# Thermo-Mechanical Degradation and Mitigation by Molten Volcanic Ash Wetting on Thermal Barrier Coatings of Jet Engine Turbine Blades

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# **Extended** Abstract

Modern gas turbine engines employed in power and aerospace industries extensively utilize thermal barrier coatings (TBCs) to protect the structural integrity of engine components against any rapid degradation at extremely high temperatures (1300-1500 °C). TBCs typically consist of 7 wt% yttria-stabilized zirconia (YSZ/7YSZ) and are mainly produced by atmospheric plasma spray (APS) and electron beam-physical vapor deposition (EB-PVD). In the course of ever higher engine operation temperatures due to a continuous increase of aircraft engine efficiency, the coatings have become vulnerable to interactions with and degradation by atmospheric contaminants (environmental dust) such as volcanic ash and desert sand. In particular, damage to TBCs by molten volcanic ash pose a serious threat to the durability of YSZ TBCs. The deterioration of the TBCs, originate by surficial wetting of by molten volcanic ash, followed by infiltration into the TBCs and solidification of the melt, an increased thermo-mechanical stress within the coating occurs. This leads to crack formation due to the alternating thermal excursion during operation of the engine, which could potentially lead to the spallation of TBCs.

In order to gain a deeper understanding of the initial cracking, the mechanical properties of solidified volcanic glass within the infiltrated TBCs were determined experimentally in this thesis. For the first time, thermal shock experiments (from 1300 °C to room temperature) were performed on silicate melt wetted TBCs, followed by a characterization of the resulting thermomechanical damage. To investigate the influence of different chemistries, 3 different volcanic ashes were used: Kilauea, Hawaii, USA (basaltic); Eyjafjallajökull, Iceland (trachy-andesitic); Cordon Caulle, Chile (rhyolitic). Mechanical properties of the volcanic ash glasses were determined and Eyjafjallajökull volcanic ash was chosen for this study, as it possessed a higher elastic modulus compared to Kilauea and Cordon Caulle volcanic ash. Low fracture toughness and a high elastic modulus within the infiltrated area of the TBCs during the thermal shock regime was attributed to the generation of microcracks.

EB-PVD-TBCs are characterized by a columnar structure, whereas APS-TBCs have a lamellar layer structure. For jet engine turbine blades, EB-PVD coatings are preferred over APS-TBCs as they offer a higher in-plane strain tolerance. However, compared to the lamellar APS structure, they are more susceptible to infiltration of molten volcanic ash. In this thesis, the deposition of volcanic ash on EB-PVD TBCs was investigated experimentally. For this purpose, Eyjafjallajökull ash was deposited on EB-PVD TBCs by thermal spraying. The morphological development of the melting volcanic ash micro globules during infiltration into the columnar TBC structure was characterized by in-situ high-temperature dilatometry measurements. The results show the deposition dynamics of the volcanic ash particles on TBCs and thus allow conclusions on possible effects regarding interaction of volcanic ash with coated turbine blades.

Finally, the mitigation potential of novel TBCs with hexagonal boron nitride (*h*-BN) additives against the deposition of molten volcanic ash was investigated in this dissertation. The experiments show that pure *h*-BN substrates have non-wetting properties under vacuum conditions at 1250 °C. The conclusions from these studies were useful for the subsequent comparison of conventional YSZ-TBCs with *h*-BN doped YSZ-TBCs under atmospheric conditions. It was shown that *h*-BN doped YSZ-TBCs are more resistant to molten volcanic ash than conventional YSZ-TBCs due to reduced infiltration and improved wetting resistance. This work serves as a proof of concept that more candidate materials exhibit resilience towards molten silicate attack.

