.% YO_{1.5} (Table 4).

Figure 8B is a TEM image of the specimen extracted from ~30 μm below the top surface (see Fig. 4A), showing small, equiaxed *t'*-ZrO₂ grains (*e.g.* Z6), which are identified as such using SAEDP (Figs. 8D) and EDS (Table 4). EDS analysis of those ZrO₂ grains in Fig. 8B reveal that they typically contain >6 mol.% YO_{1.5}. The larger ZrO₂ grains (*e.g.* Z8 in Fig. 8B) are also identified to be *t'*-ZrO₂ using SAEDP (Fig. 8E). At the bottom of the TBC (Fig. 8C), remnants of the columnar grains within the splats can be seen (*e.g.* Z10 in Fig. 8C). These grains show evidence of coarsening and re-arrangement but retain their initial crystal structure (*t'*-ZrO₂) and composition (~8 mol.% YO_{1.5}). The large, globular grains are found to be homogeneous in composition (EDS) and contain excess Ca²⁺ and Y³⁺ (*e.g.* Z9 and Z13 in Fig. 8C and Table 4). The SAEDP (Fig. 8F) shows tetragonal reflections that are forbidden for the cubic structure, thus confirming the presence of *t''*-ZrO₂ (*e.g.* Z13 in Fig. 8A). A few small grains with low Y-content (5 mol.% YO_{1.5}) were observed as well (*e.g.* Z12 in Fig. 8C and Table 4).

The CMAS glass is chemically homogeneous throughout the thickness of the coating, except for isolated SiO₂-rich pockets, as seen in Table 5. Compared to the initial composition, the CMAS glass appears to have lost significant amounts of Ca²⁺, and has gained some Y³⁺ and Zr⁴⁺. Note that some Ca²⁺ is incorporated into the ZrO₂ grains (Table 4) during the solution-reprecipitation process.

'Model' Experiments

Figures 10A-10D are cross-sectional SEM micrographs showing F&C *t'*-ZrO₂ powder particles in 'model' CMAS after 1 h heat-treatment (1300 °C). The overall view in Fig. 10A shows that the particles are clustered near the top surface of the CMAS (the dashed line indicates the periphery of the particle cluster). The higher-magnification SEM image from the top region (Fig. 10B) shows CMAS attack of the particle surfaces, but the interior of the particles appears to be intact. Raman spectra from the particle surface and interior region confirm the presence of tetragonal (*t*) phase, as indicated in Fig. 10B. (Note that it is not possible to distinguish between *t*, *t'*, and *t''* phases using Raman spectroscopy.) This morphology suggests that a solution-reprecipitation process is at work, resulting in the network of small tetragonal ZrO₂ grains along the particle surface and a well-defined planar CMAS-attack front. Also, note the high density of particles found in the cluster, as seen in Fig. 10B. The SEM image in Fig. 10C, which is from Region C in Fig. 10A, shows further penetration of CMAS glass into the particles. The interior of the grains remain *t'*-ZrO₂ (confirmed by WDS), but the outside CMAS-penetrated region consists of small *m*-ZrO₂ grains (confirmed by Raman spectroscopy). The original morphologies are still discernible for the particles in Region C (Fig. 10A and 10C). In contrast, the region near the periphery of the particle-cluster (Region D in Fig. 10A), where the particles are further apart,

consists only of small, rounded m -ZrO₂ grains, and the original particle shapes are no longer discernible (Fig. 10D). Table 6 shows significantly higher Y³⁺ content in the CMAS glass within the particle-cluster, as compared with region below the particle-cluster periphery. However, the Zr⁴⁺ content in the CMAS glass is uniform throughout (Table 6). The cross-section of the 4 h heat-treated (1300 °C) sample is shown in Figs. 10E and 10F. Although the particles are clustered near the surface (Fig. 10E), the morphology and the phase of the ZrO₂ grains are no longer dependent on their location within the CMAS reservoir. The morphology of these grains, identified as m -ZrO₂ using Raman spectroscopy, resembles that of the grains in Fig. 10D. The CMAS glass composition is found to be uniform throughout the sample (Table 6).

