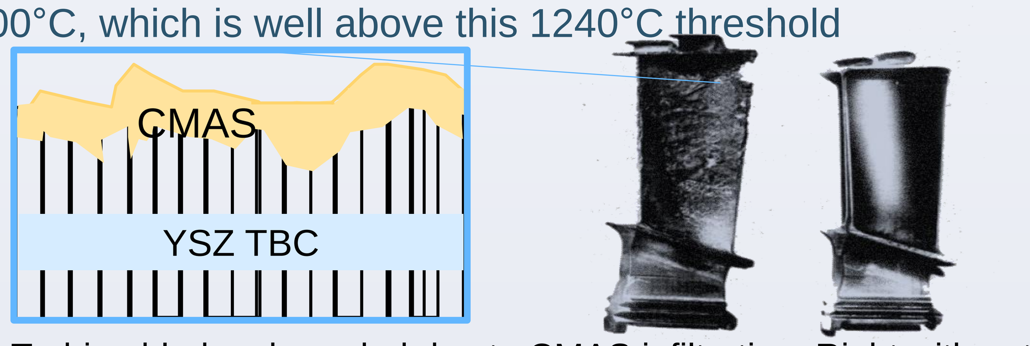
X-Ray Diffraction Studies of CMAS Infiltrated Thermal Barrier Coatings

Stein Z.[a], Bohorquez E.[a], Rossmann L.[a], Naraparaju R.[b], Raghavan S.[a]

a Department of Mechanical and Aerospace Engineering, University of Central Florida, 4000 Central Florida Blvd., Orlando, FL 32816, USA
b German Aerospace Center, Linder Höhe, 51147 Colonge, Germany

Background and Introduction

Yttria-stabilized zirconia (YSZ) serves as a ceramic topcoat for thermal barrier coatings (TBCs) in gas turbines in the aviation and power generation industries to improve their efficiency. TBCs lower temperatures of turbine blades during operation. Siliceous surface contaminants, such as sand, volcanic ash, and runway debris, infiltrate and rapidly degrade TBCs. Calcium-magnesium-aluminum-silicate (CMAS) is a mixture used to represent these particulates. CMAS melts into the TBC at around 1240°C, depleting the yttrium into the CMAS. In industry, operating temperatures can reach up to 1400°C to 1600°C, which is well above this 1240°C threshold



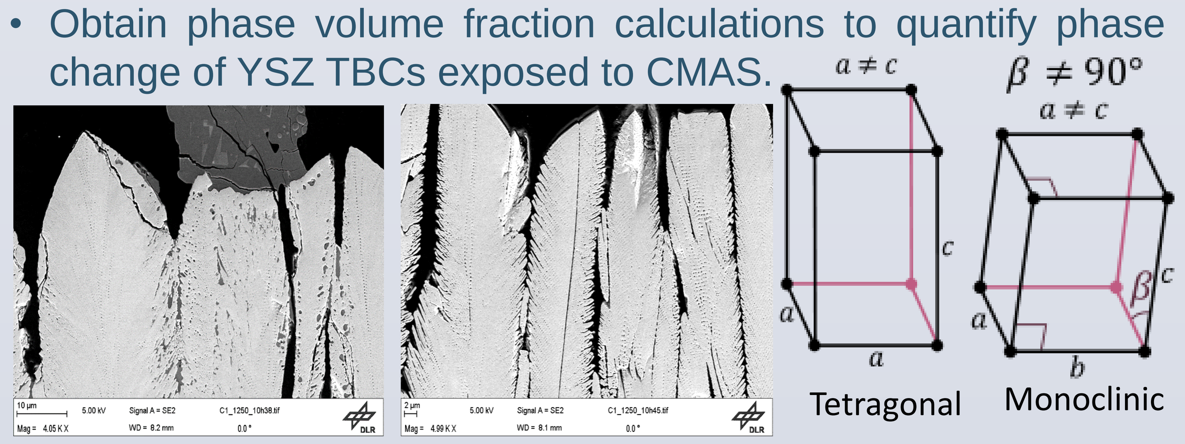
Left: Turbine blades degraded due to CMAS infiltration. Right with out CMAS.

Motivation and Objectives

- When CMAS depletes nearby yttrium, it causes the zirconia to change phase - from a tetragonal (t-phase) crystal structure to monoclinic (m-phase).
- The m-phase phase has a larger volume, causing stresses in the coating.
- Trace amounts of cubic (c-phase) is also present and transforms into either t- or m-phases; however the c-phase has a similar volume to t-phases so typically YSZ coatings would be composed of t- and c-phases.