#### Zusammenfassung

Heutige Gasturbinentriebwerke sind auf Wärmedämmschichten (thermal barrier coating -TBC) angewiesen um strukturelle Komponenten des Triebwerks vor extrem hohen Temperaturen (1300-1500 °C) zu schützen. TBCs bestehen typischerweise aus 7 Gew.-% Yttrium stabilisiertem Zirkonoxid (YSZ) und werden hauptsächlich durch atmosphärisches Plasmaspritzen (atmospheric plasma spray–APS) und Elektronenstrahlverdampfung (electron beam-physical vapor deposition – EB-PVD) hergestellt. Im Zuge der kontinuierlichen Effizienzsteigerung von Flugzeugtriebwerken durch immer höhere Betriebstemperaturen, wurden die Beschichtungen anfällig für Ablagerungen geschmolzener Partikel aus dem Luftstrom, wie Vulkanasche, Sand oder Staub. Insbesondere die Schädigung von TBCs durch geschmolzene Vulkanasche stellt eine ernsthafte Bedrohung für die Haltbarkeit von YSZ-TBCs dar. Aufgrund der oberflächlichen Benetzung mit einer silikatischen Schmelze und deren anschließenden Infiltration und Verfestigung kommt es zu einer erhöhten thermo-mechanischen Belastung innerhalb der Beschichtung. Dies hat auf Grund der thermischen Wechselbelastung während des Betriebes des Triebwerks eine Verfestigung der Vulkanasche zur Folge, die zum finalen Versagen der Beschichtung führen kann. Um ein tieferes Verständnis über die initiale Verfestigung der Vulkanasche zu erlangen, wurden im Rahmen dieser Dissertation die mechanischen Eigenschaften von verfestigtem Vulkanglas innerhalb der infiltrierten TBCs experimentell bestimmt. Dabei wurden erstmalig Wärmeschockexperimente (von 1300 °C bis auf Raumtemperatur) an Silikatschmelze benetzten TBCs durchgeführt, gefolgt von einer Charakterisierung der dadurch entstandenen thermomechanischen Schädigung. Um den Einfluß unterschiedlicher chemischer Zusammensetzungen zu untersuchen, kamen 3 verschiedene Vulkanaschen zum Einsatz: Kilauea, Hawaii, USA (basaltisch); Eyjafjallajökull, Island (trachy-andesitisch); Cordon Caulle, Chile (rhyolitisch). Es wurden die mechanischen Eigenschaften der Vulkanaschegläser und der Eyjafjallajökull-Vulkanasche bestimmt, da sie im Vergleich zu Kilauea- und Cordon Caulle-Vulkanasche ein höheres Elastizitätsmodul besaß. Als Ursache für die Ausbildung von Mikrorissen wurden eine niedrige Bruchfestigkeit sowie ein hohes Elastizitätsmodul innerhalb des infiltrierten Bereichs identifiziert. EB-PVD-TBCs sind durch eine säulenförmige Struktur gekennzeichnet, wohingegen APS-TBCs einen lamellaren Schichtaufbau besitzen. Bei Turbinenschaufeln von Strahltriebwerken werden EB-PVD-Beschichtungen bevorzugt gegenüber APS-TBCs verwendet, da sie eine höhere Flächendehnungstoleranz aufweisen. Allerdings sind sie im Vergleich zur lamellaren APS-Struktur anfälliger gegenüber einer Infiltrierung geschmolzener Vulkanasche. In dieser Arbeit wurde experimentell die Ablagerung von Vulkanasche auf EB-PVD TBCs untersucht. Zu diesem Zweck wurde Eyjafjallajökull-Asche mittels thermischen Sprühens auf EB-PVD-TBCs aufgebracht. Die morphologische Entwicklung der schmelzenden Vulkanasche-Mikrokügelchen während der Infiltration in die säulenförmige TBC-Struktur wurde mit Hilfe von in-situ-Hochtemperatur-Dilatometrie Messungen charakterisiert. Die Ergebnisse zeigen die Ablagerungsdynamik der Vulkanaschepartikel auf TBCs und erlauben somit Rückschlüsse auf mögliche Auswirkungen hinsichtlich einer Wechselwirkung von Vulkanasche mit beschichteten Turbinenschaufeln. Schließlich wurde im Rahmen dieser Dissertation das Minderungspotenzial neuartiger TBCs mit Zusätzen aus hexagonalem Bornitrid (*h*-BN) gegenüber Ablagerung von geschmolzener Vulkanasche untersucht. Die Experimente zeigen, dass reine h-BN-Substrate unter Vakuumbedingungen bei 1250 °C keine Benetzungseigenschaften aufweisen. Die Schlußfolgerungen aus diesen Studien waren nützlich für den anschließenden Vergleich von konventionellen YSZ-TBCs mit h-BN dotierten YSZ-TBC unter atmosphärischen Bedingungen. Dabei konnte gezeigt werden, dass h-BN dotierte YSZ-TBCs auf Grund einer verminderten Infiltration und einer verbesserten Benetzungsbeständigkeit widerstandsfähiger gegenüber geschmolzener Vulkanasche ist als konventionelle YSZ-TBCs. Diese Arbeiten zeigen, h-BN dotierte **YSZ-TBCs** und weitere noch untersuchende dass zu Materialkombinationen für eine Verbesserung der Widerstandsfähigkeit von TBCs gegenüber geschmolzener, atmosphärischer Partikel dienen können.

Most of the content of this Doctoral dissertation has been published in peer-reviewed journals, are in the state of revision or in the process of preparation for submission

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"Ladies and gentlemen, this is your captain speaking. We have a small problem. All four engines have stopped. We are doing our damnedest to get them going again. I trust you are not in too much distress."