Discussion

CMAS-Attack Mechanism

The CMAS-attack characteristics observed in both the TBC and the ‘model’ experiments appear to be consistent with each other. In particular, the formation of Y-depleted ZrO₂ grains and their transformation to m -ZrO₂ phase is highly dependent on their location within the TBC thickness for a given overall heat-treatment duration. It is important to note that at temperatures ≥ 1300 °C, the CMAS glass has a low viscosity (≤ 3 Pa.s⁻¹) [30], and in the case of the TBC it is expected to penetrate the entire thickness of the TBC within minutes. In the case of the ‘model’ experiments, it is expected that the interaction time between the F&C t' -ZrO₂ particles and the CMAS glass is the same for all the particles. Thus, for a given overall heat-treatment duration, the location-dependent differences observed in the ZrO₂ microstructures can be attributed to the relative volume of the CMAS ‘sink’ available in the vicinity.

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4 First consider the results from the ‘model’ experiments. At 1300 °C the dissolution of the
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6 t' -ZrO₂ grains at the surface of the F&C particles introduces Zr⁴⁺ and Y³⁺ into the CMAS melt.
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8 Zr⁴⁺ diffuses relatively rapidly, and thus, the solubility limit of Zr⁴⁺ in the CMAS glass is
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10 reached quickly, resulting in the reprecipitation of Y-lean ZrO₂ grains [9, 30]. Here the stabilizer
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12 content in the reprecipitated ZrO₂ grains depends on the Y-content in the CMAS glass, locally.
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14 Along the particle-cluster periphery, the Y-content in the CMAS glass is low, and, therefore, the
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16 CMAS can accept more Y³⁺ as the ZrO₂ grains continue to dissolve. Subsequently, the Y³⁺ can
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18 diffuse away into the large CMAS glass ‘sink,’ maintaining a low Y-content locally (Table 6),
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20 which is responsible for low Y-content in the ZrO₂ causing them to transform to m -ZrO₂ upon
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22 cooling (Fig. 10D). Within the particle cluster, there is a greater flux of Y³⁺ into the glass due to
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24 the higher concentration of the particles, and thus, the Y-content in the smaller CMAS glass
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26 ‘sink’ is high (Table 6). This leads to higher stabilizer content in the ZrO₂ grains, resulting in the
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28 retention of the tetragonal phase (Figs. 10B-10C). With longer overall heat-treatment duration (4
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30 h), Y³⁺ has diffused throughout the CMAS glass (Table 6), resulting in all grains being Y-lean
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32 and m -ZrO₂ phase upon cooling (Figs. 10E-10F).
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41 In the case of TBCs experiments, the situation is analogous. Initially, the t' -ZrO₂ grain at
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43 the top surface of the TBC are exposed to a large volume of CMAS glass that can incorporate
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45 large amounts of Y³⁺. Therefore, Y-depleted grains reprecipitate out and transform to m -ZrO₂
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47 upon cooling (Figs. 8A and 9; Table 4). Deeper within the TBC, the grains are exposed to
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49 smaller pockets of CMAS glass that are saturated in Y³⁺ (Table 4). Thus, more Y³⁺ is available
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51 locally, resulting in a high Y-content in the reprecipitated ZrO₂ grains that maintain their
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53 tetragonal phase (Figs. 8B-8F; Table 4).
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After 72 h heat-treatment, the TBC shows two different types of grains: Y-depleted m -ZrO₂ and t'' -ZrO₂ with a high stabilizer content, Ca²⁺ and Y³⁺ (Figs. 6B and 6D; Table 3). The chemical compositions and the phases of these grains are consistent with the equilibrium situation depicted in Fig. 1, suggesting destabilization by phase partitioning. The fact that the stabilizer-rich t'' -ZrO₂ phase is not found at shorter heat-treatment duration (24 h) when large CMAS glass 'sink' is present (top surface), suggests that t'' phase forms only when sufficient Y³⁺ is available in the CMAS glass pockets. This also suggests that Y³⁺-saturated CMAS glass may provide a kinetic pathway for facilitating such phase partitioning.

In any case, the formation of m -ZrO₂, either due to simple Y-depletion and/or phase partitioning mediated by Y-saturated CMAS glass, is detrimental to the TBC durability. This is because, in addition to the partial loss of strain tolerance due to CMAS penetration, the $t \rightarrow m$ martensitic transformation in the TBC during cooling, and the attendant tensile strain (3-5%) it generates, is likely to assist in the delamination of TBC [28]. The onset temperature of the $t \rightarrow m$ transformation (T_{transf}) in APS 7YSZ TBCs is determined to be ~600 °C [28], which is well below the glass transition temperature of the CMAS glass ($T_g \sim 700$ °C [21]), and, thus, the transformation strain is not likely to be relaxed. In order to demonstrate this effect quantitatively, thermomechanical analysis is performed for the most prevalent case of delamination at the TBC/metal interface (also referred to as deep-delamination) due to partial CMAS penetration under temperature-gradient conditions. This analysis and the results are described below.

