

# Comparison of 3D confocal Raman and high energy X-ray diffraction for the measurement of molten sand infiltration in turbine blade coatings

Vanessa D'Esposito<sup>1</sup>

*University of Central Florida, Orlando, FL, 32816, USA*

Seetha Raghavan<sup>2</sup>

*University of Central Florida, Orlando, FL, 32816, USA*

Thermal barrier coatings (TBCs) are used to protect metallic blades subjected to the extreme temperatures found within the turbine sections following the combustion chamber of jet engines. Yttria-stabilized zirconia (YSZ) is the standard high temperature ceramic material used for TBCs. One of the primary deposition methods of these TBCs on the metallic blades is electron-beam physical vapor deposition (EB-PVD), which gives YSZ a characteristic columnar, porous structure. This allows for a higher strain tolerance than that of other deposition methods; however, it also increases the susceptibility of the coating to molten sand and volcanic ash infiltration, referred to as calcium-magnesium-alumino-silicates (CMAS), which greatly reduces the lifetime of TBCs. A variety of techniques are used to analyze and quantify the damage to the coating; two of which will be discussed and compared in this paper. 3D confocal Raman spectroscopy and high-energy x-ray diffraction (XRD) measurements were acquired non-destructively from CMAS-infiltrated samples. The results were compared to show how the similarities and differences in the data collected can reveal a complete picture of the chemical degradation within the TBC due to CMAS. This includes the comparison of phase volume fractions found by each method. Both methods showed that higher temperatures and longer annealing times lead to a greater volume of the monoclinic phase, which is linked to the eventual failure of the coating. 3D confocal Raman provides local phase volume fractions, spatially resolved for the assessing the effects of infiltration on single columns. Meanwhile, XRD provides a more global quantification of phase volume fractions throughout the probed volume. This work highlights the complimentary nature of 3D confocal Raman and XRD for high accuracy determination of degradation mechanisms for improved lifetime predictions of TBCs.

## I. Nomenclature

<i>CMAS</i>	= calcium-magnesium-alumino-silicates
<i>EB-PVD</i>	= electron-beam physical vapor deposition
<i>XRD</i>	= high-energy x-ray diffraction
<i>mPVF</i>	= monoclinic phase volume fraction
<i>TBC</i>	= thermal barrier coating
<i>TGO</i>	= thermally grown oxide
<i>YSZ</i>	= yttria-stabilized zirconia

---

<sup>1</sup> Undergraduate Student, Mechanical and Aerospace Engineering, University of Central Florida, Orlando, USA

<sup>2</sup> Professor, Mechanical and Aerospace Engineering (Joint appointments CREOL and MSE, Affiliated with CATER, NSTC), University of Central Florida, Orlando, USA, AIAA Associate Fellow, seetha.raghavan@ucf.edu.

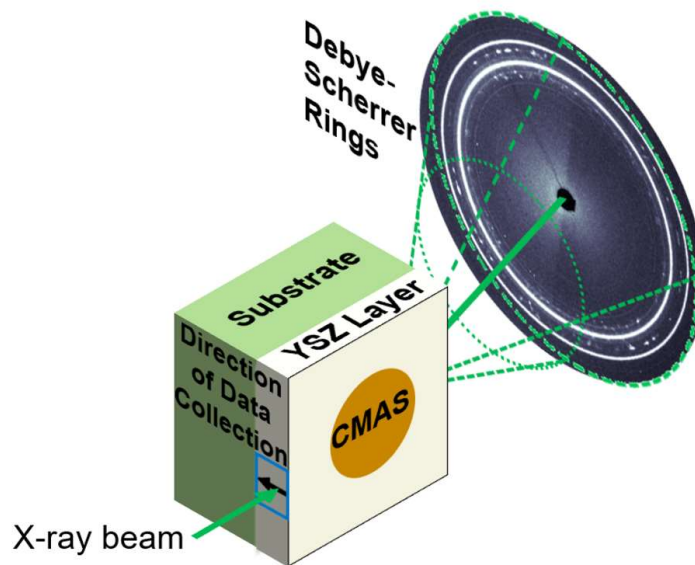
## II. Introduction

The ability to properly dissipate heat from turbine blades in the extreme environments of jet engines, which are often above the melting temperature of metal substrates used [1], is crucial for the safe operation of these engines. One method of doing so is the use of thermal barrier coatings (TBCs) [2], which is commonly three layers on top of the metal substrate of a turbine: a ceramic top coat, such as 7 wt.% yttria stabilized zirconia (YSZ), a thermally grown oxide layer (TGO), and a bond coat [3]. This not only includes the application of different methods to dissipate heat, but also the monitoring, maintenance, and prevention of damage to them when possible. In the effort to find ways to monitor and quantify the chemical degradation of TBCs due to sand and volcanic ash, referenced as calcium-magnesium-alumino-silicates (CMAS), without destroying the sample in question, research has led specifically to techniques such as high-energy x-ray diffraction and confocal Raman spectroscopy [4, 5, 6]. Both of these methods allow for the non-destructive analysis of TBCs, each with their own perspectives in data collection that form a full picture when used together.

