CMAS Ingression Study on EB-PVD Thermal Barrier Coatings using Synchrotron X-Ray Diffraction

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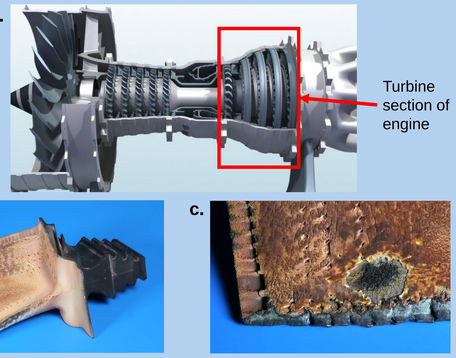
Introduction

- Thermal barrier coatings (TBCs) are applied to turbine blades to insulate superalloy blades in jet engines
- Yttria-stabilized zirconia (YSZ) is the standard material for TBCs
- Coating is applied through Electron-Beam Physical Vapor Deposition (EB-PVD) resulting in a columnar microstructure
- Deposits, such as sand or volcanic ash, enters the engine, melts and ingresses into the coating during operation [1,2]



Images of turbine blades have been used with permission by the German Aerospace Center (DLR)

a. Depiction of a jet engine with the turbine section labelled
b. Image of a turbine blade exposed to CMAS during operation
c. Close-up of coating failure due to CMAS exposure

Motivation and Objective

Motivation

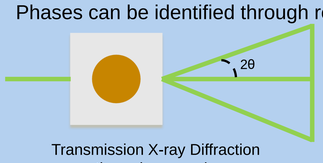
- During CMAS ingression, yttria is depleted
  - Causes phase transformations within the coating
  - Increases strain and risk of failure
  - Decreases lifetime expectancy
- High-energy X-ray diffraction can quantify phases present

Objective

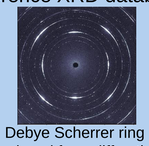
- Determine the effect of CMAS ingression on TBC by measuring the phase volume fraction (PVF) of the monoclinic phase (mPVF) present in the coating

2D XRD & Phase Volume Fraction Theory

- High-energy X-rays transmit through material, producing unique Debye-Scherrer rings according to the lattice spacing of the present crystalline phases
- Rings hold information regarding the amount of phases present, texture, and strain within the material
- Phases can be identified through reference XRD databases



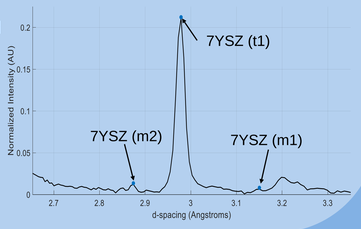
Transmission X-ray Diffraction through a sample



Debye Scherrer ring produced from diffraction

- mPVF can be calculated by finding the integrated intensities as given by [3]:

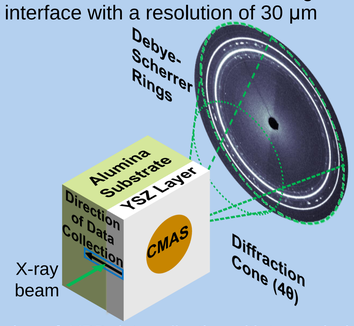
$$\mathrm{mPVF} = \frac{I_{m1} + I_{m2}}{I_{m1} + I_{m2} + I_{t1}}$$



(right) Peaks used to determine the mPVF

Experimental Setup

- 7YSZ coatings (~150 µm thick) were deposited through EB-PVD with a characteristic columnar width of ~20 µm onto alumina substrates (12 x 12 x 1.5 mm^3)
- CMAS was deposited at the center of some samples and brought to temperatures 1225°C and 1250°C and held for a set amount of time (refer to Sample Table)
- A high-energy (71 keV) X-ray beam of 30 x 300 μm^2 size impinged on samples throughout the coating (YSZ layer) starting from the surface of the coating to the coating-substrate interface with a resolution of 30 µm



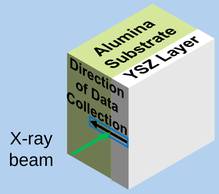
Schematic view of XRD data collection with transmission mode

Sample Table: of samples used during this study with their parameters

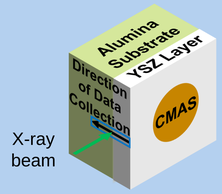
Label	Composition	Temperature (°C)	Total Time (h)
A0	Pure 7YSZ	0	0
A2	Pure 7YSZ	1225	10
A3	Pure 7YSZ	1250	10
B2	7YSZ+CMAS	1250	1
B3	7YSZ+CMAS	1250	10

The chemical composition of CMAS by weight percentage

CMAS Chemical Composition						
Elements	SiO_2	CaO	Al_2O_3	FeO	MgO	TiO_2
Wt %	40	22	18	10	8	2

