Degradation of $\text{La}_2\text{Zr}_2\text{O}_7$ and other novel EB-PVD thermal barrier coatings by CMAS ($\text{CaO}–\text{MgO}–\text{Al}_2\text{O}_3–\text{SiO}_2$) and volcanic ash deposits

Uwe Schulz *, Wolfgang Braue

German Aerospace Center (DLR), Institute of Materials Research, 51170 Cologne, Germany

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Corrosive attack of CMAS deposits is studied for a series of advanced EB-PVD thermal barrier coatings including 14YSZ, HSZ, 29DySZ, CeSZ, La$_2$Zr$_2$O$_7$, and Gd$_2$Zr$_2$O$_7$ upon a 2 hour anneal at 1260 °C in air. Furthermore, the effects of volcanic ash deposits on La$_2$Zr$_2$O$_7$, and Gd$_2$Zr$_2$O$_7$ are studied. A 7YSZ standard coating is employed for benchmarking the resulting microstructures and the coating performances in terms of infiltration depth and chemical reactivity. While all investigated zirconia-based coatings become fully infiltrated by the deposits, the zirconates form crystalline reaction products that prevent complete infiltration. The La$_2$Zr$_2$O$_7$ system is treated as a case study with detailed insight on the newly formed phases via analytical TEM.

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1. Introduction

Substantial efforts have been put into raising the operating temperature of turbines for aero engines which is demanded to increase their efficiency and to lower specific fuel consumption. This has not only led to a much higher load on the materials in the hot section, but has also revealed a new premature failure mechanism in the commonly applied thermal barrier coatings (TBCs) on components of the combustion chamber as well as the high pressure turbine section. In addition to bond coat oxidation and cyclic driven failure, these thermally insulating coatings are damaged by oxide particles that are ingested into the engine by the intake air. Ingestion may occur preferentially during takeoff and landing where the particle concentration is higher, but dust can also be found in higher altitudes during cruise. In earlier TBC applications and in older engines operating at lower surface temperature the particles form solid deposits which may lead to cooling hole clogging, stiffening of the TBC, or to erosion. In contrast, beginning in the early 90’s in military applications and later on in civil aircraft the attack of coatings by molten deposits was reported [1–3]. This was clearly a consequence of the increased surface temperature that exceeded the deposit melting temperature which is typically between 1150 and 1250 °C.

The chemical composition of ingested particles typically reflects the composition of sediments and dusts; thus, their main components are calcium–magnesium–aluminum–silicates (CMAS). Those mixtures have been widely studied in laboratory under controlled conditions and with mostly fixed compositions. There is ample literature that describes the high-temperature interaction of artificial CMAS with 7YSZ (7 wt.% yttria stabilized zirconia) TBCs [4–6].

The effects of ingested volcanic ash particles on TBC performance have recently stirred considerable interest. In spring 2010, the plume of the massive eruption of the Eyjafjallajökull volcano in southern Iceland released ash in high altitudes imposing serious limitations on European air traffic. According to the chemical analyses, the Eyjafjallajökull volcanic ash exhibits a much higher SiO$_2$ content and a higher chemical complexity than the CMAS-type deposits reported in the literature [7,8]. Typically, different volcanic provinces around the globe exhibit characteristic chemical compositions that may substantially differ from the Iceland eruption.

The common understanding is that both CMAS and volcanic ash rapidly infiltrate the 7YSZ TBC once their melting temperature is exceeded. As a consequence, they fill the pores and columnar gaps in TBCs manufactured by electron beam physical vapor deposition (EB-PVD). This effect drastically raises the Young’s modulus and lowers the strain compliance. Depending on the temperature gradient in the blade and the associated penetration depth, local cold shock spallation of the TBC occurs. In addition, CMAS and volcanic ash react with 7YSZ and destabilize the top coat. Depending on deposit chemistry, a variety of reaction settings exists ranging from dissolution of the TBC in the CMAS melt with subsequent re-precipitation of undesired monoclinic zirconia up to leaching Y out of the metastable tetragonal zirconia solid solution and concurrent formation of silicide-type reaction products as found for volcanic ash [4–8]. All effects together eventually cause premature TBC failure. The thermal conductivity of 7YSZ EB-PVD TBCs is only slightly increased by CMAS infiltration at 1260 °C while pore coarsening controls the substantial increase in thermal conductivity at higher temperatures [9]. Similar damage initiated by deposits occurs in plasma
sprayed TBCs that are not within the focus of this paper. Complement-
ary work was performed on CMSA attack on real engine hardware
[1,4,10,11] that may additionally involve CaSO₄ deposits and a Fe–Ti-
rich CMSA composition [12,13], which drastically changes the reaction
scheme between deposits and TBC.