YSZ is a commonly used material for the ceramic top coat of TBCs. This is due to its material properties regarding its handling of extreme heat and ability to dissipate it from a substrate below it, including its low coefficient of thermal expansion, ability to withstand stress, and manufacturability [2, 7]. On its own, Zirconia is subject to changes of phase without the stabilizing yttria. In the terms of the chemical degradation caused by CMAS ingress, a primary way of quantifying the level of this damage present, is the amount of phase transformations that we see of the ceramic in the TBC [1,2,3]. This transformation happens due yttria and ZrO<sub>2</sub> dissolving into the molten CMAS, with the yttria doing so in greater proportions [8, 9, 10]. This leads to a lack of the stabilizing yttria in the yttria-stabilized zirconia coating, which causes the initial tetragonal prime phase of the YSZ to become the unstable tetragonal phase of ZrO<sub>2</sub>, which then, in turn, becomes the globular monoclinic phase once cooled [9, 10, 11, 12, 13]. When this transformation to the TBC happens, multiple properties of the ceramic also change. This includes the thermal conductivity of the ceramic, which leads to increased stresses within our coating when the engine is in use [8, 14, 15]. Given this, the chemical degradation of a TBC due to CMAS is evaluated by the percent volume fraction of the monoclinic phase found within the coating. This work presents methods used in the study of CMAS infiltrated samples at various exposure times and compares the results of these experimental methods.

## III. Experimental Methods

As an introduction to the evaluation methods of this chemical degradation, a synchrotron is used to produce high-energy x-ray diffraction, which are then applied to a sample. This then leads to the crystal lattices of the different phases of ceramic found within the TBC, diffracting the incoming x-rays, which are read by an area detector to produce readouts that are known as Debye-Scherrer rings. In these rings, it is possible to obtain data on the different phases that are present in our TBC, and to quantify the volumes they occur in [5, 6]. Figure 1 demonstrates the setup of the high energy x-ray measurements taken for our sample oriented vertically. The size of the x-ray microbeam was 30 by 300 microns and this beam penetrated the entire sample volume across moving across into the depth to provide the Debye-Scherrer rings shown in the Figure.



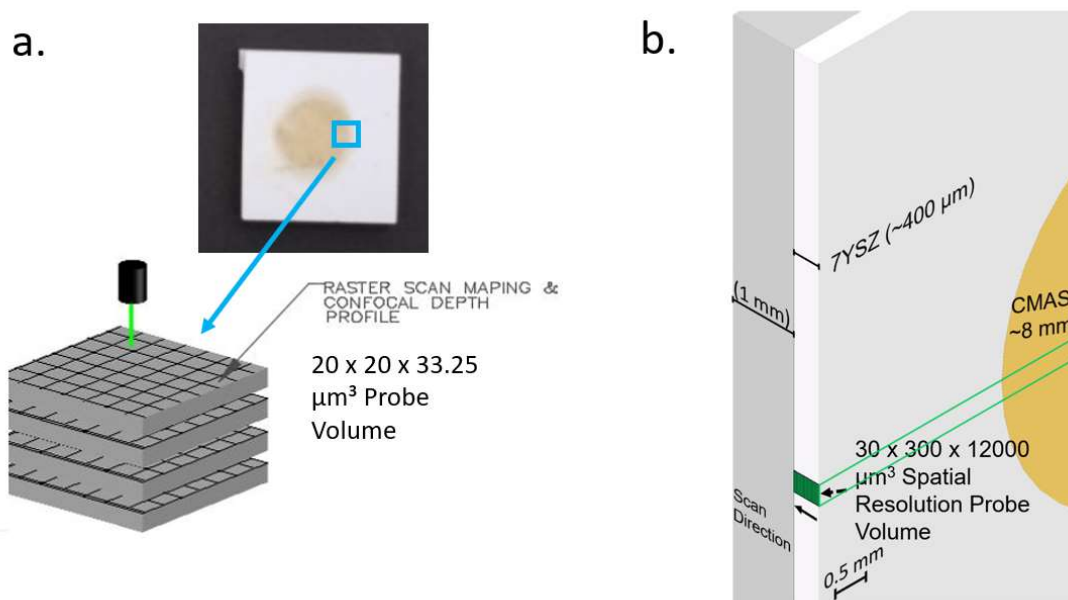
**Fig. 1 Sample set-up using high-energy x-ray diffraction (adapted from [1])**