Thermomechanical Analysis of CMAS-Penetrated TBCs and Delamination Maps

Evans and Hutchinson (E-H) derived a simplified model to predict deep delamination in CMAS-penetrated TBCs subjected to thermal excursions under thermal gradients [27]. The strain

in the TBC partially penetrated by CMAS (Fig. 11A) is calculated from the difference in the thermal expansion between the TBC and the substrate. Therefore, the cooling trajectory and the temperature profile through the TBC will determine its failure. The thermal strain, ϵ_{therm} , at any position, y , is given by the following equation [27]:

$$\epsilon_{\text{therm}}(y) = \alpha_{\text{TBC}}\Delta T_y - \alpha_{\text{sub}}\Delta T_{\text{sub}} , \quad \text{Eqn. 1}$$

where α_{TBC} and α_{sub} are the coefficients of thermal expansion (CTE) of the ceramic TBC and the metallic substrate, respectively, ΔT_y and ΔT_{sub} are the temperature differences between the initial and final temperature at y and the substrate-surface, respectively. As CMAS penetrates the TBC, it reduces the compliance of the TBC by filling into the cracks and pores. Therefore, a TBC that is partially-penetrated by CMAS (thickness H or $y=H$) can be treated as a two-layer TBC, as shown in Fig. 11A, where the CMAS-penetrated layer (thickness h , or $y=h$) has a significantly higher elastic modulus, E_1 , compared to that of non-penetrated layer ($y=(H-h)$), E_2 . However, the E-H model does not take into account strain due to the martensitic $t \rightarrow m$ phase transformation (3-5 vol% expansion) during cooling of the Y-depleted CMAS-penetrated layer [28]. To incorporate this important strain contribution, the E-H model is modified to include the additional isotropic strain from the phase transformation (ϵ_{transf}):

$$\epsilon_{\text{total}} = \epsilon_{\text{therm}} + \epsilon_{\text{transf}} , \quad \text{Eqn. 2}$$

where

$$\epsilon_{\text{transf}} = \frac{p\Delta V}{3V} . \quad \text{Eqn. 3}$$

The $\Delta V/V$ represents the transformation volume expansion, which is assumed to be 0.03 [35] and p is the volume fraction of the t' -ZrO₂ grains that have undergone the $t \rightarrow m$ phase transformation. The stress at position y , $\sigma(y)$, in the TBC is given by Eqn. 4 when the temperature of the surface layer is below the phase transformation temperature (T_{transf}):

$$\sigma(y) = \begin{cases} \frac{E_1 \alpha_{\text{TBC}} \Delta T_{\text{sur/sub}}}{(1 - \nu)} \left\{ 1 + \frac{y}{H} - \frac{\Delta \alpha \Delta T_{\text{sub}} + \epsilon_{\text{transf}}}{\Delta \alpha \Delta T_{\text{sur/sub}}} \right\}, & 0 > y > -h \\ \frac{E_2 \alpha_{\text{TBC}} \Delta T_{\text{sur/sub}}}{(1 - \nu)} \left\{ 1 + \frac{y}{H} - \frac{\Delta \alpha \Delta T_{\text{sub}}}{\Delta \alpha \Delta T_{\text{sur/sub}}} \right\}, & -h > y > -H \end{cases} \quad \text{Eqn. 4}$$

where ν is the Poisson ratio of the TBC (same for both layers), $\Delta T_{\text{sur/sub}}$ is the difference between ΔT_{sur} and ΔT_{sub} , where ΔT_{sur} and ΔT_{sub} , are the ΔT 's undergone by the top surface of the TBC and the surface of the substrate, respectively (Fig. 11A). Note that $\epsilon_{\text{transf}} = 0$ in Eqn. 4 for $T_{\text{sur}} > T_{\text{transf}}$.