TBC research during the last decade was mainly directed towards
further improvements of major coating properties. The focus was on
lower thermal conductivity, increased temperature capability including
reduced sintering and enhanced phase stability, and longer TBC life.
Promising TBC materials have been identified in the following material
classes: zirconia-based (weakly stabilized zirconium oxide), hafnia-
based, pyrochlores, hexa-aluminates, and perovskites [14–20]. Among
others, rare-earth zirconates offer a reasonable potential for TBC applica-
tion. Reduced thermal conductivity as well as improved sintering resis-
tance have been obtained with EB-PVD pyrochlore-like TBCs, especially
Gd₂Zr₂O₇ (GdZ) [21] and Sm₂Zr₂O₇ [22]. Despite some processing diffi-
culties [23], La₂Zr₂O₇ (LaZ) was also identified as a promising candidate
coating. Dopping with 3–10% yttria reduced the compositional scatter
during evaporation for this material [24].

Studies on CMSA/volcanic ash-type hot corrosion of TBC materials
other than 7YSZ and GdZ are rather rare. Gd₂Zr₂O₇ shows rapid reaction
with CMSA and crystallization of an apatite bearing thin reaction layer
which mitigates further infiltration of CMSA and volcanic ash [15,25–29].

This paper compares the infiltration behavior and chemical reactiv-
ty of seven TBCs (7YSZ, 14YSZ, HfSZ, 29DySZ, CeSZ, La₂Zr₂O₇, and
for comparison Gd₂Zr₂O₇) upon CMSA attack given relatively harsh ther-
mal loading conditions of 1260 °C for 2 h. The effects of volcanic ash
are studied for La₂Zr₂O₇, and Gd₂Zr₂O₇ as well. All coatings investigated
were deposited by EB-PVD. The La₂Zr₂O₇ is introduced as a detailed case
study with further insight via analytical TEM (transmission electron
microscopy) on the reactive interfaces introduced upon reaction with
CMSA and volcanic ash respectively.

2. Experimental

Flat Ni-based superalloys, FeCrAlY, and polycrystalline alumina cou-
pons served as substrates for the coating experiments. An 80 to 120 μm
thick standard NiCoCrAlY bond coat with a nominal composition of
Ni–22Co–20Cr–12Al–0.2Y (wt.%) was deposited by EB-PVD on the
Ni-based superalloys. The bond coat received the common peening pro-
cedure and a vacuum heat treatment for 4 h at 1080 °C. The ceramic top
bondings served as substrates for the coating experiments. An 80 to 120
μm thick NiCoCrAlY bond coat with a nominal composition of the
base metal, while alumina substrates were annealed in air.

Seven different TBCs were deposited by EB-PVD at various thick-
nesses, namely: 7YSZ as a reference (standard thickness), 14YSZ
(14 wt.% Y₂O₃–ZrO₂), 29DySZ (29 wt.% Dy₂O₃–ZrO₂), CeO₂ stabilized
zirconia CeSZ (concentration of ceria varied between 9 and 25 wt.%
on different samples), and Gd₂Zr₂O₇ (GdZ). All these TBCs had a thickness
between 128 and 210 μm. Samples that had a thicker TBC between 220
and 370 μm included 7YSZ, HfYSZ (28 wt.% HfO₂–12 wt.% Y₂O₃–
ZrO₂), and La₂Zr₂O₇ doped with 3 wt.% Y₂O₃ (LaZ). The variance in TBC
thickness owes to the origin of the samples from various previous
research projects. The stabilized zirconium oxide versions 7YSZ,
14YSZ, 29DySZ, and CeSZ are named in this paper “zirconia-based” in
contrast to the two “zirconates”. The stabilizing ions for zirconia-based
were chosen to cover both tetragonal t’ (7YSZ) and cubic phases, and
to investigate the effect of different ionic masses and radii.

A CMSA standard model composition of 33.2% CaO, 6.5% MgO, 11.8%
Al₂O₃, and 48.5% SiO₂ (in wt.%) adopted from [6] was synthesized by
mixing of appropriate powders and solutions, melting them at
1260 °C, and crushing the glassy CMSA into fine powder. A small
amount of ethanol CMSA solution was applied onto the TBCs, followed
by drying, and finally infiltration at 1260 °C for 2 h. Heating rates of
10 K/min were applied for both, air and vacuum annealing. CMSA was
applied to all seven TBC systems studied. The artificial volcanic ash
(AVA) employed in this study consisted of 5.2% CaO, 2.15% MgO, 15.5%
Al₂O₃, 57.9% SiO₂, 9.65% FeO, 1.6% TiO₂, 5.25% Na₂O, 1.75% K₂O, 0.27%
MnO, and 0.73 P₂O₅ (in wt.% and represents a typical bulk composition
of the Eyjafjallajökull event during the April 2010 eruption. Synthesis
and application of AVA is described elsewhere [7]. AVA was applied
with 12 mg/cm² of solid was applied on samples with a TBC thickness of 220 μm and smaller. Thick TBCs received 20 mg/cm² deposits.