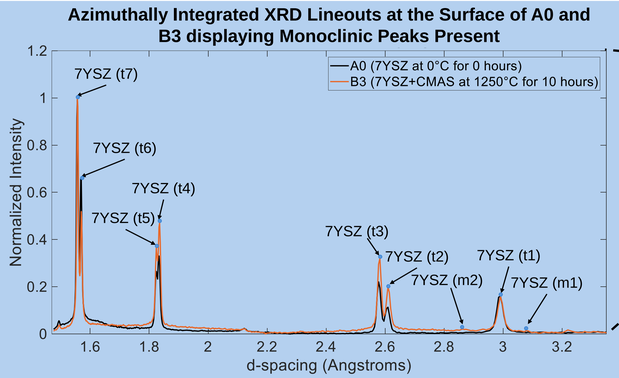


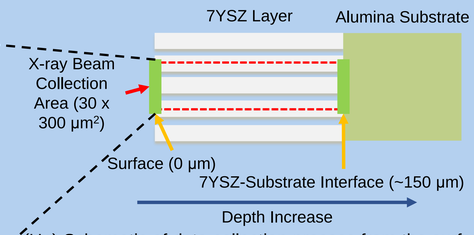
Sample without CMAS (A0)



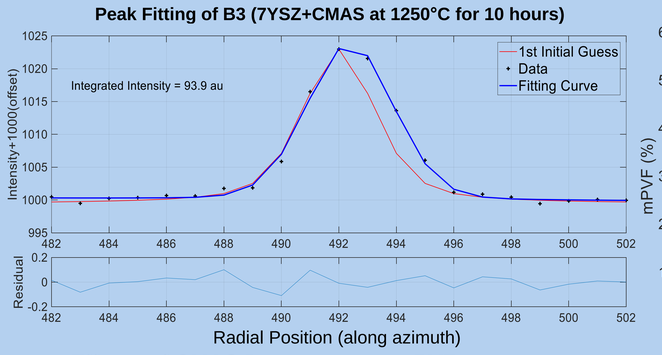
Sample with CMAS (B2,B3)

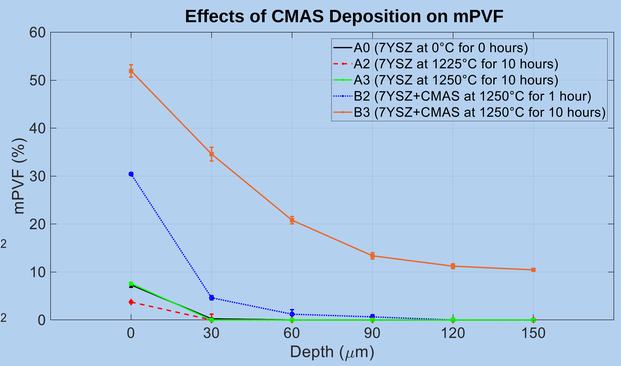
Phase Volume Fraction Results





(Up) Schematic of data collection process from the surface of the coating (0 µm) to the interface between the 7YSZ coating and Alumina Substrate (~150 µm from the surface)
(Left) Lineouts for A0 and B3, displaying only tetragonal and monoclinic peaks. Verifying there are no other phases present within the sample





Effects of CMAS Deposition on mPVF

- Both samples that were held at 1250°C during their respective annealing time of 1 hour (B2) and 10 hours (B3) have higher monoclinic phase volume fraction compared to samples with no CMAS (A0, A2, A3)
- The longer annealing time results in higher monoclinic phase volume fraction due to longer reaction time between the coating and CMAS
- The surface of the samples react more to the CMAS than further into the coating due to CMAS deposition starting at the surface

Conclusion

- Depth of CMAS ingression can be quantified through mPVF
- CMAS has a significant effect on the amount of monoclinic phases present within the coating
  - This effect can be seen throughout the depth of the coating
  - mPVF decays exponentially throughout the depth of the coating
- Annealing time strongly effects the tetragonal to monoclinic phase transformation
  - Longer annealing times result in higher monoclinic phase
  - CMAS is able to ingress further into and react with the coating

Future Work

Temperature Effects of CMAS

- Determine the effect of annealing temperature at which the deposit ingresses the coating

Residual Strain Analysis

- How does the deposit ingression effect the strain state of the coating

In-situ CMAS Ingression Synchrotron X-ray Diffraction Study

- 65YSZ TBC system samples with CMAS deposited on top
- Sample is heated during XRD measurements for real-time ingression

Acknowledgements & References

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References:
[1] 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.
[2] 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
[3] Garvie R. C., & Nicholson P. S., “Structural and Thermomechanical Properties of Partially Stabilized Zirconia in the CaO-’LrO, System.” ibid.. 55[3] 152-57(1972).