- Captain Eric Moody

(British airways flight 9 announcement, as the airline passed into a cloud of volcanic ash thrown up by the eruption of Mount Galunggung)



CHAPTER 1 INTRODUCTION

### **1.1 Thermal barrier coatings**

## **1.1.1 Evolution of Thermal barrier coatings**



Figure .1 Evolution of TBCs



#### 1.1.2 Structure of Thermal barrier coatings

Conventional TBCs consists of a porous ceramic top-coat (typically made of tetragonalphase ZrO<sub>2</sub> ceramic stabilized by 7 wt.% Y<sub>2</sub>O<sub>3</sub>, commonly referred to as 7YSZ) and a middle metallic bond coat (MCrAIY) which improves adhesion of TBC to the substrate, and is specially designed to protect the underlying superalloy engine parts against corrosive gases present under the routinely harsh operating environment. Thermally grown oxide (TGO,  $\alpha$  Al<sub>2</sub>O<sub>3</sub>), is formed as a resultant of the Al-rich bond coat and acts as an oxidation barrier to the superalloy substrate. The superalloy substrate is essentially composed of Nickle based superalloy, it offers mechanical resistance by taking the structural loads, during the operational cycle of the engine. The superalloy is resistant to creep, fatigue, and intense thermo-mechanical cycles (Fig.2). Thermal flux difference of ~170 °C is estimated from the topcoat to the substrate, spallation and delamination resistance of the top-coat can occur due to the thermal cycling during heating and cooling cycles (Clarke & Levi, 2003).



Figure 2. Schematic illustration of the structure of TBCs

#### 1.1.3 Yttria stabilized zirconia

 $ZrO_2$  is stabilized into its cubic, tetragonal phases, and unique metastable tetragonal prime (*t'*) phase as shown in figure 3. The stabilization of Zirconia is achieved by the addition of Yttria (Y<sub>2</sub>O<sub>3</sub>)-YSZ, which also introduces oxygen vacancies to the system. The choice of 7 wt. % Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub> (7YSZ) as the thermal barrier coating material is due to the ferroelastic toughening mechanism (Mercer, Williams, Clarke, & Evans, 2007), at high operating temperatures and thermal stress generated in the system.



Figure 3. ZrO<sub>2</sub> YO<sub>1.5</sub> phase diagram

### 1.1.4 Atmospheric spraying method (APS)

Atmospheric plasma-spraying (APS) is commonly used to fabricate ceramic coatings with the desired tolerances and properties (e.g., low thermal conductivity) onto vulnerable surfaces of components in the hot sections of jet engines. The air plasma spray process is a thermal spray deposition method in which the YSZ is heated to a semi-molten state by an electric heat source and deposited on the substrate. APS process can be performed in both atmospheric and vacuum conditions. Fig. 4 shows the schematic representation of the APS spray process, where the top-coat material in semi-molten form is carried along with a stream of argon/nitrogen and flows through a cylindrical nozzle onto the substrate propelled through the plasma jet. Parameters like the Spray velocity, powder size, and distance of the substrate from the nozzle influence the APS spray process.



Figure 4. Schematic illustration of atmospheric plasma spraying

The YSZ powder is deposited in the form of splat overlay (Fig.5) and consists of inter splats and intra splat voids. The coating is formed by rapid solidification of the splats and each splat is deposited parallel to the direction of spraying (Sevostianov & Kachanov, 2009). APS method is cost-effective, compared to the electron beam physical vapor deposition. The topcoat possesses low thermal conductivity, high strain tolerance, and provides thermal insulation to the metallic substrate. Phase transition at higher temperatures of topcoat is pivotal for structural stability.



Figure 5. Schematic illustration of APS TBCs microstructure

#### 1.1.5 Electron beam physical vapor deposition (EB-PVD)

The basic principle of the EB-PVD process is the creation of a melt pool consisting of YSZ feedstock, by heating it in an evacuated chamber with a high-energy electron beam, as shown in Fig. 6. The melt pool generates vapor. The vapor generated from the melt pool is coated on the target material, by means of the deposition of molecules present in the vapour. The EB-PVD process offers extensive advantages such as a smoother surface finish when compared to the APS spray process (Bernard et al., 2017).



Figure 6. Schematic illustration of electron beam physical vapor deposition

EB-PVD coating is composed of columnar grain structure YSZ generated perpendicular to the coating direction (Fig. 7), architectural modification can be achieved during the fabrication of EB-PVD coatings. In this thesis, both APS and EB-PVD coatings are employed to study the degradation, due to molten volcanic ash wetting.



Figure 7. Schematic illustration of the microstructure of EB-PVD TBC

#### 1.2 Effect of volcanic ash on TBCs

As the air traffic across the world has been growing steadily, the occurrence of volcanic ash plume encounters by aircrafts has soared and the hazards generated by the ingestion of molten silicate deposits into the engines have garnered greater attention and subjected to deeper investigation in the aviation sector. Since 1950, there have been over 125 documented aircraft encounters with volcanic ash, with 79 of these encounters ending up in severe engine damage (Prata & Tupper, 2009). In 2010, the eruption of Eyjafjallajökull Iceland triggered the largest aviation shutdown in Europe since World War II and caused an enormous economic loss estimated at ~2 billion euros (Brooker, 2010). The most recent eruptive event of Taal volcano in Philippines (January 13, 2020), resulted in the cancellation of flights from Jakarta airport (Fig. 8).