The stress $\sigma(y)$ is then used to calculate force (P) and moment (M) per unit length, which are given by [27]:

$$P = \int_{-H}^0 \sigma(y) dy \quad \text{Eqn. 5}$$

$$M = \int_{-H}^0 \sigma(y)(D + y) dy \quad \text{Eqn. 6}$$

where D is the location of the neutral axis in bending. A solution for a two-layer system by Suo and Hutchinson [36, 37] is then used to calculate the strain energy release rate (G), mode-I stress intensity factor (K_I), and mode-II stress intensity factor (K_{II}):

$$K_I = \frac{P}{\sqrt{2Ah}} \cos \omega + \frac{M}{\sqrt{2Ih^3}} \sin \omega \quad \text{Eqn. 7}$$

$$K_{II} = \frac{P}{\sqrt{2Ah}} \sin \omega - \frac{M}{\sqrt{2Ih^3}} \cos \omega \quad \text{Eqn. 8}$$

$$G = \frac{1}{2E_2} \left(\frac{P^2}{Ah} + \frac{M^2}{Ih^3} \right), \quad \text{Eqn. 9}$$

where A is the nondimensional effective cross section, I is the moment of inertia, and $\omega = 52.1^\circ$ [36, 37].

Since TBC/substrate interface fracture is known to be mixed-mode, the following relations are used to calculate the fracture energy (Γ_C^i) of that interface [27]:

$$\Gamma_C^i = \Gamma_{IC}^i [1 + \tan^2((1 - \lambda)\psi)], \quad \text{Eqn. 10}$$

$$\psi = \tan^{-1} \left(\frac{K_{II}}{K_I} \right), \quad \text{Eqn. 11}$$

where ψ is the phase angle, λ is the mode-mixity, and Γ_{IC}^i is the mode-I fracture energy; the critical condition for fracture is $G=\Gamma_C^i$.

Several assumptions have been made in this analysis, and they are as follows. The presented solutions are for equilibrium temperature distributions upon cooling, and the transient conditions derived in the E-H model are not included. Elastic modulus (E) is the only material property different between the CMAS-penetrated TBC and non-penetrated TBC, whereas the CTE mismatch is defined by the difference between the entire TBC and the substrate. The thermal diffusivity and CTE are assumed to be the same for both TBC layers. Since $\sigma(y)$ is dependent on T_{transf} and ΔT_y , the starting temperature conditions must be taken into consideration. A parametric analysis is performed as a function of two important variables, the CMAS-penetration depth (h) and the volume fraction of m -ZrO₂ transformed (p). The $t \rightarrow m$ phase transformation is assumed to occur homogeneously throughout h . Table 7 lists the material properties and other parameters used in this analysis.

Figure 11B is a calculated map showing regions of TBC delamination and no-delamination for as a function of p , and at a constant $h/H=0.17$, a reasonable CMAS penetration depth from field experience [10]. The p is varied from 0 to 0.25, where the maximum value is conservative as compared with ~ 0.5 estimated from Rietveld analysis for fully penetrated APS 7YSZ under isothermal conditions (1340 °C, 24 h). The dashed line indicates a linear cooling trajectory from $T_{\text{sur}}^i=1300$ °C and $T_{\text{sub}}^i=1100$ °C (initial temperature gradient of 200 °C) to $T_{\text{sur}}=T_{\text{sub}}=25$ °C. For no $t \rightarrow m$ phase transformation ($p=0$), the cooling trajectory is wholly within the no-delamination region. However, with increasing p , the cooling trajectory starts to enter the

delamination region, indicating TBC failure. The effect of p on TBC delamination illustrates the importance in the formation kinetics of $m\text{-ZrO}_2$. Figures 12A-12C show results for constant p ($=0.15$) but with different h/H (0.03 to 0.33). Once again, the cooling trajectory is wholly within the no-delamination region in Fig. 12A ($h/H=0.03$). However, as the CMAS penetration (h/H) increases, the overall non-delamination regions becomes smaller, and the cooling trajectory crosses into the delamination region in Fig. 12C ($p=0.15$, $h/H=0.33$) as a result of transformation strain. As seen in the isothermal TBC/CMAS interaction tests, the depth at which transformation occurs and p are dependent on exposure time. Therefore, the temperature conditions during operation can provide a better insight for predicting TBC delamination. These results also highlight the importance of including the $t \rightarrow m$ phase transformation strain in the TBC failure analysis.

