Title: Application of Biofuel Impurities and Effect on the Hot Corrosion of Yttria-Stabilized Zirconia Thermal Barrier Coatings

Article Type: Full Length Article

Keywords: YSZ; TBC; CMAS; Biofuel; Corrosion.

Abstract: The contaminants found in biofuels include alkali and alkaline metals along with sulfur, phosphorus and silicon oxides. Furthermore, while calcium-magnesium-aluminum silicates (CMAS) are typically ingested as particulate in middle-east theaters, the impurity list in biofuels includes the necessary elements to form CMAS without exposure to any environment. This is significant as CMAS is particularly destructive for operating temperatures above its melting temperature (~1250 °C), particularly affecting the lifetime of 7 wt.%Y2O3-ZrO2 (YSZ) thermal barrier coatings (TBCs). In the work reported currently, solutions containing the individual and unreacted constituents of CMAS were prepared and sprayed onto either air plasma sprayed (APS) or electron beam physically deposited (EB-PVD) TBCs and subsequently subjected to dynamic heating up to 1400°C, simulating the deposit and thermal conditions of the biofuel impurities during combustion. Microstructure analysis revealed that the individual constituents of CMAS accelerated degradation of the TBCs compared to the same samples heated without impurities.

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December 12, 2017

Dear Editor of Journal of European Ceramics Society,

Please find enclosed our article entitled “Application of Biofuel Impurities and Effect on the Hot Corrosion of Yttria-Stabilized Zirconia Thermal Barrier Coatings.”

The contaminants found in various biofuels are known to include alkali and alkaline earth metals including calcium, magnesium, sodium, potassium, along with sulfur, phosphorus and silicon oxides. Furthermore, while calcium-magnesium-aluminum silicates (CMAS) are typically ingested as particulate in middle-east theaters, the impurity list in biofuels includes the necessary elements to form CMAS without exposure to any specific environment. Our present work focuses on developing a methodology to incorporate biofuel impurities in a single solution and evaluating contaminated TBCs in similar thermal conditions as encountered in a gas turbine. In the current study, we validated such methodology with an impurity solution having a reference CMAS composition and by analysing the effects of the solution in air plasma sprayed and electron beam physical vapour deposited thermal barrier coatings. Thus, our methodology will set a precedent for studies aiming to understand the adverse effects of biofuel impurities when interacting alone or combined with TBCs.

Thank you in advance for your time and consideration!

Sincerely,

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Summary of Novel Conclusions:

- Biofuels contain impurities that are different than those in conventional Jet A fuel; in some instances these fuels contain the individual and unreacted constituents found in calcium-magnesium-aluminum silicates (CMAS). Thus, it is possible for these constituents to react and form CMAS without the gas turbine being located in a middle east or volcanic cloud environment.

- In this study we have made “impurity cocktails” by blending different alkaline nitrates with tetraethylorthosilicate and we have developed methods to apply them to the surface of air plasma-sprayed and electron beam physical vapor deposited thermal barrier coatings.

- The effect of impurity cocktails comprised of the constituents in CMAS on thermal coatings have been evaluated using ablation testing to 1400°C, with decreased lifetimes noted for the topcoat of 7 wt.% Y₂O₃-ZrO₂.
Application of Biofuel Impurities and Effect on the Hot Corrosion of Yttria-Stabilized Zirconia Thermal Barrier Coatings

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Abstract

The contaminants found in biofuels include alkali and alkaline metals along with sulfur, phosphorus and silicon oxides. Furthermore, while calcium-magnesium-aluminum silicates (CMAS) are typically ingested as particulate in middle-east theaters, the impurity list in biofuels includes the necessary elements to form CMAS without exposure to any environment. This is significant as CMAS is particularly destructive for operating temperatures above its melting temperature (~1250°C), particularly affecting the lifetime of 7 wt.%Y\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} (YSZ) thermal barrier coatings (TBCs). In the work reported currently, solutions containing the individual and unreacted constituents of CMAS were prepared and sprayed onto either air plasma sprayed (APS) or electron beam physically deposited (EB-PVD) TBCs and subsequently subjected to dynamic heating up to 1400°C, simulating the deposit and thermal conditions of the biofuel impurities during combustion. Microstructure analysis revealed that the individual constituents of CMAS accelerated degradation of the TBCs compared to the same samples heated without impurities.