Confocal Raman spectroscopy does a similar job of finding these phases present within the sample, but does so using inelastically scattered light to excite phonons within the material, which are characteristic to the specific materials of a sample. This allows for the identification of the phases present in the TBC, as well as to quantify the volume present. Confocal Raman differs from standard Raman spectroscopy due to the presence of a confocal aperture. This allows a confocal system to take 3D measurements of a sample, just below its surface, unlike a standard Raman system [4, 6]. Figure 2 shows the typical confocal Raman setup with the microprobe over the sample placed horizontally or flat on the sample holder. The laser is focused through the microprobe to interrogate a local spot and the laser light can penetrate transparent and semi-transparent samples to some effective depth depending on the level of transparency. By defocusing the probe, measurements below the surface can be achieved for depth resolution.



**Fig. 2 Example of confocal Raman system setup**

The similarities between XRD and confocal Raman spectroscopy are great in number. Both can be used to establish the presence of the difference phases throughout the ceramic of a TBC, and volume in which they occur. In addition, they can also do this over a volume of a sample, rather than just its surface, and do so without any damage being done to it. The data collected from both can also be used to calculate specifically the monoclinic phase volume fraction (mPVF) of the sample, which can be used to create a clearer picture of the chemical degradation of a TBC due to ingress and interaction with CMAS [4, 5, 6]. This is important because it allows for the collection of comparable data from both of these methods. Even with all the similarities between high-energy XRD and confocal Raman spectroscopy, both have their specializations in variations of data that they collect. The biggest difference between the two is the scale of the data that is taken depending on the spatial resolutions used. High-energy XRD with microbeams is better for use in the global and averaged measurements, with data representing larger volumes of the sample rather than nanoscale localized regions of it. Confocal Raman, however, when used at the nanoscale is more useful for getting data on a local level and seeing the effects of CMAS ingress on that basis. This allows for the mPVF to be analyzed and displayed on a columnar level on an electron-beam physical-vapor-deposition (EB-PVD) sample [6]. In this work, data from each method that we published [4,5,6], were compared to establish and validate finding from the other.



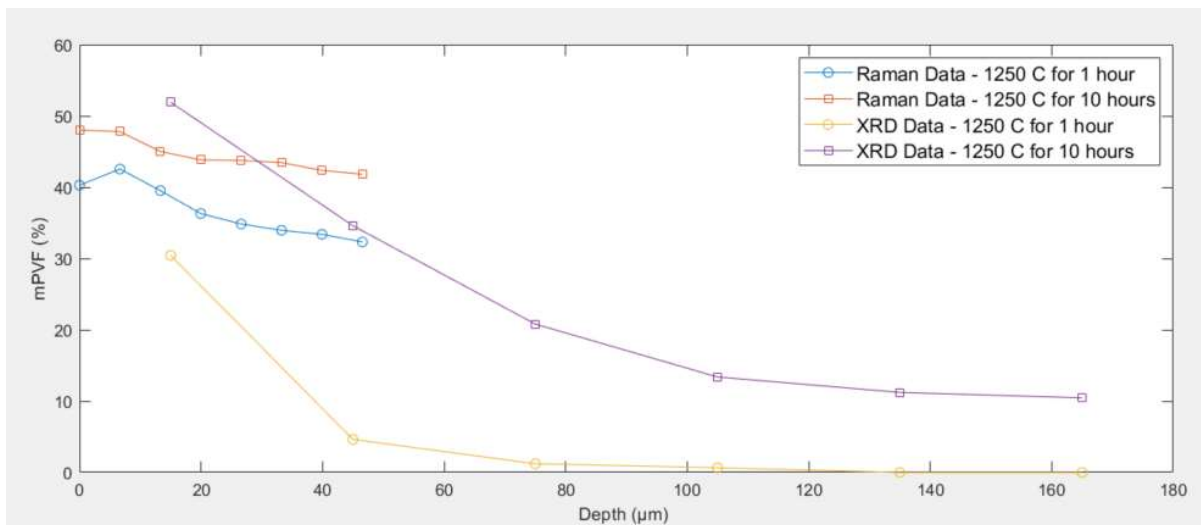
**Fig. 3 Probe sizes comparison of Raman (a.) and XRD (b.)**