5. Conclusions

The mechanisms of CMAS attack of APS 7YSZ TBCs are revealed by studying high-temperature interactions between free-standing TBCs and CMAS glass at 1340 °C, and through complementary ‘model’ experiments where 7YSZ powder particles are immersed into a reservoir of molten CMAS glass at 1300 °C. The ‘model’ experiments show that the products of the 7YSZ/CMAS interactions are initially dependent on the relative volume of the CMAS glass ‘sink’ for Y^{3+} in the vicinity of the particles. In particular, locally low Y-content in the CMAS glass due to its relatively large ‘sink’ volume produces Y-depleted ZrO_2 grains nearby that experience $t \rightarrow m$ phase transformation upon cooling. Whereas ZrO_2 grains in the vicinity of a relatively small CMAS glass ‘sink’ remain tetragonal. However, at a longer heat-treatment duration, all ZrO_2 grains are Y-depleted and monoclinic. These results complement those from

the TBC/CMAS interaction studies, where, initially, Y-depleted *m*-ZrO₂ grains are found only at, and near, the top surface of the TBC in contact with a large-volume CMAS glass ‘sink’ for Y³⁺. Deeper within the TBC, the CMAS glass ‘sinks’ (pockets) for Y³⁺ are much smaller, resulting in the Y³⁺ enrichment of the CMAS glass and a high stabilizer content in the reprecipitated ZrO₂ grains. After prolonged high-temperature exposure, solution-reprecipitation induces the formation of *m*-ZrO₂ and *t*’-ZrO₂ throughout the TBC in accordance with the phase diagram. The strain induced by the *t*→*m* martensitic phase transformation in the CMAS-penetrated TBC during cooling plays a significant role in the delamination failure of the TBC. This is demonstrated quantitatively by including the transformation strain in a thermomechanical model, and constructing delamination-failure maps as a function of CMAS-penetration depth and relative volume of ZrO₂ transformed to the monoclinic phase.

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Table 1. APS processing parameters for the deposition of 7YSZ APS TBCs.

Gas Flow Rates (std. lit/min)			Current (A)	Power (kW)	Spray Distance (mm)	Raster Speed (mm/s)	Powder Rate (g/min)	Number of Passes
Primary Ar	Secondary H ₂	Carrier Ar						
47.5	6	4	550	36	100	500	30	~30

Table 2. The CMAS [21, 29, 30] and ‘model’ CMAS [26, 31] (mol.%) compositions used in this study.

	SiO ₂	CaO	MgO	Al ₂ O ₃	Na ₂ O	K ₂ O	Fe ₃ O ₄
CMAS	50.0	38.0	5.0	4.0	1.0	1.0	1.0
‘Model’ CMAS	51.5	39.2	5.2	4.1	-	-	-

Table 3. EDS elemental compositions (cation at.%) of ZrO₂ grains marked in Figs. 6B and 6D.

Grain	Ca	Y	Zr
Z1	-	9	91
Z2	5	11	84
Z3	2	13	85

Table 4. EDS elemental composition (cation at.%) of ZrO₂ grains marked in Fig. 8.

Fig.	Grain	Ca	Y	Zr
8A	Z4	1	7	92
	Z5	-	2	98
8B	Z6	-	9	91
	Z7	-	8	92
	Z8	-	8	92
8C	Z9	4	11	85
	Z10	-	7	93
	Z11	-	10	90
	Z12	-	5	95
	Z13	4	11	85

Table 5. EDS elemental composition (cation at.%) of CMAS glass regions marked in Fig. 8. The overall composition of the CMAS (cation at.%) from Table 2 is also given.

Fig.	Region	Ca	Si	Y	Zr	Al	Mg	Fe	Na	K
8A	G1	26	54	3	2	10	4	1	-	-
	G2	23	54	3	3	11	5	2	-	-
8B	G3	6	88	1	1	3	1	-	-	-
	G4	26	55	3	2	10	4	1	-	-
8C	G5	5	92	1	1	2	-	-	-	-
	G6	27	52	3	2	10	4	1	-	-
	G7	24	56	3	1	10	4	1	-	-
CMAS		35.5	46.7	-	-	7.5	4.7	1.8	1.9	1.9

Table 6. WDS elemental composition (cation at.%) of the CMAS glass at different locations in the ‘model’ experiments (1300 °C for 1 h or 4 h).

Location	Ca	Si	Y	Zr	Al	Mg
Inside Cluster (1 h)	29.7	46.6	2.5	3.5	12.2	5.5
Away from Cluster (1 h)	32.4	47.7	0.8	4.3	9.5	5.4
General (4 h)	32.7	47.9	0.7	4.4	9.3	5.1
‘Model’ CMAS	37.6	49.5	-	-	7.9	5.0

Table 7. Materials properties and other parameters used in the thermomechanical analysis of failure of CMAS-penetrated TBCs under temperature gradient [27].