Given the ever-burgeoning air traffic and its catalytic role in shaping the socioeconomic forces across the globe, diminishing the impact of environmental dust in general and volcanic ash in particular on aviation safety has become imperative. The nature of damage imparted by volcanic ash to jet engines assumes multiple technical and economic dimensions, and hence, this problem can be categorized under the broad arena of multirisk phenomenon (Alexander, 2013). In 2000, all four engines of the DC-8 (NASA airborne research aircraft) were damaged by mere *seven-minute* exposure (equivalent to a flight distance of 50 nautical miles) to the diffuse edges of an ash cloud, which originated from an eruption Hekla volcano (Iceland). The cost of repairs was 3.2 million USD, demonstrating that exposure even to highly dispersed ash clouds can be very costly (Grindle, Burcham, & W, 2003). The short-term failure of the DC-8 engines, serve as a motivation to study the aspect of thermal shock resistant properties of the TBCs affected by molten volcanic ash in chapter 2.



Figure 8. satellite images of the volcanic ash dispersed from 2020 Taal, Indonesia eruption (credits: Copernicus Sentinel data (2020), processed by ESA)

When volcanic ash is ingested into a modern jet engine, it may initially erode/abrade compressor blades, leading to a reduction in operational efficiency, the ash subsequently enters the combustion chamber where peak flame temperatures can reach 2000 °C. Such temperatures far exceed the glass transition (~600-800 °C) and melting temperatures (~900-1300 °C) of the (glassy versus mineral) constituents of volcanic ash (Song et al., 2016). As a result, the ingested ash particles liquify (by one or both of by glass softening or mineral melting) and may adhere to, and flow across (i.e., impaction, spreading, and wetting) (Song et al., 2019). Spreading of molten volcanic ash on these components may physically clog cooling holes (as shown in Fig. 9), thereby blocking air intake and causing heat accumulation. Molten volcanic ash deposits can also infiltrate and chemically react with TBCs at operating temperatures, causing subsequent spallation of the coating upon cooling and ultimately exposing the underlying metal to corrosive gases (Vidal-Setif et al., 2012). As a result, jet engine performance may deteriorate substantially, leading to catastrophic failure (Xia et al., 2019). In chapter 3, for the first time, lab-scale simulation of the deposition of molten volcanic ash droplets was performed and, the penetration of the molten volcanic ash micro-globules was tracked by *in-situ* high-temperature dilatometry.



Figure 9. Deposition of volcanic ash on the compressor blades, high-pressure turbine vanes (W. R. Chen & Zhao, 2015)

Efforts to constrain the impact of volcanic ash on jet engines have grown following the 2010 eruption of Eyjafjallajökull. Such efforts range inter alia include:

- 1. The characterization of volcanic ash deposits in jet engines following natural encounters.
- 2. understanding the rate of molten ash deposition, investigating the wetting of the engine part (Song et al., 2016).
- 3. infiltration and chemical reaction of ash with TBCs (Padture, 2019).
- 4. The simulation of engine operation airflow and temperature evolution in the presence of volcanic ash (Jiang, Han, & Patnaik, 2017).

All such efforts are aimed at improving the durability of next-generation engines. The durability of TBCs is thus greatly affected by the deposition of molten volcanic ash on APS TBCs as well as the subsequent infiltration leading to chemical and mechanical interactions between molten volcanic ash and the YSZ TBC. Wetting of molten volcanic ash on the surface of TBCs is considered to be the preliminary step in initiating the degradation of TBCs, in chapter 4 wetting resistance offered by novel TBCs with hexagonal boron nitride additives are presented and discussed in detail.



## CHAPTER 2 THERMO-MECHANICAL DEGRADATION OF APS TBCS BY MOLTEN ASH WETTING

The results presented in this chapter were published in: Lokachari, S., Song, W., Yuan, J., Kaliwoda, M., & Dingwell, D. B. 2020. "Influence of molten volcanic ash infiltration on the friability of APS thermal barrier coatings". *Ceramics International*. doi.org/10.1016/j.ceramint.2020.01.166

# Chapter2. Thermo-Mechanical Degradation of APS TBCs by Molten Ash Wetting

### 2.1. Introduction

This chapter highlights the consequences of rapid wetting on the thermomechanical properties of molten volcanic ash on TBCs, and provide a substantial contribution to understanding the friability of APS TBCs subjected to severe degradation by molten volcanic ash, which has become a research and development imperative on aviation safety. Figure. 10 illustrates the effect of molten volcanic ash infiltration into the APS topcoat, whereby the melt infiltrates into the inter splat regions and as melt accumulates, the initially infiltrated region is prone to stiffening. The stiffened region thereby loses the strain tolerance ability and this further complicates to progressive cracking, resulting in delamination and spallation of the coating (Wellman & Nicholls, 2008).

Failure mechanisms in which the APS TBCs have also been observed to eventually buckle due to the thermal stress caused by the infiltration of molten silicates raised serious concerns over the mechanical longevity of APS TBCs. The phase de-stabilization in YSZ TBCs occurs due to the infiltration of molten volcanic ash, via dissolution of initial metastable tetragonal (t') YSZ grains followed by precipitation of Y-depleted monoclinic zirconia (m-ZrO<sub>2</sub>) (Zhou et al., 2019), it must be noted that the formation of monoclinic phase is detrimental to the structural property of the coating and plays a crucial role in the durability. Siliceous environmental debris (including volcanic ash) is commonly simulated using a chemically simplified CMAS (calcium-magnesium aluminum-silicate) analog (Padture, 2019).



