Degradation From CMAS Infiltration in 7YSZ EB-PVD Thermal Barrier Coatings

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DEGRADATION FROM CMAS INFILTRATION
IN 7YSZ EB-PVD THERMAL BARRIER COATINGS

by

ZACHARY STEIN

A thesis submitted in partial fulfilment of the requirements
for the degree of Bachelors of Science in Aerospace Engineering
in the Department of Mechanical and Aerospace Engineering
in the College of Engineering and Computer Science
at the University of Central Florida
Orlando, Florida

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Thesis Chair: Seetha Raghavan, Ph.D.
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ABSTRACT

The lifetime of the high temperature ceramic coating 7 wt.% yttria-stabilized zirconia (7YSZ) is reduced when calcium-magnesium-alumino-silicate (CMAS) particulates enters aero-engines during operation in a sandy or dusty environment, melts, and infiltrates into the coating. 7YSZ undergo both chemical and mechanical degradation from CMAS infiltration during cycling. Characterization methods with synchrotron X-ray diffraction (XRD) provides a non-destructive means to measure the impact of time and temperature on coating degradation with high spatial resolution of 7YSZ coatings infiltrated and annealed by CMAS for 1 hour and 10 hours as well as at 1225 °C and 1250 °C. Additionally, qualitative results of cross-sectional scanning electron microscopy (SEM) allows for the additional observation and validation of the extent of degradation the coatings experience from CMAS infiltration. The XRD measurements show the extent of degradation is more sensitive to temperature around the melting range of CMAS with an increase of approximately 42.8% in the concentration of the monoclinic phases present in the coating at the surface when increasing the annealing temperature from 1225 °C to 1250 °C. It was also found that the degradation was more significant in the first hour of infiltration. There was an increase of 21.5% in the concentration of the monoclinic phases present within the coating at the surface when increasing the annealing time from 1 hour to 10 hours. The results presented within this thesis resolve the impact of time and temperature on the infiltration kinetics of CMAS in coatings which are important considerations in mitigating CMAS infiltration.
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CHAPTER 1 INTRODUCTION

1.1 Background and Motivation

Thermal barrier coatings (TBCs) are multilayer coatings that are applied to insulate combustor and turbine engine components from the hot gas streams within gas turbine engines used in aeroengines and power generation. TBCs are applied to superalloy metallic components, such as turbine blades within the turbine section of the engine [1, 2]. TBCs reduce the surface temperatures of the superalloy turbine blades by approximately 200 °C due to the low thermal conductivity of a high temperature ceramic layer [3].

Currently, the two major industry standards for applying TBCs onto the superalloy components are air plasma sprayed (APS) and physical vapor deposition (PVD), more specifically electron beam physical vapor deposition (EB-PVD). Each deposition method has its own benefits and applications. APS is generally more economical as compared to PVD methods and provides a dense and porous coating that is splat-like and monolithic in microstructure [2, 3]. APS is used prevalently within the power generation industry. These coatings can be found in the combustor section and non-moving components held for long thermal cycles. EB-PVD, while more costly than the APS alternative, is capable of creating coating microstructures that provide higher in-plane strain tolerance and lower thermal conductivity in high-stress applications [3]. These characteristics are favorable to allow for thin coatings to operate under extreme environments in the turbine section with rotating turbine blades and frequent and short thermal cycling within aeroengines [2, 4].
TBC systems typically consist of four layers: the high temperature ceramic coating layer, a thermally grown oxide layer and bond coating, and the metallic superalloy substrate, which is shown in Figure 1.1. Each of these four layers serve a different function in order to increase the durability and lifetime of the underlying component [2, 5]. The thickness of the ceramic coating can vary from 150 – 400 μm depending on the deposition method and the desired temperature gradient from the hot gas stream to the surface of the substrate [1, 4]. The ceramic coating material has traditionally consisted of some weight variation of yttria with zirconia, known as yttria-stabilized zirconia (YSZ) due to the low thermal conductivity of the tetragonal and cubic phases of zirconia. Previous work has determined that 6 – 8 wt.% yttria provides the optimal lifetime of the TBC with 7 wt.% yttria being the industry standard (7YSZ) [1, 2].

An oxidation-resistant metallic bond coat (MCrAlY or PtNiAl) layer adheres the ceramic coating to the superalloy metallic substrate. During operation, oxygen diffuses inward towards the bond coat, bonds to the aluminum, and forms a thermally grown oxide layer (TGO) consisting primarily of α-Al₂O₃ between the bond coat and ceramic coating [6]. As the TGO
layer grows, it restricts further oxygen diffusion between the ceramic coating and bond coat [4, 7]. The α-Al₂O₃ is more compatible with the YSZ layer as compared to the metallic bond coat and substrate and helps to ensure long-term thermodynamic stability of the TBC system [8].

Finally, the nickel or cobalt based superalloy substrate is the component that is to be insulated with the ceramic coating. The substrate is force air-cooled through internal cooling channels in order to establish a thermal gradient across the component and to better control the residual stress required for an optimal lifetime of the ceramic coating [4, 9].

![Figure 1.2 A SEM micrograph displaying the columnar microstructure of a 400 μm 7YSZ EB-PVD TBC top coat.](image)

In EB-PVD, a high energy electron beam is used to vaporize a ceramic ingot. Through line of sight, the vapor deposits and condenses onto the target substrate and bond coat material. The condensed ceramic slowly grows upward away from the target and forms columnar structures around 10 μm in diameter as shown in Figure 1.2 [4]. The resulting microstructure is a closed porosity columnar microstructure approximately 150 – 200 μm thick. The intercolumnar gaps provide the additional strain tolerance characteristic of EB-PVD and accommodates for thermal expansion stresses during operation [2, 4].
Typical failure modes of TBCs manifest as spallation, where local separations between the topcoat and the bond coat coalesce to form a critical flaw. Separations between the TGO and TBC has been attributed to rumpling, a form of morphological instability that occurs as a result of CTE mismatch [10]. A significant cause of spallation failure is from deposits that TBCs are exposed to during gas turbine operation.