Objectives:

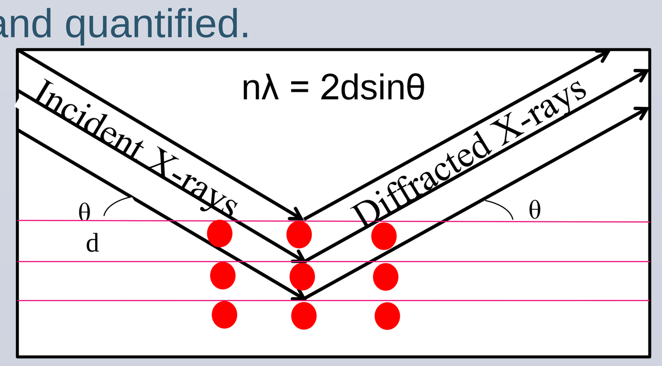
- Conduct X-ray diffraction (XRD) to determine how temperatures below and above the CMAS melting point (1240°C) and time of exposure to CMAS effects the phases of YSZ.
- Obtain phase volume fraction calculations to quantify phase change of YSZ TBCs exposed to CMAS.



SEM images of CMAS ingression in YSZ. Left: Appearance of monoclinic YSZ globular formations. Right: Intact columnar microstructure.

Experimental and Theory

- XRD reveals information about a material's atomic structure by observing the way an X-ray beam interacts with the sample.
- The angle of diffraction relates to the spacing of the atomic planes by Bragg's Law, shown below.
- From XRD data, the phases present in a sample can be identified and quantified.



X-ray diffraction and how the rays interact with molecules within a sample

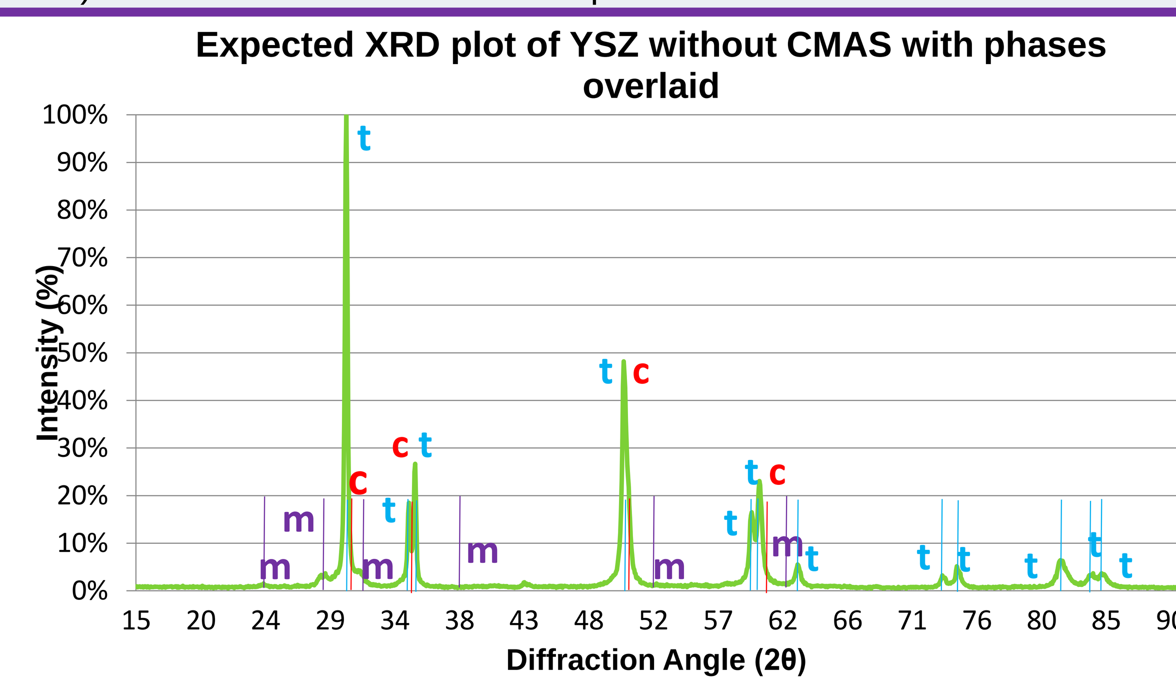
Analysis and Results

Since 1225°C is below the melting point of CMAS, only one sample with long exposure (10 h) was chosen and since 1250°C is above the melting point of CMAS, 2 samples were chosen where one was with short exposure (1 h) and one with long exposure (10 h). The XRD data was compared to literature to identify the phases present. The left table below summarizes the crystal structure of the phases present in YSZ; meanwhile the right table displays the PVFs obtained from analyzing the XRD plots shown below.