Figure 10. (a) Illustration of molten volcanic ash clogging the cooling holes of the turbine blade and the TBCs chipped off due to the deposition of molten volcanic ash. (b) The molten volcanic ash is deposited on the TBCs, which overlays the underlying superalloy substrate with an adhesive bond coat and a thermally grown oxide (TGO). (c) Schematic of the crack generation in the TBCs, due to the infiltration of molten volcanic ash.

The vulnerability of TBCs subjected to CMAS infiltration for a prolonged duration of exposure is presented in many studies (Naraparaju, et al., 2014). However, direct experimental evidence of the wetting (initiating factor leading to the degradation of TBCs, as mentioned in chapter 1), subsequent infiltration of the melt, and the origin of cracks during thermal shock conditions (similar to the rapid quenching of TBCs, due to an engine shutdown) lacks to date. In this chapter, a first step in understanding the concurrent effects of the degrees of wetting and infiltration on the mechanical properties (micro-hardness, and fracture toughness) are explored by thermal aging experiments. I perform *in-situ* thermal shocking tests (or flash heating experiments) to observe the emanation and propagation of cracks, following the densification of molten volcanic ash infiltrated layer of TBCs. The results provide a substantial contribution to our understanding of the friability of TBCs under severe degradation by molten volcanic ash.

#### **2.2 Experimental Procedure**

#### 2.2.1. Fresh volcanic ash characterization and homogenization

In this study, three volcanic ashes of different total alkali-silica content were chosen for preliminary experiments. Fresh volcanic ash from Eyjafjallajökull-referred to as Eyja in this thesis (Iceland-2010 eruption), Cordon Caulle (Chile-2011 eruption), and Kilauea (Hawaii-2018 eruption) was re-melted at 1650°C for 48 hours, in order to generate a homogeneous reproducible sample state. Samples were quenched to glass, which was crushed and sieved to obtain a fine ash fraction. The bulk chemical composition of the ashes was determined by X-ray fluorescence spectrometry (Philips Magix XRF spectrometer) and is tabulated in Table 1, based on the composition, Eyjafjallajökull was classified as a trachyandesite, Cordon Caulle a rhyolite, and Kilauea a basalt.

Volconic och	Oxide (Wt. %)								
v olcanic asii	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	Mg	CaO	Na <sub>2</sub>	K <sub>2</sub> O
				<b>(T)</b>		0		0	
Eyja	59.90	1.38	15.76	7.91	0.21	2.40	4.55	5.61	2.29
Cordon caulle	70.43	0.67	14.19	3.94	0.11	0.53	2.13	5.19	2.81
Kilaeuea	51.36	3.11	13.78	12.8	0.19	5.11	10.2	2.81	0.55

**Table 1.** Bulk chemical composition of Volcanic ash

The experimental melt viscosity of each sample was measured in air through concentric cylinder viscometry. We used a Brookfield DVIII programmable rheometer with a measuring head (full torque range: 0 - 0.7187 mNm) suspended over a Deltech furnace. A cylindrical spindle of 14.4 mm of diameters made of Platinum/Rhodium (Pt<sub>80</sub>Rh<sub>20</sub>) hangs from the head and is immersed in a cylindrical crucible, the spindle is rotated at a constant speed. The torque exerted by the sample on the rotating spindle is directly proportional to the melt viscosity ( $\eta$ ). The crucible-spindle pair and the furnace were calibrated against standard glass DGG1. The precision of the viscosity determination is  $\pm 3\%$  (Dingwell, 1986). During the experiment, the temperature is reduced stepwise from the super liquidus temperature of 1500 °C until the liquidus is reached at 25 °C decrements, with an equilibration time of one hour. This is detected by the gradual increase in melt

viscosity at a constant temperature. As a final step, the sample is reheated to 1500 °C to check for instrumental drift. At 1500 °C the rotation speed is 40 rpm; this value is then automatically halved every time that torque exceeds 100% as the temperature is decreased, down to 0.3 rpm. The multi-component viscosity evaluation model by Giordano model et.al (Giordano, et al., 2008) was used to estimate the viscosity as a function of temperature. The resultant viscosities of the volcanic ashes are plotted in figure 11.







Figure 11. Viscosities of the volcanic ash samples over the temperature range of 1000–1400 C and the corresponding BSE images.

Scanning electron microscopy (SEM) images of the respective ashes shown in Fig.11 were used to confirm the absence of crystals post re-melting (homogenization).

## 2.2.2 Fabrication and characterization of the TBC

7YSZ TBCs were fabricated by the APS method, at the German Aerospace Center (DLR) in Köln (Fig. 12a).