Calcium magnesium aluminosilicate (CMAS) compositions, which are dominant in particulates such as sand or volcanic ash, are abundantly present in deserts and sandy areas as well as in areas with high volcanic activity. It has been found that concentrations as small as 4.8 mg/cm² are able to instigate rapid coating degradation and cause premature coating failure [11]. This unexpected failure results in more frequent maintenance cycles, causing increased downtimes for aircrafts working within these high-risk environments and increased costs in repairing and replacing TBCs and turbine blades exposed to and damaged by CMAS.

CMAS enters the engine from the surrounding environment during aircraft operation and melts in the combustor section. The molten CMAS then follows the hot gas path and deposits on the TBCs. The CMAS is able to rapidly infiltrate into the intercolumnar gaps and feather arms of the coating due to capillary effects [12]. CMAS infiltration into the TBC manifests both in terms of thermomechanical and thermochemical impacts. Thermomechanical degradation occurs when the molten CMAS crystallizes within the coating and results in an increase in coating stiffness. During the operational cycles of the aero-engine, the TBCs undergo thermal cycling where CMAS associated TBC stiffening is regarded as a major contributing factor in reducing the durability and lifetime of the coating. In addition to the mechanical degradation, molten CMAS thermochemically reacts with the TBCs causing phase destabilization. The melting points of CMAS compositions vary geographically and are heavily based on their chemistry, typically occurring in a range between 1135 °C and 1270 °C. Upon cooling, molten CMAS crystallizes, closing the intercolumnar gaps and stiffening the TBC.
This crystalline CMAS primarily consists of pyroxene, anorthite, and additional amorphous phases and the coating reprecipitates into a more Y-depleted composition, susceptible to phase transformations into a globular monoclinic phase (mYSZ).

Figure 1.3 (a) Schematic of the thermochemical effects of CMAS infiltration in 7YSZ. (b) An example XRD pattern acquired by an area detector of a CMAS infiltrated 7YSZ coating (infiltrated at 1250 °C and held for 10 hours). (c) A lineout acquired from integrating the XRD pattern in (b) along with the labelled tYSZ and mYSZ phases indicated by the dotted line.

The stiffening and phase transformation of the coating as a result of CMAS infiltration plays a role in diminishing the strain tolerance and introducing thermal mismatch, which results in the formation of microcracks within the TBC and ultimately causing coating failure [13, 14]. A schematic of the thermochemical and thermomechanical degradation of the coating due to CMAS infiltration is shown in Figure 1.3a.

The CMAS-TBC interaction severely limits the operational capabilities of both commercial and military aircrafts in CMAS abundant regions. Therefore, understanding the
mechanisms behind this ingress and quantifying its subsequent degradation is vital and will allow for lifecycle monitoring and development of more CMAS-resistant coatings.

1.2 Factors affecting CMAS infiltration

Several field studies stemming from investigations with aircrafts operating in the Middle East have investigated the composition and effects of CMAS entering into aeroengines and found CMAS to be a major life-limiting factor on TBCs [15, 16]. These field studies then led investigations towards the development of experimental methodologies and the synthesis of CMAS in a laboratory setting in order to simulate infiltration conditions and effects found in field studies on APS and EB-PVD coatings [17, 13, 18, 19, 20]. Additionally, many investigations have tried to better characterize the effects of CMAS degradation on coatings at various experimental parameters such as CMAS concentration and annealing conditions. At temperatures lower than the melting range of CMAS, damage induced by particle impact enabled by CMAS penetration was determined to be a major contributor towards coating failure impact and erosion damage from CMAS [20, 21, 22]. Meanwhile, within and above the melting range, it was found that thermomechanical and thermochemical degradation played prominent roles in the degradation of TBCs. This work in this thesis will focus around the melting range of CMAS due to the detrimental effects it has on the degradation on the coatings.

It was observed with Krämer and Evans et al. that CMAS is able to infiltrate to a certain depth of the coating, when under thermal gradient, and causes the surface of the coating to experience tensile stresses upon cooling as the coating stiffness increases and porosity decreases [17, 14, 23, 24, 25]. Mercer et al. identified a critical infiltration thickness, in which the coating is at high risk of delamination beyond the critical infiltration thickness [24]. Findings from Evans et al. found when CMAS comes into contact with the TGO, it can also
result in a chemical interaction and form cavities, incurring delamination along the TGO [26, 27]. Microcracks begin to form within the coating due to coefficient of thermal expansion mismatch and changes in the thermal conductivity between the CMAS infiltrated and non-infiltrated regions [26]. Depending on the rate of CMAS infiltration and operational conditions, the coating may fail due to the addition of thermomechanical induced stresses before thermochemical interactions between the coating and molten CMAS can occur [19].

Krämer et al. and Li et al. found that discernable thermochemical degradation of the coating from CMAS occurs in longer exposures of time of several minutes to hours [17, 19]. This suggests that the duration of time that molten CMAS is infiltrating into the coating is significant in relation towards measuring thermochemical degradation. Therefore, the annealing times chosen within this work, 1 hour and 10 hours, needs to be long enough to ensure the molten CMAS has not only interacted with the coating, but can elucidate the evolution of degradation with prolonged exposure.

When interacting with the molten CMAS, the coating starts to dissolve, having the Y$_2$O$_3$ deplete from the coating and causing the non-transformable, metastable tetragonal YSZ phase to transform into intermediary phases and complete its reprecipitation into the less desirable globular monoclinic phase upon cooling. Garces et al. found through in-situ Raman spectroscopy experiments this final phase transformation into the monoclinic phase starts to occur around 600 °C [28]. The transformation from the non-transformable tetragonal phase to the monoclinic phase has an associated volumetric expansion of approximately 4%, which introduces additional strains into the coating and may cause microcracks and spallation to occur at these points within the coating [12, 13, 14, 23, 29]. It was found through the thermochemical investigations of Wellman et al. that CMAS concentrations of approximately 4.8 mg/cm$^2$ after 4 hours of annealing at 1300 °C was the minimum level at which degradation occurs uniformly over the columnar tips [11]. While Wellman et al. conclude that this finding is specific to their
CMAS composition and testing conditions, there is some minimum level that is required for degradation on a significant level to occur and selecting a concentration above 4.8 mg/cm² will ensure thermochemical degradation within the coating.