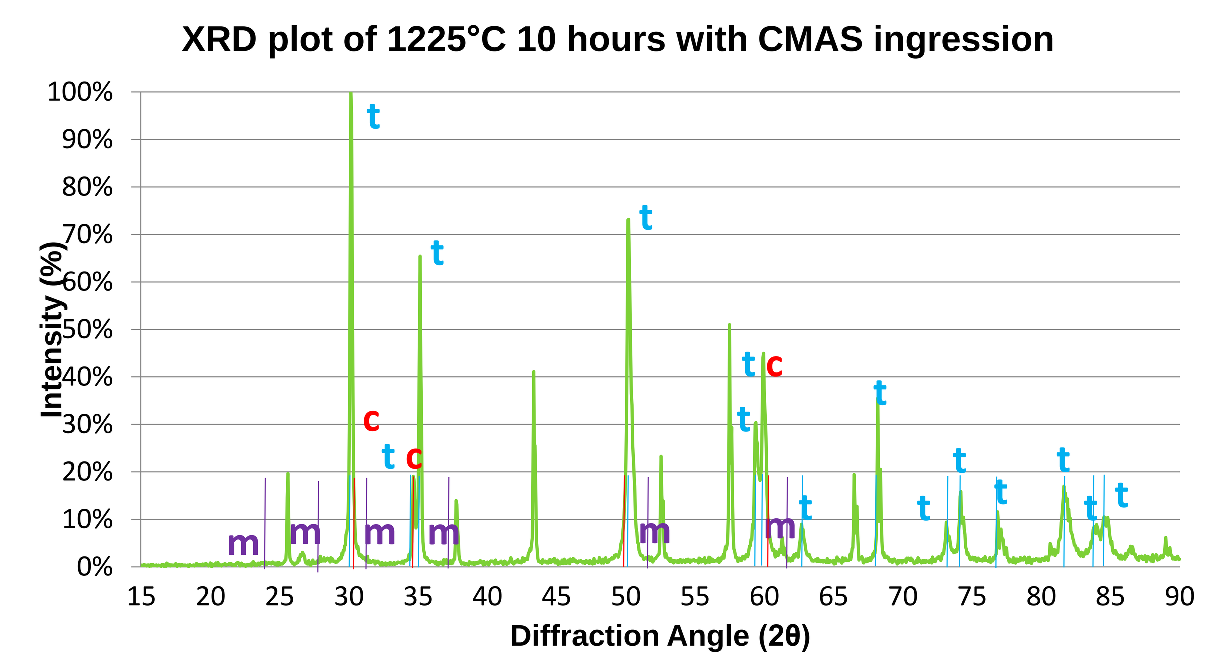
Phase	A (Å)	B (Å)	C (Å)	β (°)	Volume (*10[6] picometer[3])
Tetragonal	3.63	3.63	5.14	90.00	67.55
Monoclinic	5.15	5.21	5.31	99.23	140.54
Cubic	3.64	3.64	5.15	90.00	68.33

Phase	PVF 1225°C 10 h (%)	PVF 1250°C 1h (%)	PVF 1250°C 10h (%)
Tetragonal	91.2	90.8	95.2
Monoclinic	2.2	1.9	3.5
Cubic	6.5	7.3	1.3

Left: Summary of crystal structure for each phase of YSZ. Right: PVF of m-, t-, and c- phases for each sample (obtained from analysis from the XRD plots below). There are increases in the m-phases from 1h to 10h as well as compared to 1225 and 1250°C.