The infiltration annealing was performed in vacuum for Ni-based su-
perlloys and FeCrAIY substrates in order to avoid severe oxidation of
the base metal, while alumina substrates were annealed in air.

Following infiltration the samples were cross-sectioned according to
standard metallographic procedures and then analyzed in a DSM Ultra
55 scanning electron microscope (SEM) (Carl Zeiss NTS, Germany with
Inca EDS and EBSD, Oxford, U.K.). Focused- ion-beam (FIB)-assisted an-
alitical transmission electron microscopy (TEM) from CMAS and AVA
infiltrated LaZ samples were performed in a Strata 205 FIB system and
an analytical Tecnai F30 TEM/STEM microscope utilizing a field-
emission gun (FEI Inc., The Netherlands).

3. Results

3.1. Zirconia-based TBCs under corrosive attack (CMSA, AVA)

The standard 7YSZ TBCs were attacked by CMSA in the common
way. The reaction scenario includes infiltration of the whole TBC
down to the substrate, complete filling of the inter-columnar pores,
and disintegration of feather-arms. CMSA infiltration and reaction be-
behavior were independent of annealing atmosphere (vacuum or air)
and TBC thickness. All observations on EB-PVD 7YSZ TBCs were in
good agreement with literature data available for standard CMSA
[6,8,30] and modified Fe-CMAS [30]. Therefore, 7YSZ is addressed here
only to benchmark the new TBC systems.

Fig. 1 depicts alternative zirconia-based TBC compositions after
CMSA attack. All grades showed a reaction scenario similar to 7YSZ
with subtle differences only. Infiltration has progressed towards the
TBC root area. The CMSA composition in the inter-columnar gaps
and larger feather-arms was essentially the same as on top of the TBCs.
The high annealing temperature of 1260 °C promoted chemical reac-
tions at the column tips (Fig. 1a and e). The columnar structure got
dissolved and material was reprecipitated with a slightly different com-
position than the original TBC incorporating minor amounts of CMSA
constituents, similarly as found in [6] for 7YSZ. Some zirconia got
dissolved into the CMSA melt close to the reaction regions. Large hori-
zontal cracks were also occasionally observed in the infiltrated TBCs
(Fig. 1d) that are usually quite untypical for EB-PVD TBCs not subjected
to deposits. For deposit free samples annealed under the same condi-
tions the columnar structure with its feather-arms and pores was still
intact. It only underwent the typical morphological changes caused by
sintering such as pore coalescence which have been described for
7YSZ in detail elsewhere [31,32].

CMSA on 14YSZ and 29DySZ on alumina substrates reacted also with
the TBC in the root area (Fig. 1b and d). The TBC reprecipitated as glo-
bular grains with a composition close to 14YSZ or 29DySZ with some
dissolved Ca (~2 wt.%). This reprecipitation was also observed when a
small diffusion barrier of platinum (bright gray layer highlighted by
the arrows in Fig. 1d)) was deposited between the DySZ TBC and the
alumina substrate.

HYSZ was evaporated from two sources, namely (i) a 7YSZ ingot
and (ii) a hafnia and yttria rich ZrO₂ ingot. The rotation through the
two vapor clouds over the two crucibles created the distinct stria-
tions visible in Fig. 1(e). The column tips were also heavily attacked and
globular Ca-doped fully stabilized zirconia grains are evident with the latter
also abundant in inter-columnar gaps and close to the substrate. A sim-
ilar attack of the TBC with complete infiltration by CMSAS was found for
CeSZ TBCs with the thickness of the reaction zone depending on the
CeO₂ content of the top coat. To avoid duplications, pictures of this TBC version are not given.

3.2. Pyrochlore-type TBCs under corrosive attack by CMAS

In Fig. 2 gross-scale microstructures of the reaction zones between CMAS and both, Gd₂Zr₂O₇ (GdZ) and La₂Zr₂O₇ − 3 wt.% Y₂O₃ (LaZ) EB-PVD TBCs are shown. The situation is quite different from the zirconia based compositions (Fig. 1) as the formation of crystalline reaction products is promoted via rapid CMAS/TBC interaction at the column tips as well as within the inter-columnar gaps. Column tips of GdZ were dissolved and reaction products reprecipitated within a 3 to 5 μm thick reaction layer which is retained along the column tips and the rims of wider inter-columnar gaps. Restriction of the reaction to the column rims becomes evident in Fig. 2b which displays a composite image of an EDS silicon map with the corresponding SEM image. CMAS constituents were not detected inside the columns. The more feathery and open-columnar structure of GdZ (as compared to 7YSZ) is not necessarily detrimental for CMAS mitigation, but on more narrow inter-columnar gaps the infiltration depth is slightly lower than within larger gaps. Small probe microanalysis data of the reaction products agreed well with the data given in [25–29] suggesting the presence of Ca–Gd–apatite of needle-like morphology and a globular cubic zirconia phase. For these annealing conditions, a mitigation of CMAS in infiltration inside inter-columnar gaps was observed at a depth of 60 to 80 μm from the coating’s surface.