Additionally, Naraparaju et al. demonstrated that slight increases in infiltration temperatures within the CMAS melting range can increase the rate of infiltration [13]. While the fully molten CMAS was able to infiltrate through a coating isothermally annealed within a few minutes, a partially molten CMAS only infiltrated approximately 20% of the coating depth in the same duration of time. It was determined that the rate of infiltration and its depth is dependent on the annealing temperature and the subsequent viscosity of the CMAS. These findings indicate that temperature, especially around the melting range of CMAS, is also a major factor in coating degradation that must be considered within this work. With similar annealing conditions as the partially molten and fully molten CMAS will not only aid in the expected CMAS infiltration depths within this study found by Naraparaju et al., but also provide insight on how coating degradation is influenced by these slight changes in temperature and viscosity within the melting range of CMAS.

The results found within this thesis will provide a better understanding on the mechanisms behind CMAS infiltration and its interaction with coatings. The conclusions obtained will guide future experiments in determining temperatures and times of key interest to explore more as well as to use as a benchmark on more novel TBCs. Raman spectroscopy investigations are currently being conducted for the samples presented within this study, as well as on thermal gradient 7YSZ EB-PVD TBC samples [30]. The work with Raman spectroscopy also investigates the thermochemical interactions between CMAS and the coating, but on a more localized level, which is highly dependent on the microstructure and deposition parameters of the EB-PVD coating. Meanwhile the work presented here investigates these interactions averaged across the sample and resolved with depth. The changes in the residual
stresses, as benchmarked from non-infiltrated samples under similar annealing conditions, were also measured and determined through Raman spectroscopy for the samples used with this study as well as on the thermal gradient samples. In both cases, the surface of the coating exposed to CMAS experienced tensile stresses and became more compressive further into the depth of the coating, agreeing with what was found by Krämer et al. [17]. The findings within this work and current work are to provide a better idea of full thermomechanical and thermochemical interactions between the CMAS and 7YSZ coating. These findings characterizing CMAS infiltration and its interaction with the coating can also be applied to future work investigating mitigation strategies and the possibility of more CMAS resistant alternative coatings.

Many studies are currently focusing on mitigation strategies to either reduce the rate of or inhibit CMAS infiltration as solutions towards the problems highlighted in studies being performed for characterizing the mechanisms influencing CMAS infiltration. Naraparaju et al. found that tailoring the microstructure of 7YSZ EB-PVD coatings to have longer feather arms reduced the rate of infiltration when the CMAS was partially molten by nearly half as compared to the traditional EB-PVD microstructure [12]. This reduction in infiltration speed lowers the stresses the TBC would experience and may be able to prolong the lifetime of EB-PVD TBCs exposed to CMAS [12]. Within the same study, a mathematical model to better predict infiltration depths was proposed that accounts for the shape of the capillary tubes of the intercolumnar gaps and feathery arms.

Previous CMAS infiltration characterization studies concluded that the CMAS infiltrates first and then interacts with the coating. This has led the scientific community towards investigating novel zirconia coatings to limit the depth CMAS is able to infiltrate by doping the zirconia with rare-earth elements (rare-earth zirconates, REZ) such as gadolinium (GZO) instead of yttria. REZ are of high interest due to their lower thermal conductivity and
higher resistance towards sintering as compared to traditional 7YSZ coatings. The idea of GZO coatings are for the coating to react quickly with the CMAS and form a reaction layer of an apatite phase that will prevent further CMAS infiltration. Krämer et al. noticed in their experiments that the apatite phase was approximately 6 μm thick after 4 hours of isothermal annealing at 1300 °C and the CMAS had only infiltrated about 30 μm into the depth of the coating [31]. These promising findings are a result of the knowledge obtained from previous investigations on the composition of CMAS and how CMAS infiltrates into and interacts with YSZ coatings during operation. This also illustrates how previous investigations can serve as a benchmark for GZO coatings and other alternative coatings currently being investigated.

Similarly, Harder and Faber et al. have conducted many high-energy XRD studies studying the chemical and mechanical changes of environmental barrier coatings (EBCs) exposed to CMAS [32, 33]. EBCs are a multilayer high temperature coating similar to TBCs in function. Si-based ceramics are excellent for high temperature operations due to their lower thermal conductivity and high thermomechanical stability [34]. Different compositions of EBCs are currently being explored, such as Ba_{1-x}Sr_{x}Al_{2}Si_{2}O_{8} (BSAS) and other rare-earth silicates, in order to protect the highly reactive Si-based ceramic [34]. However, EBCs are still susceptible to CMAS and requires extensive work towards understanding how CMAS and EBCs interact with each other. Though the specific phases and changes in the residual stresses are different in EBCs compared to TBCs, the characterization techniques such as high-energy XRD and SEM are similar. Similar experimental setups were used for the high-energy XRD in both this work and from high-energy XRD work performed by Harder and Faber et al. [32]. Future work can adapt some methods such as in-situ experimental setups unique to TBCs and EBCs and apply them to the other. This will enable further exploration in how various operating conditions influence the rate of CMAS infiltration in these different coatings and assist in the development of more effective and CMAS-resistant coatings.
Many studies have explored the issues relating towards CMAS infiltration and its thermomechanical and thermochemical interactions with 7YSZ coatings. Similarly, these studies have highlighted that annealing temperature and annealing time are major contributors on coating degradation. However, the extent by how sensitive temperature and time are and how their significance changes with an increase in temperature and time have not yet been fully explored and serve as the objectives for this thesis.