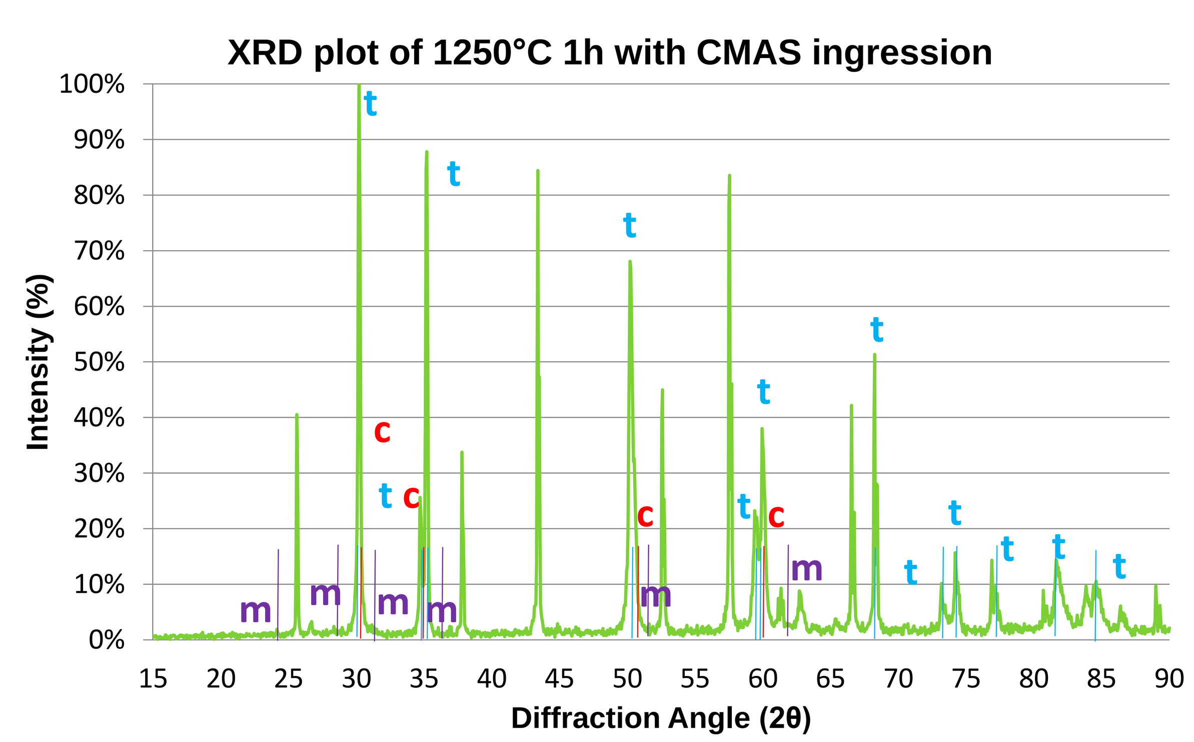


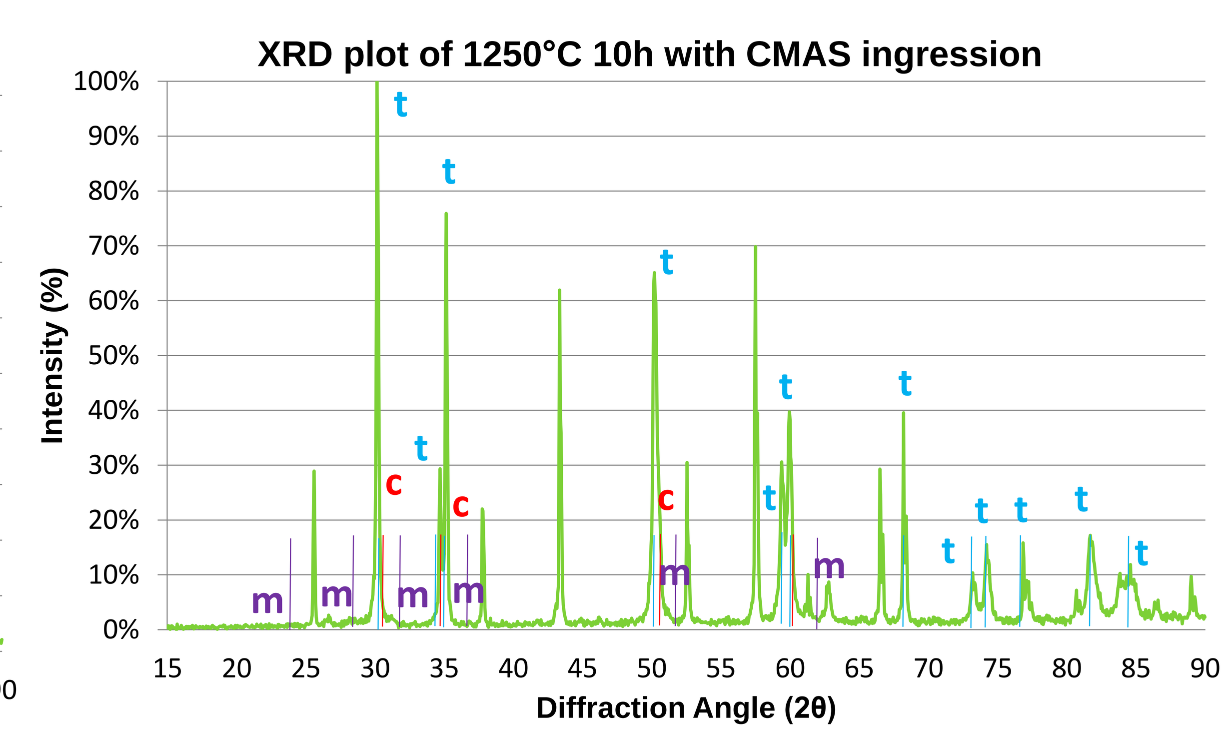
Graph 1: The expected peaks of YSZ without CMAS. Mainly t- and c- phases. Minimal m-phases should be present, hence small peaks present at m.