#### IV. Data Analysis and Results

These difference in data collection methods used also lead to a difference in the calculation of the mPVF found throughout the samples, overall and locally. Figure 4 shows the plots from the data taken by high energy XRD [5] and Raman confocal measurements [4] in a single plot. The confocal Raman measurements are taken at specific points in the depth of the coating, and the XRD data is taken at depths of 30 $\mu$ m. To account for this, the midpoint of each depth for the XRD data is used with the average mPVF found in that section.

The first observation is that the Raman data was only taken for a part of the depth. This is because as the depth increases the intensity of the readings are reduced. Confocal Raman is capable of surface and subsurface measurements up to a point and depending on the transparency of the sample. The mPVF range of values and drop in mPVF with depth is however in general agreement for both results with slight differences attributed to be possibly due to the differences in probe volumes between XRD and confocal Raman, with the much larger probe volume of

XRD being better suited for representing the average mPVF values for the overall coating, unlike the confocal Raman measurements which are greatly affected by the local microstructure differences throughout the coating.



**Fig. 4 Comparison of mPVF and depths found by high energy XRD and confocal Raman**

### V. The Complimentary Nature of XRD and Confocal Raman Spectroscopy

Given the similarities and difference between the evaluation methods of high-energy XRD and confocal Raman spectroscopy, the two can be used to paint an overall more complete picture of the chemical degradation of a TBC due to CMAS ingress. XRD can be used to showcase the overall, global details of a sample in a more consolidated and accurate manner, while confocal Raman can give more information on the specifics of the monoclinic phases found throughout a sample and where there are occurring most. The results in Fig 4 show that with more exposure time, from 1 hour to 10 hours, mPVF increases overall in the sample over the depth and this is shown in both the Raman and high energy XRD results. In addition, both results show that the surface of the sample has the highest mPVF and therefore is most affected by the CMAS and this reduces with depth. The confocal measurements provide some more details on the variation of CMAS effects within a column of the YSZ [4] while the high energy X-ray results quantifies the overall degradation over the depth. Having both these measurements are important to build a better idea of the fundamental mechanisms at play between CMAS and YSZ TBCs, which allow for the development of TBCs that better mitigate the effects of CMAS and extend their lifetime, as well as better quantification of the damage that is done to give a better predict the lifetime of these TBCs.

### VI. Conclusion

Knowledge of the effects of CMAS on coatings on- turbine blades in jet engines is vital to making sure these engines are safe for use. This information drives the maintenance and reduction of damage when possible. CMAS ingress into TBCs is detrimental to the lifetime of these coatings, due to both the mechanical and chemical complications it causes. Therefore, it is extremely important that the fundamental mechanisms at play between CMAS and YSZ TBCs are known and understood, which requires having methods that allow for the in-depth analysis and data collection of samples that have undergone this interaction at different scales. High-energy XRD and confocal Raman spectroscopy not only both allow for this data to be collected on their own, but create an even more clear picture when both are used, and can do so without destroying samples in the process. High energy XRD using a transmission microbeam in our sample allows for an overall assessment of the chemical degradation of a TBC, averaging the differences in microstructure throughout, while confocal Raman at the nanoscale gives a detailed idea of the local degradation.

## Acknowledgments

This material is based upon work supported by the National Science Foundation [Grant Nos. DMR 1337758 and OISE 1460045] and by the German Aerospace Center (DLR), Cologne, Germany. The author acknowledges Dr. Ravisankar Naraparaju and Dr. Uwe Schulz from DLR, Cologne for their scientific collaboration on this research. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357