Keywords: YSZ; TBC; CMAS; Biofuel; Corrosion.
1. Introduction

Gas turbines are an essential element of the modern world, being used to generate electrical power or thrust in commercial and military aircraft. In an effort to improve gas turbine efficiency they have been operated at progressively higher temperatures, with ceramic thermal barrier coatings (TBCs) being employed in the combustion chamber to protect the underlying superalloy structure from temperature extremes. The processes used for depositing YSZ TBCs are typically either air plasma spray (APS) or electron beam physical vapor deposition (EB-PVD). APS coatings are typically used for large stationary components such as the combustion chamber walls while EB-PVD coatings are applied to small or rotating components such as blades and vanes. The most utilized TBC material is 7 wt.% Y$_2$O$_3$-ZrO$_2$ (YSZ) due to its low thermal conductivity and the relatively slow destabilization kinetics of the as-deposited $t'$-ZrO$_2$ phase to $c$-ZrO$_2$ and $t$-ZrO$_2$ phase (and ultimately $m$-ZrO$_2$) upon heating.$^1$ With the maximum operating temperature of gas turbines increasing to 1250°C and above, a new problem has emerged for TBCs that has been well documented over the last decade.$^{2,3,4}$ Calcium-magnesium-aluminum silicates or CMAS, a particulate common to the middle east regions or found in volcanic ash, can be pulled into a gas turbine. Depending on the composition of the particulate, it can melt and infiltrate into the TBC via the porous pathways in either the APS or EB-PVD microstructures. Upon cooling, the compliance difference between infiltrated and non-infiltrated coating regions causes residual stresses that can delaminate the infiltrated coating. Repeated heating/infiltration/cooling cycles can remove the entire TBC.
There is currently momentum to shift to the use of biofuels in gas turbines. For example, United Airlines flights between Los Angeles and San Francisco, have been using a blend of 70% Jet-A and 30% biofuel since 2016. Biofuels can be formed via numerous biomass processing approaches, using a multitude of different biomasses to include wheat, willow, and even olive waste.\(^5\) It has been well established that contaminates found in fossil fuels such as Jet A can be incorporated into TBCs, ultimately hastening their failure through a variety of different corroding mechanisms. Contaminants found in fossil fuels include S, V, Na, Ca, K, P etc.\(^6\) With the use of biofuels, however, a new group of contaminants must be considered. It has been determined that the amount of impurities present in biofuels depend directly on the biomass source. The composition of impurities in the biomass source is highly variable due to its dependence on factors such as harvest season, composition of the soil, and drying temperature.\(^7\) This list includes Al, Ba, Ca, Fe, K, Mg, Na, P and Si.\(^8\) Inspection of this list reveals that those same elements found in particulate forms of CMAS are found as individual constituents in biofuels. Thus, a gas turbine operating with biofuels maybe exposed to the constituents of CMAS without ever being operated in a middle east or volcanic ash environment. While extensive studies of the effect of fossil fuel impurities have been performed previously,\(^9\) the effect of impurities and oxides of alkali and alkaline metals found in commercial and military biofuel blends (e.g. HEFA, FT-S8, SIP) is still unknown. Because of the growing importance of biofuels worldwide, a specific understanding of the possible negative effects of these impurities is extremely important to avoid premature failure of TBCs used in gas turbines.

In the work reported here, we have developed a methodology to incorporate the individual impurities found in biofuels into TBCs made either via APS or EB-PVD. The approach uses
impurity “cocktails”, solutions combining the impurities of interest that are subsequently sprayed on TBCs. Their effect on the microstructure is subsequently evaluated after heating/cooling in an ablation rig to temperatures of 1400°C. The goal is to understand the mechanisms of degradation that take place when biofuel impurities are incorporated into a TBC.