1.3 Overview of Thesis

In order to investigate the effects of infiltration in this study, a synthetic CMAS was used to represent sand-like compositions, which was taken from the composition of desert sand from Middle Eastern countries [23, 35]. The rate at which CMAS interacts with the coating can be influenced by the infiltration temperature and the duration of infiltration. Therefore, it is important to understand to what extent these factors influence the thermochemical reaction between CMAS and the coating. Mapping the phase volume fraction of the crystalline phase constituents in a CMAS infiltrated TBC using high-energy X-ray diffraction (XRD) can elucidate the impact of these factors. In this work, XRD was used to study the effects of temperature and time on the CMAS/EB-VD 7YSZ interactions by investigating the thermochemical degradation of the coating. The two temperatures of 1225 °C and 1250 °C were chosen since it was found in a previous study that the CMAS composition used in this work is fully molten at 1250 °C and partially molten at 1225 °C. The resulting CMAS infiltration depths for each temperature as a result of viscosity suggests that temperature and viscosity may also influence the interaction between CMAS and the 7YSZ [36]. The two times of 1 hour and 10 hours were selected due to previous findings from studies demonstrate that the molten CMAS does not noticeably interact with the coating until some initial time, 1 hour in this case, has
passed. Meanwhile, 10 hours allow for a more significant amount of time for the CMAS to interact with the coating, which will serve to gauge how thermochemical degradation evolves over time [17, 19]. Quantification of the constituent crystalline phases, more specifically the phase volume fraction concentrations of mYSZ and tYSZ, using a high-spatially resolved X-ray beam (30 x 300 μm²) across the depth of the coating, was done to study the phase degradation throughout the coating depth due to CMAS infiltration. The results from these XRD measurements were then qualitatively compared with scanning electron microscopy (SEM) cross-sectional micrographs for the samples used within this study.
CHAPTER 2 METHODS: X-RAY DIFFRACTION AND SCANNING ELECTRON MICROSCOPY

2.1 X-ray Diffraction

In general, X-ray diffraction (XRD) is a characterization technique that utilizes high-energy electromagnetic radiation from electrons accelerated from a cathode at high velocities colliding an anode. At low energies, incident X-rays are produced and reflect off the lattice planes of a crystalline material. The diffracted beam of X-rays can then characterize the atomic and molecular structure of an impinged crystalline material. At higher energies, the X-rays are able to transmit through the material and is known as High-energy X-ray diffraction.

High-energy X-rays impinge onto a material and diffracts from the lattice planes of the crystalline phases present within the that material producing full Debye-Scherrer diffraction rings downstream of the incident X-ray beam rather than the partially obscured diffraction rings at lower energy XRD. The full Debye-Scherrer rings for a CMAS-infiltrated 7YSZ coating is depicted in Figure 1.3b, with the radius indicating the d-spacing in Angstroms. If no texturing is present throughout the probed volume, the rings would be a uniform intensity along the ring throughout the azimuth. Otherwise, the ring would be disconnected with higher intensities in the preferred orientation direction of the material, which is based on the lattice planes the X-ray beams reflected from. An advantage of high energy XRD is that it allows for fast data acquisition at a high spatial resolution. The information held by diffracted X-rays are able characterize the state of probed volume of the TBCs, including information on the preferred orientation of the grains (texture), phases present within the probed volume, and the lattice strains in the volume, which has been done in previous studies [37, 38, 39, 40]. Often, the raw diffraction pattern of Figure 1.3b is integrated along the azimuth for each d-spacing, producing a one-dimensional intensity vs. d-spacing lineout as shown in Figure 1(c). Figure 1.3c also
indicates the d-spacings of the expected peaks for the tetragonal and monoclinic YSZ phases. Investigations performed by Garvie and Nicholson were able to formulate an equation based from varying known concentrations of the tetragonal and monoclinic phases of zirconia in terms of the monoclinic phase [41]. Their equation is capable of providing an approximation of the phase volume fraction of the monoclinic and tetragonal YSZ phases in terms of the monoclinic phase (mPVF) from XRD lineouts. The equation, presented as Equation 2.1, takes the integrated intensity of the (\(\bar{1}11\)) and (111) for the monoclinic phase and of (101) for the tetragonal phase. Since the formation of the monoclinic phase is representative interactions between CMAS and the coating, this mPVF can be correlated to the thermochemical degradation of the coating.

\[
mPVF(\%) = \frac{I_{m}(\bar{1}11) + I_{m}(111)}{I_{c}(101) + I_{m}(\bar{1}11) + I_{m}(111)}
\]  

(2.1)

2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) a tool that is capable of producing surface images of samples through a focused beam of high energy electrons. SEM is able to achieve high magnification images typically with a resolution between 1 and 10 nm [42]. SEM has been used extensively with polished cross sections of TBCs to provide insights on the microstructure of the top coat. SEM has been used to observe the state of the coating and any microcracks that may have formed due to the age of the coating or from external influences, in the case of CMAS infiltration. Wellman et al. Wu et al., and Krämer et al. have utilized SEM along with additional characterization techniques such as XRD and Raman spectroscopy to observe how the thermochemical interactions between the coating and molten CMAS changed the microstructure of the coating [11, 14, 17].
SEM has also revealed details on the effects of changing the EB-PVD deposition parameters. Naraparaju et al. used SEM when tailoring the microstructure of the coating in their efforts to observe how the microstructure of the coating influence CMAS infiltration at varying annealing temperatures and times. SEM allowed for approximating the CMAS infiltration depth with these varying microstructures and while under varying annealing conditions [12, 13]. Within this thesis, SEM cross-sectional micrographs served to validate and optically depict the mPVF results obtained from XRD measurements.
CHAPTER 3 CMAS SAMPLE PREPARATION AND EXPERIMENTAL SETUP

3.1 Sample Preparation

The samples used for infiltration were 7YSZ EB-PVD coatings which were deposited by means of a 150 kW EB-PVD dual-source pilot plant coater system on a 1 mm thick alumina substrate (12mm x 12 mm) at the German Aerospace Center (DLR) in Cologne, Germany with a substrate temperature of 1000 °C and rotational speed of 12 rpm. The scanning electron microscopy (SEM) image in Figure 3.1 shows the coated substrates A0 that is not infiltrated by CMAS and without heat treatment. Samples A2 and A3 were also not infiltrated by CMAS with different heat treatment times and temperatures as described in Table 3.1.

![SEM image at the surface of the columnar 7YSZ EB-PVD deposited coating of sample A0 with no heat treatment.](image)

The images show the closed-porosity columnar microstructure typical of EB-PVD coatings where the columns have a center core and a porous outer feathery region. The estimated thickness of the coating from the SEM images is 400 μm. A columnar microstructure provides a higher strain tolerance than a monolithic microstructure typically characteristic in other deposition methods. This is due to the presence of intercolumnar gaps in EB-PVD
coatings that allow for thermal expansion to occur during operation without introducing significant stress.