A variety of reaction scenarios and microstructures was found on LaZ TBCs, ranging from complete disintegration of the TBC top region and fully reacted compact layers as shown in Fig. 2c) up to reactions that took mainly place on the outer column rims inside and along larger inter-columnar gaps (see Fig. 3). The latter reaction is similar to GdZ where this setting is predominantly found. For LaZ, the reaction layer depth of around 10 μm is somewhat thicker than on GdZ, even under the scenario of exclusive reaction on column rims. The morphology of LaZ processed via EB-PVD is characterized by a more compact microstructure of branching columns having small diameters and quite narrow inter-columnar gaps, and on the other hand frequently occurring larger columnar gaps of varying width that possibly developed by the large shrinkage of the material during manufacture [18,24,33]. As a consequence, CMAS can penetrate locally quite deep into the coating in those gaps, occasionally reaching the substrate surface in case of very large inter-columnar gaps. Inside inter-columnar gaps of moderate width crystalline reaction products are formed up to a depth of 30 to 50 μm inhibiting further CMAS infiltration.

Fig. 3 highlights the cross-section microstructure of the phases found in the LaZ/CMAS system in an area where inter-columnar gaps are well developed and reactions are limited to the column rims. A FIB section of the reaction layer was prepared in the vicinity of a former column and analyzed in TEM. This investigation of the fine-grained La₂Zr₂O₇/CMAS reaction layer (Fig. 3) just above the zirconate top coat revealed a total of three different crystalline phases and an amorphous phase located at grain junctions and grain boundaries, as shown in the
The crystalline phase assemblage included (i) the lath-shaped Ca$_2$La$_8$(SiO$_4$)$_6$O$_2$ La-apatite phase\(^{34,35}\) holding small amounts of Y and Zr, (ii) the Ca$_2$Al$_2$SiO$_7$ gehlenite phase with 2 mol% MgO in solid solution and, (iii) the Ca$_3$ZrSi$_2$O$_9$ phase, also known as the mineral baghdadite\(^{36,37}\). Apart from quantitative X-ray microanalysis these phases were unambiguously identified via electron diffraction. The corresponding zone axis patterns are implemented in Fig. 4. The amorphous phase is a CMAS-bearing silica-rich glass with holding approximately 1 mol% La$_2$O$_3$. Y uptake of the amorphous phase is close to the EDS detection limit.

The reactive interface as described is also retained along the inter-columnar gaps. As shown in the electron-backscattered diffraction (EBSD) image (Fig. 5), the apatite phase is joined by La-doped fully stabilized zirconia along with gehlenite and minor amounts of baghdadite and anorthite. These are essentially the same phases found in the TEM investigation with additional appearance of zirconia and minor amounts of the anorthite phase. Note that different locations were selected for TEM vs. EBSD. While TEM was performed on the column rims, the EBSD pattern was collected in an inter-columnar gap approximately 30 \(\mu\)m below the column tips. On the wider inter-columnar gaps, the reaction front has progressed into the column interior (perpendicular to the column axis) by about 3 to 8 \(\mu\)m, which is slightly less than the reaction zone thickness of about 10 \(\mu\)m found on the column tips.

### 3.3. Pyrochlore-type TBCs under corrosive attack by AVA

For both pyrochlore based-TBCs the reaction depth is higher under AVA attack as compared to CMAS under the same annealing conditions, as shown in Fig. 6. In addition, the corrosive attack of GdZ by AVA (Fig. 6(a)) is more severe than the reaction of the same coating with CMAS (Fig. 6(b)). The varying depth of the reaction front implies that inter-columnar gaps are partly filled by both deposits, but for AVA almost the whole column interior has completely reacted while under CMAS attack the reaction is restricted to the outer column rim (compare Fig. 6(a) and (b)). The reaction has proceeded to a depth between 70 and 100 \(\mu\)m, leading to a partial loss of Gd in the reaction zone with Si, Ca and Fe being incorporated into the coating. On top of the columns a thin zone of about 10 \(\mu\)m thickness is visible that contains large globular grains of 1 to 5 \(\mu\)m dimensions rich in zirconia holding substantial amounts of Gd and some Fe. In the former AVA numerous precipitates
of varying shape and size occur. The highly complex thermo-chemical interaction of volcanic ash with Gd$_2$Zr$_2$O$_7$ EB-PVD coatings requires more fundamental work including TEM and investigation of powder based mixtures of the reactants, as described in [29].