Figure 12. (a) BSE image of the cross-section of 7YSZ TBC (b) Surface profile of the 7YSZ.

The coating was deposited onto Al<sub>2</sub>O<sub>3</sub> substrates of 1mm thickness. 7YSZ coatings were separated from the Al<sub>2</sub>O<sub>3</sub> substrate, using a precision diamond wire saw of diameter 0.1 mm. The cross-section and topographical profile of the AS-sprayed 7YSZ TBC are shown in Figs. 12a and 12b, the thickness of 7YSZ was  $405 \pm 10 \,\mu$ m. The surface roughness (R<sub>a</sub>) plays a vital role in the wetting of liquid on a solid substrate (Huh & Mason, 1977), for the surface profile of the coating in figure 12b R<sub>a</sub> is defined as the mean arithmetic roughness. R<sub>a</sub> of YSZ TBC was found to be  $3.3 \pm 0.5 \,\mu$ m.

#### 2.2.3 Wettability measurement

Finely sieved powdered volcanic ash (with a 32  $\mu$ m sieve) was compacted into a cylindrical form, using a compact die press. The resultant ash compacts of dimension 1×1 mm was placed at the geometrical centre of the TBC. The sample was thermally aged at 1250 °C with a ramping rate of 10 °C min<sup>-1</sup> (cooling rate 10 °C min<sup>-1</sup>) and a hold duration of 1 hour in an optical dilatometer (EM301 Hesse instruments). The silhouette of the ash compact was observed with increasing temperature using a charge-coupled camera, with a temporal resolution of 60 frames per second. The contact angle and the spreading diameter were observed by monitoring the change in silhouette of the ash compact.

#### 2.2.4 Thermal shock treatment

The use of a state-of-the-art optical dilatometer enabled us to observe the *in-situ* thermal shocking of molten volcanic ash spreading on free-standing 7YSZ TBCs. The dilatometer furnace was held at a constant temperature of 1300 °C. The free-standing YSZ TBC and VA compact assembly into the furnace at 1300 °C for five minutes duration and then rapidly quenched to room temperature. The samples were subjected to thermal shock treatments of five and ten cycles, respectively. The change in the cylindrical morphology
of the volcanic ash pellet was observed during the first cycle of thermal shock regime, using a charge-coupled camera (Fig.13).



Figure 13. Schematic illustration of the furnace and heating cycle for the thermal shock process, and photograph of the coating post the thermal shocking at 13000 °C for a hold time of 5 minutes.

#### 2.2.5 Infiltration and characterization procedure

The post-experimental free-standing 7YSZ coatings were cleaned using de-ionized water and stored in a vacuum desiccator, in order to avoid any surface contamination. The coatings were cold mounted in an epoxy resin, and standard metallographic techniques were employed to section the coatings across the cross-section. A scanning electron microscope (SEM-Hitachi SU5000), configured at high vacuum mode- 60pa, and a spot size of 30 dp. Electron dispersive spectroscopy (EDS) was used for examining the maximum infiltration depth in the volcanic ash affected coatings, by tracking the presence of elements across the cross-section of the coating. Comparative phase analysis of the TBCs (post degradation by VA infiltration), was performed using X-ray diffraction (XRD) with CuK $\alpha$ -1 radiation and a detection range of  $2\theta = 25-85^{\circ}$ . Raman spectroscopic analysis was performed using a Horiba Jobin Yvonne (Xplora) system, mounted on an Olympus BX15 microscope, within a Raman shift range of 100-800 cm<sup>-1</sup>. Raman measurements were performed at the Mineralogical state collection, Munich.

#### 2.2.6 Micro-hardness measurement

Micro indentation technique was employed to determine the mechanical properties of the volcanic ash glass shard and TBCs. Vickers and Knoop micro indentation apparatus (VH-1202 Wilson) was used to place micro-indents onto the polished cross-section of the coatings with an exerted load of 500 gram-force, and a hold time of 10 seconds. The Vickers micro-hardness ( $H_v$ ) was evaluated by using the following equation:

$$H_{\nu} = 0 \cdot 102 \frac{F}{s} \tag{1}$$

where F is the indentation load (N) and S is the indented surface area ( $mm^2$ ) (Fig. 14 a). Fracture toughness ( $K_{IC}$ ) is evaluated by the Anstis relation (Anstis, et al., 1981):

$$K_{IC} = 0.16 \cdot H_{\nu} \cdot \sqrt{a} \cdot (c / a)^{-3/2}$$
(2)

Where, a is the diagonal length (mm) and c the crack length (mm).



Figure 14 (a) Schematic illustration of Vickers hardness (b) Schematic illustration of Knoop hardness

The elastic modulus of the infiltrated region was measured by Knoop indentation method, by using the following relations:

$$H_k = 0.102 \frac{F}{A} \tag{3}$$

$$\frac{d_2}{d_1} = \frac{b}{a} - \frac{\alpha \cdot H_k}{E} \tag{4}$$

Where  $H_k$  is the Knoop hardness value (GPa), F is the test load (N), A is the projected indent area (mm<sup>2</sup>) (Fig. 14 b), E is the elastic modulus (GPa); d<sub>2</sub> is the short diagonal, and d<sub>1</sub> the long diagonal, b/a is the ratio of known Knoop indenter geometry (1/7.11) and  $\alpha$  is a constant (0.45).