Table 3.1 Samples information regarding composition, annealing temperature, and annealing time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Annealing Temperature (°C)</th>
<th>Annealing Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>7YSZ</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>A2</td>
<td>7YSZ</td>
<td>1225</td>
<td>10</td>
</tr>
<tr>
<td>A3</td>
<td>7YSZ</td>
<td>1250</td>
<td>10</td>
</tr>
<tr>
<td>B1</td>
<td>7YSZ + CMAS</td>
<td>1225</td>
<td>1</td>
</tr>
<tr>
<td>B2</td>
<td>7YSZ + CMAS</td>
<td>1250</td>
<td>1</td>
</tr>
<tr>
<td>B3</td>
<td>7YSZ + CMAS</td>
<td>1250</td>
<td>10</td>
</tr>
</tbody>
</table>

The CMAS composition used in this study, (in mol.%: 24.6% CaO, 12.4% MgO, 11% Al₂O₃, 41.7% SiO₂, 8.7% FeO & 1.6% TiO₂), was based on deposits obtained by analyzing different aero-engine parts that flew over Middle Eastern countries. CMAS was synthesized by co-decomposition of Al, Ca, Mg, and Fe nitrates along with SiO₂ and TiO₂ powders (Merck, in Darmstadt, Germany) followed by heat treatment at 1250 °C for 1 h. A roughly 8-mm diameter circle of the CMAS was then applied on top of the 7YSZ coating. CMAS was deposited in the amounts of 10 mg/cm² in the center of the samples and isothermally heat treated in a Netzsch chamber furnace at 1225 °C (Sample B1) and 1250 °C (Sample B2 and B3) to allow for CMAS infiltration for different annealing times as described in Table 3.1. Samples B1 and B3 were then prepared for SEM through standard metallographic techniques typically used in preparing cross sections of samples. The methods used to infiltrate and prepare the samples for SEM were similar to previously conducted CMAS infiltration studies [12, 13, 36]. Three other samples were annealed at similar temperatures and times without CMAS deposits. All of the sample parameters are given in Table 3.1 and a picture of the prepared samples in Figure 3.2. The SEM images of the infiltrated samples are shown in Figure 3.3.
During annealing, the CMAS is able to infiltrate quickly into the intercolumnar gaps present throughout EB-PVD through capillary effects and wet the feathery arms region [12]. SEM imaging allows for qualitative observation of the depth CMAS has infiltrated into these gaps and to ensure that the infiltration was successful. In Figure 3.3, in both B1 and B3, it is observed that the CMAS has indeed infiltrated into the samples and have completely sealed the intercolumnar gaps. This allows for qualitative validation of the depths at which we should expect to see the influence of CMAS within the infiltrated samples. Additionally, the effects of CMAS infiltration, when compared to Figure 3.2, can be observed with the columnar tips becoming more eroded with an increase in annealing temperature and time.

Figure 3.3 SEM image at the surface of CMAS infiltrated 7YSZ EB-PVD samples (a) B1 annealed at 1225 °C for 10 hours and (b) B3 annealed at 1250 °C for 10 hours.
The samples without CMAS infiltration are used as a reference in order to determine the effect of CMAS attack on the monoclinic phase formation of the coating. The melting range of the CMAS composition used is between 1225-1250 °C [36]. These two temperatures were chosen to determine the effect of temperature on the CMAS infiltration depth and on the chemical degradation of the coating. The annealing times of 1 hour and 10 hours were chosen to observe the influence of time on the rate of phase transformation within the coating.

3.2 Sample dimensions, set up and data collection

High-energy XRD measurements were performed at beamline 1-ID of the Advanced Photon Source at Argonne National Laboratory. Data was collected on the profile of the 12 x 12 x 1.4 mm³ sample with an incident X-ray beam size of 30 μm horizontally and 300 μm vertically with a beam energy of 71.68 keV. Debye-Scherrer rings between 1.48 Å - 4.89 Å were captured using a GE a-Si 2048 x 2048-pixel area detector located approximately 1697.5 mm away from the sample. CeO₂ powder was used to calibrate the experimental setup. The high energy of the X-ray beam impinges on the profile of the sample for a 1s exposure time, transmits through, and diffracts the Debye-Scherrer rings throughout 12 mm of coating, which can be seen in Figure 3.4b. This resulted in a probed volume of 0.108 mm³, which remains consistent for each sample. Data was collected this way in order to attain high spatial resolutions throughout the depth of the coating while also minimizing localized effects within the coating while capturing the effects of CMAS on the coating along a constant depth. With a 30 μm step size, 15 data points were collected from the surface of the coating to the YSZ-alumina interface. Of the 15 data points, one of the measurements was taken directly above the sample and another was right below the YSZ-alumina interface. These additional points were taken to ensure data was properly attained throughout the depth of the coating.
Figure 3.4 (a) Schematic view of the XRD data collection in transmission mode. (b) A side profile view is provided with the dimensional thickness of the 7YSZ coating (~400 μm) and alumina substrate (~ 1 mm) as well as how the scans were performed and the spatial resolution of the probe volume dimensions (30 x 300 x 12000 μm$^3$) of the X-ray beam.

It should be noted that although the CMAS was deposited only at the center of the sample, to obtain depth resolution data, the samples were measured from the profile of the sample (Figure 3.4b), meaning the X-ray beam impinged on a part of the sample that was non-infiltrated 7YSZ as well as the infiltrated 7YSZ regions throughout the samples. The beam probed through about 0.036 mm$^3$ of non-infiltrated region of the coating as compared to about 0.072 mm$^3$ of the infiltrated region. This remains consistent between all of the infiltrated samples, allowing for comparison between the effects of annealing temperature and time.
CHAPTER 4 RESULTS OF TIME AND TEMPERATURE EFFECTS ON CMAS INFILTRATION

Results of the synchrotron experiments are presented here and the findings from these results are compared and supported with the SEM images. The results for the non-infiltrated samples are presented first, which serve as reference samples to then be compared to those from the infiltrated samples measured at two different temperatures (1225 °C and 1250 °C). This comparison establishes the effect of temperature on phase transformation. Finally, the effect of time is investigated by comparing samples at a fixed temperature (1250 °C) over two different time exposures (1 hour and 10 hours).