In the LaZ coating the reaction has proceeded down as a reaction front to a depth of about 100 μm which is slightly higher than in GdZ. Unlike the CMAS system, preferred reaction within inter-columnar gaps is not observed. Due to inward diffusion of AVA elements and the outward flux of elements from the former top coat into the AVA three different reaction subzones (1–3) can be distinguished (Fig. 6(c)). Reaction zones 1 and 2 basically differ in their ratio of crystalline phases to modified AVA melt and in the grain sizes of phases precipitated, the former one increasing from top to bottom of the bulk reaction zone. Zone 1 consists of the former AVA melt and several precipitated phases of needle-like or faceted morphology while the upper reaction zone 2 is characterized by more numerous Zr-rich precipitates of predominantly globular appearance that are low in their La-content (Fig. 7). The lower reaction zone 3 is the fully reacted former TBC which looks compact. Their columnar coating structure has completely converted into small globular grains in the 1 μm range. The content of Zr and La is lower compared to the intact TBC regions, but still higher than in zones 2 and 1. AVA constituents are also confirmed in this zone but at a lower amount than in the upper and outer former AVA zone. The interface between zones 2 and 3 seems to mark the former top coat surface that might has slightly shifted due to corrosive reactions.

FIB-assisted TEM investigations were performed from various locations at the boundary between sublayers 1 and 2, and within zone 3 in order to unambiguously identify the phases involved in La$_2$Zr$_2$O$_7$/AVA inter-diffusion and reaction.

The former AVA melt reaction zone (1) consists of faceted La$_2$Si$_2$O$_7$ grains (bright phase in upper part of Fig. 7) embedded in an amorphous AVA matrix. The silicates appear mostly in a needle-type shape at various orientations with regard to the former TBC surface, leading to an either rhombic (Fig. 8) or elongated needle like appearance in cross sections. Indexing of La$_2$Si$_2$O$_7$ electron diffraction patterns was consistent with the structure and cell parameters given by [38] for the tetragonal high-temperature polymorph. Etch grooves developed in the La$_2$Si$_2$O$_7$ grain from Fig. 8 suggest the silicate phase is probably retained metastably in the AVA/LaZ reaction zone 1.

Numerous microspheres, apparently crystalline and typically between 50 and 200 nm in size, are found dispersed throughout the residual AVA melt in zone 1. This is not an unusual finding as synthetic AVA glass typically includes nanosized precipitates of ferric oxide (hematite) solid solution already in the as-processed condition glass [29]. Due to their embedded nature it is difficult to collect an EDS spectrum from a microsphere that devoids the contribution of the surrounding silaceous AVA matrix. Z-contrast imaging in STEM dark field indicates an inhomogeneous impurity distribution across the microspheres (see bright dots in Fig. 9). From EDS mapping (not shown) Fe is identified as the major constituent of the microspheres. The elements Mg, Y, P, La and Zr are enriched in the spheres relative to the surrounding modified AVA
matrix while Al and Si are significantly depleted. The 0.272 nm lattice spacing corresponding to the strongest reflections collected from the microspheres via electron diffraction excludes possible ZrO2 polymorphs, but is again consistent with a ferric oxide (hematite Fe2O3) solid solution.

Between former AVA melt (zone 1) and upper LaZ/AVA reaction zone 2 precipitation of Fe2SiO4 (fayalite) solid solution (Fig. 10) is a prominent feature which has been identified via electron diffraction (see inset) and small probe microanalysis. Fayalite grains are arranged in a needle-like texture and contain small amounts of Mg and Al along with traces of minor other AVA constituents such as P and Mn.

The lower AVA/LaZ reaction zone 3 (Fig. 11) holds three crystalline phases, the La-apatite phase Ca2La8(SiO4)6O2, tetragonal La2Si2O7 and monoclinic ZrO2. Again a non-crystalline phase is located at triple grain junctions. Its volume fraction however, is considerably lower than in reaction zones 1 and 2, respectively. The apatite and silicate phases exhibit lath-shaped grain morphologies while the heavily twinned m-ZrO2 is always globular. Small amounts of Fe, Y, and Zr did segregate to the La-apatite phase. Although previous work has derived an extended Al2O3 solubility range for La-apatite [39], no Al was detected in the apatite phase for both, the CMAS and the AVA systems which are consistent to similar findings for the GdZ/CMAS system in [25]. The amorphous phase is an aluminosilicate glass holding substantial amounts of Fe, La and Mg along with traces of Ca, Y and Zr. It presents a modified AVA melt composition upon uptake of La, Zr and Y characteristic of the penetration level of the progressing reaction.