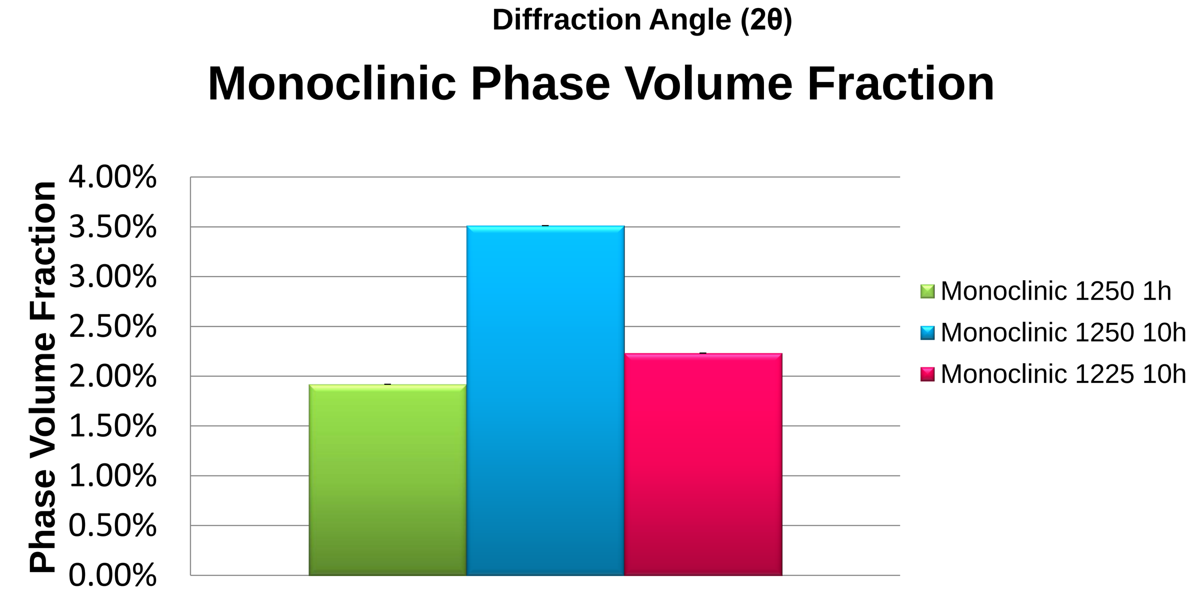


Graph 2: The c-, t-, and m-peaks of the samples.