2. Experimental Methods

2.1. Formulation and Application of the Impurity Cocktails

Nitrates of the alkaline metals, including Ca(NO$_3$)$_2$ (Sigma Aldrich), Mg(NO$_3$)$_2$ (Sigma Aldrich), and Al(NO$_3$)$_3$ (Sigma Aldrich) are soluble in ethanol. Using these nitrates, and the pre-ceramic polymer Si(OC$_2$H$_5$)$_4$ (Sigma Aldrich), an impurity cocktail with a composition in mole percent of 33CaO-9MgO-6.5Al$_2$O$_3$-45SiO$_2$ was formulated with the assumption that each nitrate or silicate solution would oxidize upon heating according to:

$$2\text{Ca(NO}_3\text{)}_2 \rightarrow 2\text{CaO} + 4\text{NO}_2 + \text{O}_2$$

$$2\text{Mg(NO}_3\text{)}_2 \rightarrow 2\text{MgO} + 4\text{NO}_2 + \text{O}_2$$

$$4\text{Al(NO}_3\text{)}_3 \rightarrow 2\text{Al}_2\text{O}_3 + 12\text{NO}_2 + 3\text{O}_2$$

$$\text{Si(OC}_2\text{H}_5\text{)}_4 \rightarrow \text{SiO}_2 + 2\text{C}_2\text{H}_3\text{OH} + 2\text{C}_2\text{H}_4$$

This composition of CMAS chosen was based on the average of deposits on aircraft turboshfts shrouds as reported by Borom et al.\textsuperscript{10} The conversion temperature of the reactions to produce the individual constituents of CMAS are all lower than 670°C. The individual constituents of CMAS were dissolved in ethanol to make a 10% concentration of the impurities in solution. In the as-mixed cocktail there was no visual evidence of the formation of precipitates to suggest that the constituents reacted with one another or stratification of the added constituents suggesting they unmixed.
Prior to deposition of the impurity cocktail, the coatings were heated up to 100°C by placing a hot plate in direct contact with the coating substrates. An air brush kit, with the air pressure held constant at 0.2 MPa, was used to spray the impurity cocktail. Impurity cocktails were sprayed on heated TBC/substrates in intervals of 5 seconds followed by 3 seconds of no spray to facilitate ethanol solvent vaporization. The impurities were applied at a concentration of 1 mg/cm². Samples were dried at room temperature for 24 hr. prior to the ablation cycle.

2.2. TBC Coatings Evaluated

Table 1 presents the APS and EV-PVD TBC coating systems (topcoat of 7 wt.% Y₂O₃-ZrO₂, and a bondcoat of either CoNiCrAlY or PtAl) evaluated in the current study. Each TBC system was applied to 25 mm diameter superalloy substrate. The APS TBC coating was produced by Praxair Surface Technologies. The topcoat of YSZ was processed to have a dimensionally vertically cracked (DVC) microstructure. The vertical cracks in the APS TBC are designed to simulate the columns observed in EB-PVD coatings. A CoNiCrAlY bondcoat was used for the APS TBCs, sprayed first on the Inconel 718. The EB-PVD TBC was supplied by GE, with a topcoat of YSZ, a bondcoat of PtAl, and a superalloy of Rene N5. Cross-sectional and surface views of each coating are shown in Figure 1. The cross-sectional image of the APS TBC (Figure 1a) show vertical cracks, while the cross-sectional image of the EB-PVD coatings shows the expected columnar microstructure.
2.3. Ablation and Characterization