In essence, three different LaZ/AVA reaction zones have been identified:

1. The reaction zone 1 of the former AVA melt consists of modified AVA glass holding nanoscale globular precipitations (presumably hematite solid solution) and La2Si2O7 needles.
2. The upper reaction zone 2 is dominated by globular zirconia-rich grains, La-silicate, and modified AVA. Fe2SiO4 (fayalite) is abundant in the transition range between the former AVA melt and upper zone respectively.
3. The lower reaction zone 3 comprises La-apatite, La2Si2O7 and twinned m-ZrO2 along with a noncrystalline phase at triple grain junctions. It represents the former TBC that has already reacted with AVA but is still rich in La and Zr.
4. Discussion

The present experiments reveal that under a 2 h isothermal annealing at 1260 °C the investigated zirconia-based TBCs were fully infiltrated by CMAS down to the substrate. Unlike the pyrochlore-type TBCs they provide no mitigation potential. The coatings are left completely infiltrated via TBC dissolution–precipitation processes and formation of new zirconia-rich phases preferably at the column tips, within the inter-columnar gaps and in the fine grained TBC root area. This implies a low chemical reactivity of the zirconia-based materials with CMAS while the propensity to infiltration is high, regardless of tetragonal or cubic zirconia polymorphs in the top coat and nearly independent of amount and type of stabilizing ion in the zirconia lattice. As a consequence, the whole TBCs got infiltrated by CMAS under laboratory conditions where a temperature gradient across the coating is absent. This leads eventually to stiffening and crack formation of the TBC which makes the coating susceptible to thermomechanical driven failure [8]. The minor variations among the zirconia-based compositions investigated here included (i) thickness of the TBC-CMAS reaction zone on the column tips, (ii) the extent of attack of feather-arms and fine-porous features at the column rims, and (iii) the amount of reprecipitated globular grains close to the substrate.

The findings of enhanced reactions between EB-PVD TBC and CMAS close to the TBC/substrate interface, particularly by using a platinum diffusion barrier between alumina TGO and 7YSZ TBC (Fig. 1b), suggest that a major reason for the heavier reaction here is the fine columnar, high grain boundary density structure adjacent to the substrate surface. Presence of a TGO might not be absolutely necessary to promote this reaction. Due to the small grain and column sizes (sub-micron range) diffusion is enhanced and hence chemical reactivity (dissolution and reprecipitation) is higher than in the bulk coating where the column diameter is in the range of 2 to 15 μm. Needless to say that alumina as the major constituent of the TGO will heavily participate in the reaction with CMAS and AVA under isothermal conditions, leading to solution and precipitation processes that yields modified phases in this area compared to the bulk of the TBC.

The reaction of the two pyrochlore-type TBCs investigated with AVA often involved the whole coating including the column interiors while under CMAS attack a fast reaction along the column periphery prevailed. This is unambiguously caused by variances in reactivity due to striking differences in deposit chemistry and consequently variations in formation of crystalline reaction products. These chemical effects are discussed below. Table 1 summarizes reaction depth inside columns, mode of reaction, and maximum global infiltration depth which was defined as the maximal distance between TBC surface and the transition between un-reacted and reacted TBC areas within inter-columnar gaps.

The reaction scenario between GdZ and CMAS found in this study agrees with previously published work. GdZ mainly served as comparison for the other pyrochlore TBC studied, and was therefore not investigated in TEM. Interestingly, the current findings mark an earlier damage stage than the one described in [25] for a nominally identical EB-PVD GdZ TBC–CMAS combination, but investigated after 4 h at 1300 °C. While the present research after 2 h at 1260 °C revealed only attack at the column outer rims to a maximum depth of 5 μm, the whole column tips were dissolved and reaction products reprecipitated at a thickness of up to 8 μm after the more severe annealing which indicates a progressing reaction into the column interior with increasing time and temperature. The current findings are fully consistent with the proposed progressing reaction mechanism proposed in [8,25]. The much deeper global infiltration and reaction inside inter-columnar gaps for the present work (up to 80 μm) as compared to 30 μm in the previous work may be due to differences in the width of the inter-columnar gaps that seem to be larger for the current coatings compared to the previous research. Obviously, larger gaps allow the CMAS to penetrate deeper before competing TBC dissolution and subsequent crystallization of the apatite blocks those channels and prevents further infiltration as shown in Fig. 6b). Differences in column morphology are known to be caused by variances in the deposition conditions [16,40], most likely the higher condensation speed here plays a role (4.6 μm/h compared to 2 μm/h). In addition to the variance in annealing temperature, a source of gradual differences in the findings might be the nature of the synthetic CMAS, i.e. amorphous versus partially crystalline depending on the processing routes during deposit synthesis.

The reaction between LaZ and CMAS is similar to the GdZ system but due to the more inhomogeneous columnar microstructure of LaZ it differs in some details. Different microstructures and reaction depths have been found. One of them is the reaction restricted to column tips and rims (see Fig. 3). The slightly lower reaction zone thickness on column rims inside larger columnar gaps compared to its thickness on top of the columns (see Table 1) is assumed to be a consequence of reduced supply of CMAS into the gaps and rapid formation of gehlenite (see Fig. 5) which limits the availability of elements needed to form apatite. In addition to the former scenario, fully reacted compact TBC layers are typical for the LaZ system (see Fig. 2c). This is assumed to be a consequence of lacking coarse and well separated columns as commonly found in 7YSZ.