# 2.3. Results and Discussion

# 2.3.1 Micro hardness properties of volcanic ash glass

Firstly, the Knoop micro hardness of the volcanic ash glasses was determined using equation 3 and it was found that there was no significant difference in the micro hardness  $(H_k)$  of the glass shards. Average  $H_k$  of Eyjafjallajökull was  $5.09 \pm 0.154$  GPa, Cordon Caulle was  $5.05 \pm 0.052$  GPa and Kilauea was  $5.05 \pm 0.135$  GPa (Fig. 15). Based on the values of micro hardness, elastic modulus was calculated by using equation 4. Image analysis was performed based on the impression of the indents for determining the diagonal lengths (b,a).

Knoop Indenter impression





Figure 15. Knoop micro hardness of the volcanic ash glasses and an example of the indent impression generated on the Eyjafjallajökull glass shard

The average elastic modulus of Eyjafjallajökull was  $83.33 \pm 1.54$  GPa, Cordon Caulle was  $82.5 \pm 1.08$  GPa and Kilauea was  $82.1 \pm 1.29$  GPa. It was observed that the value of elastic modulus of the Eyjafjallajökull glass shard (referred as VA) was higher (Fig. 16). In chapters 2 and 3, Eyjafjallajökull was thereby chosen to analyze its effect on thermomechanical aspect of TBCs.



Figure 16. Elastic modulus data of the volcanic ash glasses

# 2.3.2 Wetting and infiltration of molten VA

The properties of VA was determined by Song et.al (2019). The DSC (differential scanning calorimetry) result revealed that the melting point of VA was 1164 °C. Molten VA readily spreads the surface of TBCs at elevated temperatures above their melting point, followed by infiltration into the lamellar structure of TBC. As noted above, the morphological transition of VA during transition into the wetting regime was observed by tracking *in-situ* silhouette images recorded at different temperatures. For one hour of thermal dwell time, molten VA ultimately spread on the surface of 7YSZ TBC, making a contact angle of  $\theta_c = 14.3^\circ$  as shown in Fig. 17. At 1250 °C, it was observed that the contact angle of molten VA decreased from 44.6° to 14.3°, during the thermal dwell time of 60 minutes (Fig. 17).

The horizontal flow regime transition of molten VA was determined by the spreading diameter on the surface of TBC. The average spreading rate was evaluated by  $\bar{v} = \Delta d / \Delta t$ , where  $\Delta d$  is the difference of the spreading diameter of the molten VA;

and  $\Delta t$  is the difference in time during hold duration. Molten VA wetted the surface of TBC at a rate of 0.25 µm/sec during the thermal dwell time. Compilations of documentation of volcanic ash encounters with jet engines provide evidence that a minor exposure of 2-4 minutes of volcanic ash in the engines led to their failure (Guffanti, et al., 2011). Here, the *in-situ* wetting of the VA pellet on the surface of TBCs during thermal shock regime was observed.



Figure 17. Change in the equilibrium contact angle and spreading diameter of molten VA on the surface of YSZ at 1250 °C, during a hold time of 60 minutes.

The spreading behavior of molten VA during the first cycle, with a hold time of five minutes is illustrated in Fig. 18. It was observed that wetting was relatively unimpeded when compared with preliminary thermal ageing tests for a constant hold-time: the average change in contact angle was estimated to be 0.1 degrees per second during thermal shock regime whereas  $0.16 \times 10^{-2}$  degrees per second, during constant hold time.



Figure 18. Effect of thermal shocking on the rapid change in the equilibrium contact angle and spreading diameter of molten VA on the surface of TBC at 1300 °C.

The spreading diameter of the VA pellet (1.25 mm) to molten VA (2.62 mm), was rapid during the hold-time of the initial thermal shocking cycle Molten VA spread on the surface of TBC with an average spreading rate of molten VA on the TBC was  $1.92 \,\mu$ m/sec (Video related to the wetting process is made available online in: Lokachari et al., 2020). At 1250°C, molten VA infiltrates into the APS TBC, as observed from the wetting and spreading characteristics. Maximum infiltration depth of molten VA into the TBC was found to be 159  $\mu$ m, as determined by the elemental mapping of Si and Al across the cross-section as shown in Figs. 19a and 19b.



Figure 19. (a) BSE image of 7YSZ TBC (b) Si and Al EDS mapping, to determine the maximum infiltration depth.

Previous studies on the wetting of molten silicates on architecturally different plasmasprayed physical vapor deposited (PS-PVD) TBC and EB-PVD TBCs, have discussed the influence of wetting on infiltration, and it should be noted that a minor change in  $\theta_c$ resulted in extensive infiltration depths (Naraparaju et al., 2019). In order to obtain the overall phase content in the TBC post molten VA infiltration, XRD analysis was performed.