In the current study, the deposition of the impurities on the TBCs was performed prior to ablation cycling, affording better control of the impurity composition, surface impurity concentration and a partial separation of the mechanical effect degradation (e.g. erosion) from the thermochemical degradation effect. To ablate the samples a 5-W Victor welding nozzle was used for the torch with an acetylene to oxygen ratio of 10:12 liters per minute. The temperature of the front face (i.e. the TBC surface temperature), was measured in intervals of a second using an infrared pyrometer Omega OS3750. The back-surface temperature was measured using a type K thermocouple in contact with the superalloy substrate. Front face temperatures were maintained between 1400°C to 1500°C for APS and 1250°C to 1300°C for EB-PVD coatings. X-ray diffraction investigations in the 2θ range of 72-76° revealed that EB-PVD coatings without added impurities were rapidly transforming the as-deposited t’-ZrO₂ to other zirconia phases at 1400°C. Thus, a lower ablation temperature of 1250°C-1300°C was chosen. The APS coatings without added impurities remained t’-ZrO₂ after the 30-min ablation at 1400°C; thus, an ablation temperature of 1400°C was used for the APS coatings. The back temperature of the substrates never exceeded 1000°C for either TBC, avoiding substrate phase changes and melting temperatures reported for Inconel 718 and Rene N5.11,12 After each cycle samples were allowed to cool down to room temperature by air convection. APS and EB-PVD samples were ablated in 10 minute cycles for a total ablation time of 30 and 20 minutes, respectively. The impurity was reapplied in a 1mg/cm² concentration after each ablation cycle.
As received and after ablation X-Ray Diffraction (XRD) patterns were collected with a Bruker D8 Focus diffractometer. Samples were analyzed with an X-Ray copper source (\(\lambda=0.1544\) nm), a 2\(\theta\) interval between 20° to 90° and a scan speed of 3 degrees per minute in increments of 0.01 degrees per step. Additionally, SEM micrographs of as-received coatings and after ablation were taken. Cross-sectional images of each coating were prepared by mounting the sample in epoxy, and polishing down through 5\(\mu\)m using a diamond paste. For both cross sectional and surface SEM analysis, a carbon coating was applied to the samples to avoid sample charging.

3. Results and Discussion

3.1. Impurity cocktail validation

One-hundred ml of the impurity cocktail was heated up in an alumina crucible to 800°C and held for two hours. An XRD pattern of the reaction product, in the form of a powder, was collected. Figure 2 shows a comparison of the pattern collected for this sample as well as for a synthetically prepared CMAS with the identical composition. The synthetic CMAS was formed by reacting individual oxides of CaO, MgO, Al\(_2\)O\(_3\) and SiO\(_2\) followed by pulverization to a powder size of 10-100 \(\mu\)m. Both XRD patterns exhibited a similar smooth-curved shape, with no crystalline peaks observed. A very similar XRD pattern to those observed here have been reported by Pujol et al.\(^{13}\) when synthetizing CMAS via sol-gel process. Thus, it is proposed that the reaction product of the individual constituents in the impurity cocktail match that of CMAS.
3.2. Effect of Thermal Cycling on APS and EB-PVD coatings (No Impurities Added)

Figure 3 shows APS and EB-PVD TBC samples and a topological micrograph for each after being ablated for 30 minutes and 20 minutes, respectively. These samples did not have any impurity applied and, thus, they represent the baseline condition for each TBC type. Neither the APS or EB-PVD TBC samples showed significant degradation after being ablated. Cross sections of each coating after ablation, revealed the formation of small horizontal cracks in the APS sample due to thermal cycling (Figure 3a), and microstructural densification in the EB-PVD TBC (Figure 3c). Comparison of Figure 1b with Figure 3b reveals no difference in the APS coating surface before and after ablation. Similar observations were made for the EB-PVD coatings, as is seen in Figure 1d and Figure 3d.

3.3. Combined Effect of Thermal Cycling and Biofuel Impurities on APS and EB-PVD Coatings.

APS TBCs: Figure 4 shows the changes in the APS TBC samples after each 10-minute cycle, with biofuel impurities added prior to each successive cycle. Figures 4b, 4d, and 4f show the top surface of the coating. After the first thermal cycle of 10 minutes to 1400°C, Figures 4a and 4b show no difference in comparison to the sample surface ablated with no impurities after 30 min at 1400°C (Figures 3a and 3b). After reapplication of the impurity cocktail and another 10 minutes of ablation, evidence of spallation and crack formation was apparent (Figures 4c and 4d). Figure 4d shows a region on the surface where part of the coating has delaminated. Finally, after reapplication of the impurity solution and a total of 30 minutes of ablation, large-scale spallation was clearly visible in the sample (Figures 4e and 4f). In contrast, the sample that was
ablated with no impurities never exhibited coating spallation even after 30 minutes of ablation (Figure 3b).