H (μm)	T_{sub}^i ($^{\circ}\text{C}$)	T_{sur}^i ($^{\circ}\text{C}$)	T_{transf} ($^{\circ}\text{C}$)	E_1 (GPa)	E_2 (GPa)	α_{TBC} ($^{\circ}\text{C}^{-1}$)	α_{sub} ($^{\circ}\text{C}^{-1}$)	ν	Γ_{IC}^i ($\text{J}\cdot\text{m}^{-2}$)	λ
300	1100	1300	600	200	40	11×10^{-6}	15×10^{-6}	0.2	30	0.25

Figure Captions

Figure 1. Phase diagram for the $\text{YO}_{1.5}\text{-ZrO}_2$ system with the metastable phase transitions superimposed (dashed curves) [15, 20]. The conventional 7YSZ (t' - ZrO_2) TBC composition is indicated with a dashed line. The dashed arrows indicate the destabilization pathways of t' - ZrO_2 after: (i) high temperature exposure $\{t' \rightarrow (t+c)\}$, followed by cooling $\{(t+c) \rightarrow (t''+m)\}$ and (ii) from CMAS attack $\{t' \rightarrow t\}$, followed by cooling $\{t \rightarrow m\}$.

Figure 2. SEM micrographs of the 7YSZ (t' - ZrO_2) (A) HOSP feed powder and (B) F&C powder used for depositing the TBCs and the ‘model’ experiments, respectively.

Figure 3: SEM cross section images of a thermally etched 7YSZ free-standing TBC at (A) low and (B) high magnifications.

Figure 4. (A) SEM image of the cross section of the 7YSZ after CMAS-attack (1340 °C, 24 h). The red dashed boxes indicate the locations where the TEM samples, shown in Fig. 8, were retrieved. (B) EDS elemental Ca map showing the location of CMAS in the sample. (C) The Raman spectra line-scans collected from the regions denoted by the black dashed boxes in (A). Major bands corresponding to t - and m - ZrO_2 (gray box) are indicated.

Figure 5. (A) SEM image of the cross section of the 7YSZ after CMAS-attack (1340 °C, 72 h). (B) WDS elemental Ca map showing the location of CMAS in the sample. (C) The Raman spectra line-scans collected from the regions denoted by the black dashed boxes in (A). Major bands corresponding to t - and m - ZrO_2 (gray box) are indicated.

Figure 6. SEM images of the cross sections of APS 7YSZ TBCs after CMAS-attack (1340 °C, 30 mg/cm²) for 24 h, where (A) is the top and (C) is the bottom of the TBC, and for 72 h, where (B) is the top and (D) is the bottom of the TBC.

Figure 7. XRD patterns collected from the surface of APS 7YSZ TBCs after heat-treatment at 1340 °C for 24 and 72 h, both with and without CMAS-attack.

Figure 8. TEM micrographs of the 7YSZ coating after CMAS-attack (1340 °C, 24 h) from (A) near the surface, (B) ~30 below the surface, and (C) at the bottom of the coating, as indicated in Fig. 4A. Indexed SAEDPs of particles (D) Z6, (E) Z8, and (F) Z13 are included, where ‘*B*’ indicates the zone axis and the transmitted beam is circled. Indexed reflections with the subscript ‘*t*’ indicate those observed in tetragonal structures but forbidden in cubic structures.

Figure 9. (A) High magnification TEM micrograph of grains in Fig. 8A (the surface of 7YSZ after CMAS-attack at 1340 °C for 24 h). (B) SAEDP of *m*-ZrO₂ grain in (A), where ‘*B*’ indicates the zone axis and the transmitted beam is circled. The dashed box and corresponding reflections, which are indexed with the subscript ‘*T*’, indicate mirror reflections observed due to twinning. (C) High resolution TEM image of twin boundary from grain in (A).

Figure 10. Low-magnification SEM images showing distribution of F&C powders in CMAS-filled Pt crucible after heat treatment at 1300 °C for (A) 1 h and (E) 4 h. (B-D, F) High-magnification SEM images of regions specified in (A) and (E). The crystal structure, as determined by Raman spectroscopy, is indicated for various grains, where *t* and *m* represent tetragonal ZrO₂ and monoclinic-ZrO₂, respectively.

Figure 11. (A) TBC system schematic used for the delamination model that indicates the temperature profile during cooling. (B) Delamination maps for the system described by

parameters in Table 7 and $h/H=0.17$, where p is varied from 0 to 0.25. The purple dashed arrow indicates a linear cooling trajectory.

Figure 12. Delamination maps for the system described by parameters in Table 7 and $p = 0.15$ and solved for different values of h/H : (A) 0.03, (B) 0.17, and (C) 0.33. The purple dashed arrows indicate linear cooling trajectory.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

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Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12