4.1 X-ray diffraction peak identification

The data collected from the X-ray diffraction rings were averaged over the entire 360° azimuth and presented as 1-ID lineouts in the results in order to clearly observe and compare the peak intensities to identify the peaks. These lineouts can be seen for each sample in Figure 4.1. The resulting peaks in Figure 4.1 were identified by cross-referencing the XRD peak lineouts from the Joint Committee on Powder Diffraction Standards (JCPDS) files: JCPDS 04-008-7255 and JCPDS 04-018-6628 for the tetragonal and monoclinic YSZ phases, respectively. The cubic phase has a very similar diffraction pattern when compared with the tetragonal phase and are labeled as part of the tetragonal phase. This is because the cubic phase is only an intermediate phase in the 7YSZ phase transformation from the tetragonal to monoclinic phase and the cubic phase does not introduce significant additional stresses to the coating. It should be noted that although the (101) tetragonal peak located at approximately 2.97 Å should be the highest peak, the lineout peaks do not match fully with that of the normalized intensities found.
within these JCPDS files. This is due to the highly texturized Debye-Scherrer rings obtained during data collection.

Additional phases, pyroxene and anorthite, other than 7YSZ and its constituent phases, were also detected and identified within the lineouts for sample B1, Figure 4.1b. These two silicate phases are associated with the synthesized crystalline CMAS [13]. The pyroxene and anorthite phases were identified and cross-referenced through work done previously studying the composition of CMAS and its various compositions when interacting with 7YSZ [13, 43, 44].

Upon cooling, after becoming fully molten around 1250 °C, the CMAS solidifies fully around 1200 °C and reprecipitates into an amorphous glass of these two silicate phases with the addition of the dissolved Y2O3 and ZrO2 from the 7YSZ. During CMAS infiltration in B1,
it was observed through SEM that the partially molten CMAS did not fully infiltrate the coating, stopping somewhere around 20% or about 80 μm in the coating after 10 hours. The unmelted parts of the CMAS still displayed strong pyroxene and anorthite phases, which influenced the XRD lineouts taken throughout the coating. These silicate phases have strong peaks corresponding to the same d-spacing as the mYSZ and tYSZ peaks. Therefore, the pyroxene and anorthite peaks must be subtracted before fitting B1 YSZ peaks to determine the mPVF.

It should be noted that the crystalline pyroxene and anorthite phases were not detected in the other infiltrated samples of B2 and B3 since the CMAS within these samples were fully molten during the annealing process and a majority of the CMAS recrystallized into more amorphous phases. It is suspected that trace amounts of the pyroxene and anorthite phases may still be present within these infiltrated samples, however, the concentration of these phases are too low to be properly identified and are therefore considered to be negligible within B2 and B3, as compared to B1.

![Figure 4.2](image)

Figure 4.2 (a) Lineout of the CMAS peaks with respect to d-spacing. (b) A subtraction of the CMAS peaks from B1 at a depth of 90 μm into the coating.

A reference of the pyroxene and anorthite phases were taken from the 30 μm thick CMAS layer resting on the surface of the coating for sample B1, shown in Figure 4.2a. With this reference, the varying influence of the CMAS rings at each depth measurement on the XRD lineouts were able to be removed, leaving behind only the YSZ peaks, as shown in Figure 4.2b. In order to determine the influence of the CMAS peaks present in the lineout, the CMAS
peaks needed to be deconvoluted. However, this peak overlapped with the 7YSZ tetragonal and monoclinic peaks. In cases where the both of the CMAS anorthite (04̅2) and (101) tetragonal 7YSZ peaks did not fully overlap each other, which occurred primarily deeper in the coating, the two peaks were deconvoluted with a symmetric Gaussian shape, resulting in accurate intensities of both the CMAS peaks and of t1. In other cases where deconvolution of the CMAS and 7YSZ peaks was not possible, the anorthite (422) peak located at 1.689 Å was used as the CMAS reference. This peak was chosen as it was isolated from the other peaks present in the lineout. The 1.689 Å peak was then used to determine the highest intensity peak through a percent value equation, Equation 2, using the known peak intensity ratio between the two anorthite peaks [43].

\[ I_{(04̅2)} = \frac{I_{(422)}}{I(%)_{(422)}} \]  

(2)

With the intensity of the (04̅2) anorthite peak determined, Equation 2 can be rearranged into Equation 3 and redefined to determine the intensity of the other peaks.

\[ I_n = I(%)_n \times I_{(04̅2)} \]  

(3)

The CMAS peaks were then able to be subtracted from the lineout, leaving only the YSZ peaks, which can be seen in Figure 4.2b. B1 was then fitted along with the other samples to determine the mPVF [19].

The integrated intensities of the (101) tetragonal peak (t1) and the (1̅11) and (111) monoclinic peaks (m1 and m2, respectively) were required to determine the mPVF through Equation 1.1. The peaks were identified and fitted using a pseudo-Voigt function. An integrated intensity was determined by the area underneath this fitted function of the peaks throughout 10° intervals throughout the azimuth, as seen in Figure 4.3. Then an average of the integrated
intensities for each of the 36 sections were obtained to determine the integrated intensity of t1, m1, and m2 for each depth. The effects of texturing and nonuniformity throughout the Debye-Scherrer rings are reduced through this method. A Gaussian shaped deconvolution was performed on m1, Figure 4.3c, due to the symmetric bell-like curve nature of the present doublet during fitting.

![Graphs showing fitting of peaks](image)

Figure 4.3 Pseudo-Voigt function fittings for (a) t1, (b) m2, and (c) m1 with a Gaussian deconvolution plot. The integrated intensity of these plots is used to calculate the mPVF of each sample.

The pseudo-Voigt function was used to fit t1, m1, and m2 for each depth up to 150 μm. After which, absorption attenuation of the Debye-Scherrer rings made the data unreliable in obtaining accurate mPVF values and as a result, is not included. This attenuation most likely a result of the higher density and higher absorption coefficient of the alumina substrate, resulting in parts of the diffracted X-rays being too scattered within the sample before reaching the detector.