The mechanism by which the APS TBC delaminates can be explained by analyzing the spallation debris. Figure 5a shows a piece of debris in cross-section. There is clearly a glassy phase that has infiltrated the coating, with a clear demarcation observed between the infiltrated and un-infiltrated parts of the coating. More detailed observations of debris as in Figure 5b show horizontal cracks right next to areas where the infiltrated impurities solidified, leading to the conclusion that the layer by layer delamination of the TBC is cause by partial infiltration, solidification and horizontal crack formation in the TBC during every heating cycle.

Figure 6a shows a polished cross-section of the APS TBC after 30 minutes of ablation time showing filled vertical cracks. Note that this sample had the impurity cocktail applied 3 times. The vertical crack in this micrograph has clearly been filled with a secondary phase. Also indicated in Figure 6a is a region analyzed using a qualitative energy dispersive spectroscopy (EDS) line scan. Figure 6b shows a close-up of this region. The qualitative EDS revealed the presence of the added impurities within the vertical cracks of the TBC, with Si (presumably SiO$_2$) being the majority phase. However, peaks associated with the presence of Al, Ca and Mg were also noted in the vertical cracked regions. Furthermore, zirconium was still observed in the vertically cracked regions, indicating that it was somewhat dissolved by the presence of the glassy silica.$^{14,15,16}$

**EB-PVD TBCs**: Figure 7a-d shows the combined effects of thermal cycling and the addition of the impurity solution on EB-PVD TBCs. After the application of impurities and 10-minute
ablation near 1300°C, SEM micrographs revealed column separation in different regions (Figure 7b) as compared to the EB-PVD sample heated to 1300°C with no impurities (Figure 3d). Reapplication of the impurity followed by another 10-minute ablation cycle caused no apparent delamination of the coating (Figure 7c), in the surface, limited areas with reaction products were observed (Figure 7d).

Figure 8a shows the polished cross-section of the EB-PVD TBC after 20 minutes of ablation and two applications of the impurity cocktail, along with a detailed view of the reaction products near the EB-PVD coating/bondcoat interface (Figure 8b). Figure 8c show elemental map for Si at the interface shown in Figure 8b. Figure 8a reveals regions of severe attack in the TBC/substrate interface, as well as void regions. Comparison of Figure 8a to a coating ablated 20 min with no impurities (Figure 3c) reveals stark differences in the interface microstructure. Moreover, Figure 7b, which was taken near the coating/bondcoat interface, along with the corresponding EDS map for Si, shows that significant concentrations of this element, presumably in the form of silica, were detected there. The location of the impurities strongly indicates that the columnar structure facilitated the infiltration of the impurities through its entire thickness, reaching the denser bondcoat. As a reminder, the APS samples did not experience penetration of the modified silica phase through its thickness as the channels of filtration are more limited. Furthermore, close inspection of Figure 8b shows a horizontal crack developing in this silica rich region, a precursor to delamination of the coating.

The location of the modified silica products is consistent with the Zhao et al.\textsuperscript{17} correlation of liquid permeability/intercolumnar pore fraction for the infiltration of particulate forms of CMAS
in TBCs, with correlations made using similar thicknesses and sample compositions to those employed for this study. In their studies the columnar microstructure of the EB-PVD TBC favored the infiltration of the impurities, achieving full infiltration of the impurities (i.e. reaching the substrate) seconds after melting of the particulate form of CMAS. Thermochemical studies of molten CMAS with YSZ TBCs observed by Krämer et al.\textsuperscript{18} observed that the full infiltration of molten CMAS in EB-PVD prepared coatings is accompanied by horizontal cracks at the topcoat/bondcoat interface, similar to the observations in Figure 8b. Nevertheless, it is important to note that the infiltration of the impurity was not accompanied by a degradation of the columnar tips as suggested by previous literature. As noted by Vidal-Sétif et al.\textsuperscript{19} tip degradation phenomena are present when a large volume of CMAS is present, opposite to the methodology proposed in this study where the amount of impurities is limited during each cycle.