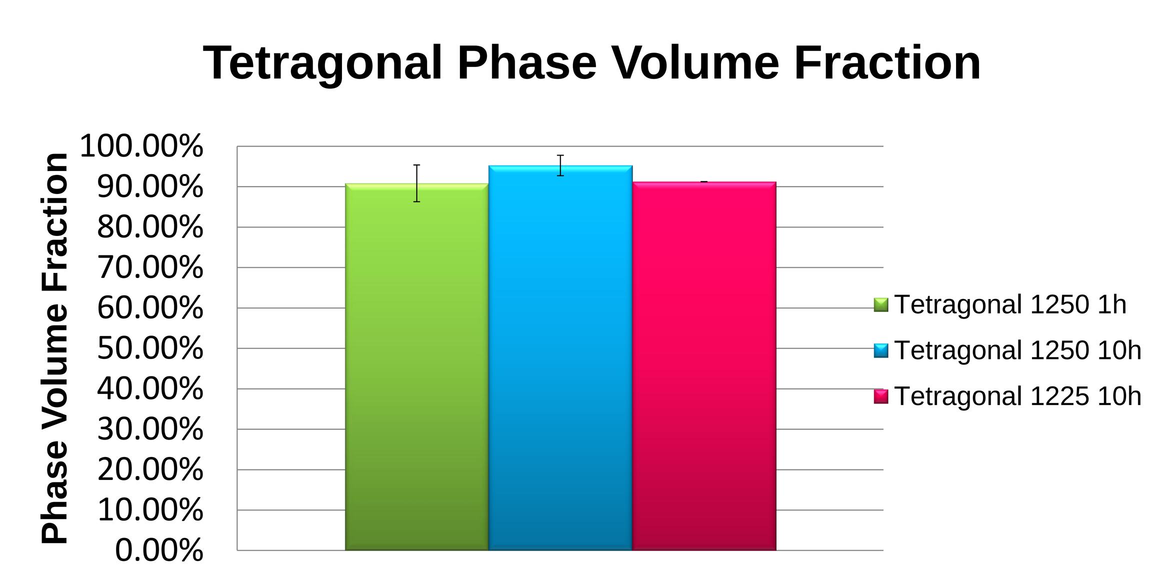
- The relative intensities of the XRD peaks were used to determine the volume fractions of t- and m-phases.
- There was an increase of about 1.6% in the m-phase between 1 and 10 hours for the 1250°C sample indicating the impact of time on the ingression effects.
- There was about a 1.3% higher m-phase volume within the 1250°C compared to the 1225°C after 10 hours indicating that the temperature of the ingression environment plays a role in ingression effects.







Monoclinic Phase Volume Fractions of Samples



Tetragonal Phase Volume Fractions of Samples

- There was also an increase of about 4.4% in the t-phase within the 1250°C sample between 1 and 10 hours of exposure.
- This increase is due to the decrease in the c-phase within the samples.

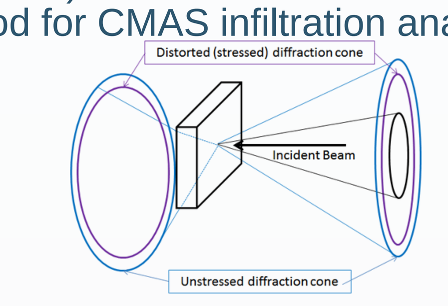
Conclusion

Siliceous containments, represented by CMAS, rapidly degrade the YSZ coating used to improve the efficiency in turbines. It was found that the ingression of CMAS is impacted by the time and the temperature of the ingression environment. This impact means that the more extreme temperatures found within the turbine over long durations of operation will dramatically increase the monoclinic phases present within the YSZ coating, causing more residual stresses to form. Eventually these stresses will lead to cracks forming in the coating and cause failure, spallation.

Future Work

- Now that the monoclinic phase has been found to be correlated with temperature and time of exposure with XRD, this correlation must be compared to previously collected Raman spectroscopy data.
- Raman is a non-destructive technique to measure vibrational scattering of a sample's molecules to determine the material, its phases, and stresses present.
- Continue and compare the stresses found between Raman and XRD samples.

- Use 2D XRD (In-situ) to further validate Raman as the non-destructive method for CMAS infiltration analysis.



- The XRD used in this study had diffraction data at different points, 1D XRD. 2D XRD giving data from an area of diffraction through a diffraction cone, holds information about atomic arrangement, texture, microstructure, defects, stresses, pans phases. 2D XRD has high speed and high accuracy.
- This would allow for analysis of CMAS infiltration into TBCs without permanently destroying samples.

References/Acknowledgements

This material is based upon work supported by National Science Foundation grants DMR 1337758 and OISE 1460045 and by the German Aerospace Center (DLR).

Bohorquez E., Sarley B., Hernandez J., Hoover R., Laurene Tetard, Naraparaju R., Schulz U. & Raghavan S., "Investigation of the Effects of CMAS-infiltration in EB-PVD 7% Yttria-Stabilized Zirconia via Raman Spectroscopy," 2018 AIAA/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, 8–12 January 2018, Kissimmee, Florida.

Naraparaju R., Hüttermann M., Schuly U. & Mechnich P., „Tailoring the EB-PVD columnar microstructure to mitigate the infiltration of CMAS in 7YSZ thermal barrier coatings," *Journal of the European Cermaic Society* 37.1 (2017) 261-270. doi: 10.1016/j.jeurcerasoc.2016.07.027