In the following sections, the X-ray diffraction results obtained using the data analysis methods described are presented for all the samples with the corresponding SEM results for comparison and validation.
4.2 Non-infiltrated samples

The SEM image of Figure 4.4a, is from an as-deposited 7YSZ sample with no CMAS infiltration (A0) and the average mPVF results calculated for all non-infiltrated samples (A0, A2, and A3) at each depth from XRD are shown in Figure 4.4b. The mPVF for the non-infiltrated samples lie within the range of 0 – 0.6 % when accounting for possible errors. There is no discernible increase in the mPVF at varying times and temperatures (1225 °C for A2 and 1250 °C for A3) as compared to an as-deposited coating. This is because there is no CMAS present within these samples to instigate phase transformation of the coating, which is also reflected in the lack of the globular monoclinic YSZ phase and CMAS infiltration present within the SEM image of A0. The errors presented in Figure 4.4b are fitting errors of the YSZ peaks contributed by the negligible intensities of mYSZ for the non-infiltrated samples.
Within the SEM image, it can also be observed that the columnar tips and feather arms are well defined throughout the depth of the coating. The surface (0 μm) depth measurements shown in the SEM starts slightly within the coating, by a range of approximately 1 – 3 μm. This is due to slight variations in the columnar tip heights. The labelled depths within the SEM cross-sectional micrographs correspond well with the calculated mPVF results at each depth and serve as a reference point for the infiltrated samples.

4.3 Infiltrated samples: temperature and time effects

Figure 4.5a shows the SEM of a sample B1, which was infiltrated by CMAS at an annealing temperature of 1225 °C for 10 hours. Figure 4.5b shows the mPVF with respect to depth of sample B1. From XRD, the mPVF was found to be roughly 9.2% ± 8.35% at the
surface and decreased to near zero by 90 μm. At 1225 °C, the CMAS composition used in this study is only partially molten. In this partially molten state, crystalline pyroxene and anorthite phases were much more prevalent within the CMAS and the XRD lineouts for B1 as compared to other infiltrated samples as shown in Figure 4.1b. In order to determine the mPVF, the pyroxene and anorthite XRD peaks that overlapped with the tetragonal and monoclinic YSZ XRD peaks needed to be removed. The removal of these CMAS peaks on the XRD lineout at each depth introduced additional uncertainties into the mPVF calculations and are taken into consideration in the error calculations. The errors introduced by this removal account for a majority of the overall mPVF error.

Additionally, it was found within a previous study that CMAS when annealed at 1225°C for 10 hours had only infiltrated approximately 20% of the coating, which is also observed in the calculated mPVF results for B1 in Figure 4.5b. This previous study concluded that their findings were a result of the CMAS having a higher viscosity in this partially molten state as compared to being fully molten at 1250 °C, which slowed down the rate of infiltration significantly [12].

It was observed within the SEM images that the CMAS only partially infiltrated and reacted with the coating. The globular monoclinic phase is indicated in Figure 4.5a and is seen through SEM imaging as a slightly darker gray in the 7YSZ columns. Signs of the globular monoclinic phase are present in higher concentrations around the columnar tips near the surface of the coating and decreases in concentration until reaching near zero around 60-80 μm into the coating. The columnar tips and feather arms are beginning to show signs of sintering, but are still well defined at this point. This observation in the SEM micrograph agrees with both the calculated mPVF results from XRD within this study as well as from the aforementioned previous study.
Figure 4.5 (a) SEM cross-sectional micrograph of a CMAS infiltrated 7YSZ coating that was infiltrated with the conditions of 1225 °C for 10 hours and shows some signs of globular mYSZ near the surface and decreasing throughout the depth. (b) The mPVF of the B1 with respect to depth as determined through high-energy X-ray diffraction measurements.

At 1250 °C, the fully molten CMAS has a much lower viscosity and fully infiltrates the coating within minutes [5]. This is followed by the coating reacting with the molten CMAS and it can be seen for the 1250 °C for 10 hours sample (B3) in Figure 4.6a and Figure 4.6b. The effects of the fully molten CMAS can also be seen in the mPVF XRD results in Figure 4.6b. At the surface, the mPVF was found to be approximately 51.9% ± 1.29% and decreases steadily throughout the depth of the coating shown here up to 150 μm.
Figure 4.6a shows the SEM cross-sectional image of B3. B3 shows high concentrations of the globular monoclinic phase and similar to B1, B3 exhibits higher concentrations of the monoclinic phase near the surface of the coating and decreases further through the depth of the coating. As a result, the columnar tips and feather arms have been highly sintered and are almost nonexistent within the SEM images. Additional SEM analysis revealed that CMAS has infiltrated completely through the 400 μm thick coating and reached the alumina substrate where it has reacted with the roots of the 7YSZ columns causing monoclinic phase formation within the region [12]. However, this was not observed conclusively through XRD in this study due to attenuation and absorption effects that decreased the XRD diffraction ring intensities past 150 μm into the coating.
Though B1 and B3 were held at similar exposure times of infiltration, B1 has a much lower mPVF overall throughout the depth of the coating. The consistently higher mPVF values for B3 as compared to B1 in Figure 4.7a would suggest the thermochemical interaction between the CMAS and coating is highly influenced by temperature. The qualitative SEM micrograph results for B1 and B3 shows similar trends in the CMAS infiltration depth of partially molten and fully molten CMAS, respectively, as to what was found in similar conditions in the CMAS infiltration depth and temperature studies performed by Naraparaju et al. [13] This would also suggest that the viscosity and the concentration of the CMAS melt present in the coating not only influence the CMAS infiltration depth within the coating, but also the thermochemical reaction rate of the coating with the CMAS melt. This would also suggest that the rate of thermochemical degradation through monoclinic phase transformation is slower with higher viscosities. The extent temperature has on the thermochemical degradation of the coating were determined through the calculated mPVF differences between B3 at 1250 °C and B1 at 1225 °C, which is approximately 42.8% ± 8.45%.
Similarly, the effects of time on thermochemical degradation can be seen in Figure 4.7b. B2 was held at the same temperature as B3, but was only infiltrated for 1 hour as compared to 10 hours. Similar to B3, the CMAS fully infiltrated B2 within only a few minutes and can be seen with the monoclinic phase being present throughout the measured depth of the coating. These results agree with studies performed by Li et al. and Naraparaju et al., where the CMAS fully infiltrates the coating within minutes and then the coating starts to react with the molten CMAS [12, 19]. When comparing the calculated difference in mPVF between B3 and B2 being about 21.5% ± 1.32%, it can be noted that a majority of the thermochemical degradation of the coating occurs at the surface and decreases further into the depth of the coating. This follows a similar trend observed by Krämer et al, which would also suggest that after some point within the coating, the thermochemical degradation and mPVF would start to increase with respect to depth towards the substrate [17].