The high reactivity of LaZ with CMAS yielded several crystalline reaction products. Depending on the local concentration, diffusion conditions, and kinetics of the reactions involved, the apatite phase formed either as a needle-like precipitate ranging into the CMAS-rich region above the TBC, or it was involved in the reaction zone within the columnar solid outer rim, designated CMAS/LaZ reaction layer in Fig. 3. In a situation of CMAS excess, the former CMAS in contact with the TBC transformed into a four-phase assemblage consisting of a La-bearing amorphous phase, La-apatite Ca₂La₈(SiO₄)₆O₂, gehlenite Ca₆Al₂SiO₇ and baghdadite Ca₃ZrSiO₆, and occasionally occurring globular zirconia grains decorating the column edges.

The reaction of AVA with GdZ yielded fully reacted column interiors and complete disintegration of the column tips, giving rise to formation of a new phase of mostly globular shape which contains high amounts of Zr, Gd and Fe. The somewhat deeper infiltration of some inter-columnar gaps (see Fig. 6a) again evidences the effect of column architecture on infiltration depth as described for the CMAS case above. Obviously, infiltration depth in more narrow inter-columnar gaps is lower yielding better sealing of these channels by crystalline phases than within wider gaps. A detailed discussion on the complex phase relationships and reaction sequences in the GdZ/AVA system can be found in [29], while this version served in the present study only as a reference to compare the results with the extensively studied LaZ TBC.

The results of SEM, EBSD, and TEM investigation of the LaZ TBC under AVA attack offer insight into several reaction schemes.

Table 1

<table>
<thead>
<tr>
<th>Version</th>
<th>Maximum reaction depth within columns (μm)</th>
<th>Reaction mode</th>
<th>Maximum global infiltration depth (μm)</th>
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<tr>
<td>GdZ/CMAS</td>
<td>5 Rims + inter-columnar gaps</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>LaZ/CMAS</td>
<td>10 On top fully reacted (front)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>GdZ/AVA</td>
<td>8 Rims within inter-columnar gaps</td>
<td>50 to fully infiltrated</td>
<td></td>
</tr>
<tr>
<td>LaZ/AVA</td>
<td>Fully reacted</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- GdZ TBC–CMAS combination, but investigated after 4 h at 1300 °C.
between AVA and LaZ is higher than the infiltration kinetics of inter-columnar gaps by AVA, the latter one being mainly governed by deposit viscosity and wetting of AVA. Simultaneously, the reactivity between AVA and LaZ must have been high enough to block gaps and channels in the coating via precipitation of crystalline reaction products.

ii.) The high Si and low Ca contents in AVA gave rise to the formation of La- and Fe-silicates in the outer and upper reaction zones, while mainly Ca–Al–or Ca–Zr-silicates are formed under CMAS attack due to the higher availability of calcium and aluminum in the CMAS system.

iii.) It is suggested that in the lower part of zone 3 the first reaction between AVA and LaZ has occurred by a classical dissolution–reprecipitation process that does not lead to a final and stable assembly of crystalline phases. Given a continuous supply of Si, Al, Ca, and Fe these initial phases further reacted to form La-apatite, La-silicate, and monoclinic zirconia.

For both deposits, the infiltration depth as well as the thickness of the reaction layer is higher for LaZ than for GdZ (see Table 1). These results suggest a high reactivity between LaZ and either deposit as compared to GdZ. Moreover, the viscosity is known to be substantially lower for La- compared to Gd-containing glasses, probably caused by the larger cation radius of La [41]. In comparison to the GdZ case, this would induce a deeper and finer infiltration of the La-modified deposit. Note that LaZ was doped with 3 wt.% yttria that might have further influenced phase stability and reactivity. In analogy to the widely studied Gd2Zr2O7 system covering both, EB-PVD [25,29] and plasma-sprayed microstructures [26–28] under a variety of deposit compositions, the La-apatite phase Ca5La8(SiO4)6O2 is one key phase identified for CMAS as well as for AVA on LaZ. Previous work [39] shows that the La-apatite represents a stable solidus phase in similar rare earth systems involving both, CMAS and AVA melts. Unlike the GdZ system where the apatite phase presents the major RE-element sink, the significance of the silicate phases must be considered in both the LaZ/CMAS and the LaZ/AVA system. Their formation changes the composition of the residual CMAS and AVA melt to a siliconleaner and possibly less viscous composition respectively. A similar effect is expected for the AVA constituent iron bound to silicon via fayalite formation at the boundary between zone 1 and 2 (see Fig. 10).