4. Conclusions

A methodology to incorporate common impurities found in biofuels has been developed by mixing alkali and alkaline nitrates and a silicon-containing preceramic polymer in an ethanol solution to form impurity cocktails. For this study, the impurity cocktail was designed to match the composition of the individual constituents found in particulate forms of CMAS. The solution was sprayed on both APS and EB-PVD TBCs, and its effect on the microstructure was evaluated after successive ablation cycles. The APS TBC exhibited extreme delamination, with the vertical cracks being filled by the modified silica glass, the oxidation product of the impurity cocktail. Each ablation cycle caused increased delamination. The oxidation product associated with impurity cocktail interacted with the EB-PVD TBC differently than in the APS TBC in that they
appear to have found a direct pathway through the columnar grains to the YSZ/bond-coat interface. Micrographs revealed nucleation and propagation of horizontal cracks in the oxide product.

5. Acknowledgments

This work was supported as part of Purdue’s NEPTUNE Center for Power and Energy, funded by the Office of Naval Research under Award Number N000141613109. Furthermore, the authors would like to thank GE (Dr. Doug Konitzer) for providing the EB-PVD TBCs and Praxair Surface Technologies (Dr. Chris Petorak) for providing the APS TBCs.

6. References


Table 1: As-received specifications of APS and EB-PVD TBCs.

<table>
<thead>
<tr>
<th>Specification</th>
<th>APS</th>
<th>EB-PVD</th>
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<tbody>
<tr>
<td>Geometry</td>
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<td>Button Ø 25.4 mm</td>
</tr>
<tr>
<td>Top coat material</td>
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<td>7YSZ</td>
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<tr>
<td>Top coat thickness</td>
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<tr>
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<tr>
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<td>Rene N5</td>
</tr>
<tr>
<td>Total thickness</td>
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<td>3.5 mm</td>
</tr>
</tbody>
</table>
Figure 1 SEM micrographs showing APS and EB-PVD TBCs in the as received condition. Images (a) and (b) show the cross-section and top surface of the APS coatings studied. Images (c) and (d) show the cross-section and top surface of the EB-PVD coatings studied.
Figure 2 X-Ray diffraction patterns of synthetically prepared CMAS and the reaction product of the impurity cocktail after heating to 600 °C.
Figure 3 APS TBC (a) cross section and (b) surface after ablation for 30 minutes without impurities at 1400 °C and EB-PVD TBC (c) cross section (d) and surface after ablation without impurities for 20 minutes at 1250 °C.
Figure 4. APS sample with biofuel impurities, ablated for 10 minutes (a,b), 20 minutes (c,d), and 30 minutes (e,f) at 1400 °C.
Figure 5 SEM micrographs of a piece of delaminated APS coating following 30 minutes of ablation. There are regions that have clearly been completely infiltrated by the reaction products. Horizontal cracks separate infiltrated from un-infiltrated regions in the coating.
Figure 6 a) SEM micrograph of an APS YSZ top coating after 30 minutes of ablation testing showing the infiltration of a glassy reaction product. b) Shows an enlarged area of this coating, with the corresponding EDS scan and the resulting elemental analysis.
Figure 7 EB-PVD sample with biofuel impurities ablated for 10 minutes (a, b) and 20 minutes (c, d).
Figure 8 EB-PVD TBC with added impurity cocktail after 20 minutes of ablation and impurity cocktail added. Cross section (a) and close view of the infiltrated products (b) with the corresponding element maps (c and d) for Zr(Lα1) and Si(Kα1).