## References

- [1] Peters, M., Leyens, C., Schulz, U., & Kaysser, W. A. (2001). EB-PVD thermal barrier coatings for aeroengines and gas turbines. *Advanced Engineering Materials*, 3(4), 193–204. [https://doi.org/10.1002/1527-2648\(200104\)3:4<193::AID-ADEM193>3.0.CO;2-U](https://doi.org/10.1002/1527-2648(200104)3:4<193::AID-ADEM193>3.0.CO;2-U)
- [2] Miller, R. A. (1997). Thermal barrier coatings for aircraft engines: History and directions. *Journal of Thermal Spray Technology*, 6(1), 35–42. <https://doi.org/10.1007/BF02646310>
- [3] Padture, N. P., Gell, M., & Jordan, E. H. (2002). Thermal barrier coatings for gas-turbine engine applications. *Science*, 296(5566), 280–284. <https://doi.org/10.1126/science.1068609>
- [4] Barrett, C., Stein, Z., Hernandez, J., Naraparaju, R., Schulz, U., Tetard, L., & Raghavan, S. (2021). Detrimental effects of sand ingestion in jet engine ceramic coatings captured with Raman-based 3D rendering. *Journal of the European Ceramic Society*, 41(2), 1664–1671. <https://doi.org/10.1016/j.jeurceramsoc.2020.09.050>
- [5] Stein, Z., Naraparaju, R., Schulz, U., Kenesei, P., Park, J. S., Almer, J., & Raghavan, S. (2020). Synchrotron x-ray diffraction study of phase transformation in cmas ingressed eb-pvd thermal barrier coatings. *AIAA Scitech 2020 Forum*, 1 Part F (January), 1–8. <https://doi.org/10.2514/6.2020-0400>
- [6] Zachary Stein, "Degradation From CMAS Infiltration in 7YSZ EB-PVD Thermal Barrier Coatings" Undergraduate Thesis, University of Central Florida, 2020 (2020 - 762).
- [7] Miller, R. A. (1987). Current status of thermal barrier coatings - An overview. *Surface and Coatings Technology*, 30(1), 1–11. [https://doi.org/10.1016/0257-8972\(87\)90003-X](https://doi.org/10.1016/0257-8972(87)90003-X)
- [8] Krämer, S., Faulhaber, S., Chambers, M., Clarke, D. R., Levi, C. G., Hutchinson, J. W., & Evans, A. G. (2008). Mechanisms of cracking and delamination within thick thermal barrier systems in aero-engines subject to calcium-magnesium-alumino-silicate (CMAS) penetration. *Materials Science and Engineering A*, 490(1–2), 26–35. <https://doi.org/10.1016/j.msea.2008.01.006>
- [9] Pujol, G., Ansart, F., Bonino, J. P., Malié, A., & Hamadi, S. (2013). Step-by-step investigation of degradation mechanisms induced by CMAS attack on YSZ materials for TBC applications. *Surface and Coatings Technology*, 237, 71–78. <https://doi.org/10.1016/j.surfcoat.2013.08.055>
- [10] Krämer, S., Yang, J., Levi, C. G., & Johnson, C. A. (2006). Thermochemical interaction of thermal barrier coatings with molten CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) deposits. *Journal of the American Ceramic Society*, 89(10), 3167–3175. <https://doi.org/10.1111/j.1551-2916.2006.01209.x>
- [11] Wellman, R., Whitman, G., & Nicholls, J. R. (2010). CMAS corrosion of EB PVD TBCs: Identifying the minimum level to initiate damage. *International Journal of Refractory Metals and Hard Materials*, 28(1), 124–132. <https://doi.org/10.1016/j.ijrmhm.2009.07.005>
- [12] Levi, C. G., Hutchinson, J. W., Vidal-Sétif, M. H., & Johnson, C. A. (2012). Environmental degradation of thermal-barrier coatings by molten deposits. *MRS Bulletin*, 37(10), 932–941. <https://doi.org/10.1557/mrs.2012.230>

- [13] Peng, H., Wang, L., Guo, L., Miao, W., Guo, H., & Gong, S. (2012). Degradation of EB-PVD thermal barrier coatings caused by CMAS deposits. *Progress in Natural Science: Materials International*, 22(5), 461–467. <https://doi.org/10.1016/j.pnsc.2012.06.007>
- [14] Wu, J., Guo, H. bo, Gao, Y. zhi, & Gong, S. kai. (2011). Microstructure and thermo-physical properties of yttria stabilized zirconia coatings with CMAS deposits. *Journal of the European Ceramic Society*, 31(10), 1881–1888. <https://doi.org/10.1016/j.jeurceramsoc.2011.04.006>
- [15] Naraparaju, R., Schulz, U., Mechnich, P., Döbber, P., & Seidel, F. (2014). Degradation study of 7wt.% yttria stabilised zirconia (7YSZ) thermal barrier coatings on aero-engine combustion chamber parts due to infiltration by different CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> variants. *Surface and Coatings Technology*, 260, 73–81. <https://doi.org/10.1016/j.surfcoat.2014.08.079>