One of the significant findings from our work is that a majority of the thermochemical degradation occurs within the first hour of CMAS infiltration, after which sintering may be more predominant in coating degradation. Similar results are observed in a Raman spectroscopy study, on B2 and B3 samples capturing the destructive phase destabilization caused by CMAS infiltration for 1 hour and 10 hours of annealing times at 1250 °C [30]. The mPVF was calculated non-invasively through high resolution Raman measurements taken at 20x objective and were validated with SEM cross-sectioned micrographs. The mPVF results from the Raman study provided localized mPVF concentration values that are highly influenced by the microstructure. It was found that higher mPVF values occurred along the edges of the columns compared to the center. This is also observed with the SEM cross-sectional micrographs for B3, Figure 4.6a. When averaging the localized mPVF depth results up to approximately a 33 μm depth from Raman to approximately compare the surface mPVF results from XRD, 30 μm, there is a difference of roughly 6.95 % ± 3.43 % and 6.72% ± 1.96 %
for B2 and B3, respectively as seen in Figure 4.8. The discrepancy could be attributed to the vast difference in probed volume size with a probed volume of 1.08e-1 mm³ (30 x 300 x 12,000 μm) for XRD and 1.33e-5 mm³ (20 x 20 x 33.25 μm) for Raman. The larger XRD probed volume allows for an averaging of any microstructural differences throughout the probed volume and provides mPVF results more representative of the entire coating along the probed depth.

![mPVF vs depth of B2](image1)

![mPVF vs depth of B3](image2)

Figure 4.8 Averaged Raman spectroscopy mPVF results (20 x 20 μm²) through a highly resolved depth (6.65 μm) within the CMAS infiltrated area of the sample annealed at 1250°C for 1 hour (B2) and the sample annealed at 1250 °C for 10 hours

Wellman et al. and Chang et al. found when coatings are exposed to CMAS for longer durations, even by only a few additional hours, high amounts of sintering occurs on microstructure, especially towards the columnar tips [11, 25]. This could be due to the CMAS throughout the coating becoming almost saturated by the Y³⁺ some point around the first hour, resulting in less Y-depleted YSZ from reprecipitating. This is because the CMAS interacts with the YSZ coating and primarily depletes the Y³⁺, which after some point depending on the concentration of CMAS and of Y³⁺ within the coating the CMAS would become saturated and would no longer deplete Y³⁺ [17, 28].

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When comparing Figure 4.7a and Figure 4.7b, the data suggests that the effects of temperature play a larger role on degradation as compared to the effects of time as CMAS becomes fully molten at 1250 °C. Past the melting range, it is expected that any further increase in temperature would not significantly increase the extent of phase transformation, but rather the time required for infiltration and for phase transformation would be shortened as viscosity is further reduced. The data also suggests that a majority of the thermochemical degradation as a result of the phase transformation of the coating from the non-transformable tetragonal YSZ to the monoclinic YSZ phase occurs within the first hour of infiltration. After which, sintering plays a more prominent role.

Experimental calculation of the monoclinic volume fraction is important in understanding the mechanical strength of the 7YSZ coatings which would define the erosion properties of the coating under CMAS attack. No such data currently exists for the development of an erosion model studying, quantifying, and comparing the thermochemical degradation of coatings infiltrated by CMAS with respect to annealing temperature and time until now. This study paves the way for the usage of high-energy XRD techniques to evaluate the phase transformations with high sensitivity and spatial resolution and can be applied on to novel TBCs such as gadolinium zirconate and yttria-rich zirconia and estimate the in plane and out of plane mechanical behavior.
CHAPTER 5 CONCLUSIONS

This work investigated the impact of annealing temperature and time on the thermochemical degradation for CMAS infiltrated EB-PVD 7YSZ coatings through high-energy synchrotron X-ray diffraction and validated through SEM cross-sectional micrographs. The thermochemical degradation was quantified throughout the depth of the coating through mPVF calculations from XRD measurements. It was found that the extent of degradation the coatings experiences is more sensitive to temperature within the melting range of CMAS when increasing the annealing temperature from a partially molten CMAS at 1225 °C to a fully molten CMAS at 1250 °C. Once fully molten, it was found that a majority of the thermochemical degradation occurred within the first hour of infiltration compared to the increase in the mPVF when increasing from 1 hour to 10 hours. The results from this thesis helps to resolve the impacts of annealing temperature and time in the CMAS infiltration kinetics in EB-PVD TBCs, which are important considerations towards mitigating CMAS infiltration. Coupled with thermomechanical analysis of the additional strains created due to the presence of CMAS and the formation of the monoclinic phase, will allow better models and prediction methods to be made of the lifetime of a coating after exposure to sand-like compositions.

The findings from this work will assist in determining vital annealing parameters to investigate further in future studies. For instance, it would be of interest to measure and track the thermochemical degradation of coatings within the first hour of infiltration. Similarly, this finding demonstrates that experiments monitoring the infiltration of CMAS into EB-PVD coatings can measure a majority of the degradation due to thermochemical interactions in 1 hour and to expect a slowly decreasing rate of an increasing mPVF over time.
Additionally, the methods for quantifying the degradation of the coating through high energy XRD and validating the XRD measurements with SEM is not limited only to 7YSZ EB-PVD coatings, but can be modified and applied to more novel TBCs, such as Gadolinium zirconate (GZO) coatings with respect to tracking the formation and growth of the reactionary apatite phase.

Future work will include analysis of the data for depth resolved strains to assess the impact of time and temperature on the thermomechanical behavior of these coatings. Full thermal barrier coating systems will be studied to establish any effects of the substrate on the behavior. In-situ infiltration experiments will provide both time and depth resolved data on infiltration kinetics that can better help design CMAS resistant coatings.
REFERENCES