CMAS and AVA differ fundamentally in terms of phase constitution and melting characteristics which control(i) the complexity of the newly-formed reactive interfaces, (ii) the depth of infiltration and reaction, and (iii) the progression mode of the reaction between the novel EB-PVD pyrochlore coatings and the deposits. While the four component standard CMAS system exhibits a congruent melting behavior [42], the AVA system used in this study was already reduced to a feasible ten component system which exhibits incongruent melting characteristics. Most importantly, due to the low glass transition temperature of 930 °C and the broad melting interval of AVA culminating at 1300 °C [7,29], infiltration starts at a lower temperature compared to the more tenacious CMAS. Moreover, the reactivity between AVA and pyrochlore TBCs seems to be higher than for CMAS. Owing to competing infiltration and phase reactions, infiltration depth and thickness of the reaction layers are larger for both LaZ and GdZ under AVA attack as compared to the CMAS case. Additionally, the whole column interior gets dissolved and the reaction progresses downwards to the substrate as a front in case of LaZ.

Further investigations are needed to find out if one of the reaction schemes described above (reaction restricted to inter-columnar gaps and column rims vs. complete reaction including column interiors) lead to a lower stiffening of the TBC and hence to a retarded thermomechanically driven TBC failure. It can only be anticipated that stiffening might be larger for AVA than for CMAS deposits due to the different reaction progression mode, the latter deposit holds some inter-columnar gaps open but only partly filled with CMAS.

The current findings suggest that short-term annealing is insufficient to finally conclude on the true mitigation potential of a specific coating. It is anticipated that the corrosive CMAS and AVA attacks may advance further into the coatings upon prolonged annealing in the 100 h range which is the topic of on-going research. The striking differences in the reactions between CMAS and AVA on the pyrochlore TBCs make comparison of the detailed mitigation potential for different coatings difficult and call for standardized deposit compositions in further research.

In essence, the present investigation leads to the following systematic categorizing of the reactions between a deposit and a thermal barrier coating.

(I) Very high reactivity of the deposit (i.e. very fast reaction with TBC) → reaction front nearly parallel to the former TBC surface that progresses downwards (found here for AVA on both LaZ and GdZ)

(II) High reactivity (fast reaction with TBC) → reaction on the column tips and column rims within inter-columnar gaps (found here for CMAS on both LaZ and GdZ)

(III) Low reactivity (slow reaction with TBC) → full penetration into inter-columnar gaps, followed by dissolution and reprecipitation processes mainly on column tips, within inter-columnar gaps, along the column rims (dissolution of feather arms), and in the root area close to the TGO. This was the case for all zirconia based TBCs investigated. Depending on time and temperature the reaction may progress into the column interior and disintegrate the whole TBC.

5. Conclusions

A variety of new EB-PVD TBCs was studied with both CMAS and AVA deposits to assess infiltration and reactivity after isothermal annealing at 1260 °C for 2 h. Zirconia-based TBCs (7YSZ, 14YSZ, HfSZ, 29DySZ, CeSZ) were fully infiltrated by CMAS followed by dissolution/ reprecipitation processes mainly on column tips and rims, within inter-columnar gaps, and in the far root area close to the TGO layer. The coatings investigated provide no mitigation potential which is due to the lack of rapid formation of crystalline reaction products.

The high reactivity of both Gd- and La-zirconate with the deposits introduced pronounced reactions along column tips, rims, and within inter-columnar gaps (CMAS case), or lead to downward moving reaction fronts parallel to the former TBC surface (AVA case), including disintegrated and fully reacted column interiors. The pyrochlore TBCs thereby provide a significant but varying potential for mitigation of TBC damage by deposits. The variation in the reaction mode under CMAS attack suggests that TBC microstructure, in particular the width of the inter-columnar gaps, seem to play a decisive role for the reaction between TBC and deposits. The infiltration depth in narrower inter-columnar gaps was lower than in wider ones which reveal effective sealing of these channels by crystalline phases. This finding opens opportunities to tailor TBC morphology towards more deposit resistant variants.

The local phase assemblage in the reaction zones upon CMAS/AVA attack is very sensitive to infiltration depth and chemistry of the deposit. It depends on local conditions such as composition, phases and interfaces present, and time available for diffusion. Metastable and stable phases may co-exist. In the LaZ system the La-apatite phase Ca5La8(SiO4)6O2 defines the key solidus phase during both, CMAS and AVA hot corrosion while the nature of minor newly formed phases depends on CMAS and AVA bulk compositions: (i) mainly Ca–Al-silicates (e.g. Ca8Al5Si2O22 gehlenite) or Ca–Zr-silicates such as the Ca11Zr2Si3O10 phase are formed due to higher availability of calcium and aluminum in the CMAS system, while (ii) La- and Fe-silicates dominate the outer and upper LaZ reaction zones due to high Si and low Ca contents in AVA.
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