Figure 20. XRD patterns of as-sprayed YSZ TBC and VA affected TBC

The phase transformation from tetragonal 7YSZ to monoclinic Zirconia (m-ZrO<sub>2</sub>) was observed in the spectra shown in Fig. 20. The presence of Zircon (ZrSiO<sub>4</sub>), as a resultant of Zr–Si reaction was evident in the spectrum of VA affected TBC. Previous studies have shown that the phase destabilization is majorly responsible for a volume change of 4 - 5%, leading to the generation of cracks in the TBCs (Schulz et al., 2004). The percentage of monoclinic phase (% m) was evaluated by using equation 5 (Toraya, et al., 1984):

$$\% m = 100 \times \frac{I_m(\bar{1}11) + I_m(111)}{I_m(\bar{1}11) + I_m(111) + I_t(101)}$$
(5)

Where  $I_m$  is the monoclinic intensity and  $I_t$  is the tetragonal intensity corresponding to the signal from the XRD pattern. The increase in monoclinic content after VA was infiltrated in the TBC was found to be 17 % and the as-sprayed TBC was 3 %. The objective of stabilizing Zirconia, by addition of Yttria is to avoid the phase transformation from tetragonal to monoclinic phase, which leads to a volume change of 3–5% due to cooling. Subsequent infiltration and phase transformation due to the reaction of molten VA with 7YSZ TBC deteriorates the mechanical properties.

#### 2.3.3 Mechanical properties

The average Vickers micro-hardness values of the as-sprayed conventional YSZ was 6.2  $\pm$  1.2 GPa. Corresponding micro-hardness values of VA infiltrated 7YSZ was measured at 50, 100, 150 and 200 µm respectively. From Fig. 21a, it was evinced that the region of the VA affected TBCs at 50 µm has a hardness value higher than the as-sprayed TBC (11.1  $\pm$  3.2 GPa). VA glass shard had an elastic modulus of 83.33  $\pm$  1.54 GPa (Fig. 16), whereas the micro-hardness of artificial volcanic glass (CMAS) was determined to be 84.3 GPa (Bansal et al., 2015).

The infiltration of the molten VA or CMAS into the splat-like lamellar microstructure of TBC, and further solidification during the cooling phase is responsible for the increase in hardness value of the penetrated region. High fracture toughness is one of the essential criteria for a TBC, fracture toughness value of the as-sprayed TBC at 50  $\mu$ m is 2.2 ± 0.08 MPa·m<sup>0.5</sup>, which was higher than VA infiltrated TBC corresponding to the same measurement depth (0.8 ± 0.1 MPa·m<sup>0.5</sup>) as seen in Fig. 21b. The elastic modulus is plotted in Fig. 21c, as-sprayed TBC had an elastic modulus of 166.5 ± 1.9 GPa at 50  $\mu$ m, whereas the elastic modulus of VA infiltrated YSZ was 262 ± 4 GPa. The increase in elastic modulus at 50  $\mu$ m, is again attributed to the solidified VA accumulation in the splats of YSZ TBCs (Kang et al., 2017). Low fracture toughness and high elastic modulus is responsible for the generation of micro-cracks in the TBCs.



Figure 21. (a) Change in the Vickers microhardness (GPa), (b) Fracture toughness (MPa $\cdot$ m<sup>0.5</sup>), at 50, 100, 150 and 200  $\mu$ m.



Figure 22. (c) Elastic modulus (GPa) of as-sprayed and VA affected TBCs, measured at 50, 100, 150 and 200  $\mu$ m.

Thermal stress of the infiltrated region is evaluated by using equation (6)

$$\sigma = \frac{E \cdot (\Delta \alpha \cdot \Delta T)}{1 - \nu} \tag{6}$$

Where,  $\sigma$  is the thermal stress, E is the elastic modulus of TBC affected by VA (262 ± 4 GPa),  $\Delta \alpha$  is the difference in thermal expansion coefficients of the TBC and VA ( $\alpha_{TBC}$ = 11×10<sup>-6</sup> K<sup>-1</sup> (Fox & Clyne, 2004);  $\alpha_{VA}$ = 7×10<sup>-6</sup> K<sup>-1</sup> (Skinner, 1966),  $\Delta T$  is the temperature difference between the furnace temperature and the temperature assumed at the infiltrated layer (~1150 °C) and v is the Poisson's ratio of YSZ (0.2). The thermal stress of the YSZ at a constant heating rate was estimated to be ~ 0.131 GPa. Qualitative analysis of the damage caused by rapid spreading of molten VA on the surface of TBCs during thermal shock regime was performed by optical observation. Cross-sectional SEM images of the TBC post 5 cycles of thermal shocking is shown in Fig. 22.



Figure 23. Cross-section and topography SEM images of VA infiltrated 7YSZ TBCs post thermal shocking for 5 cycles.

Horizontal and vertical cracks of length 193.4 µm and 310.3 µm were evinced from the cross-sectional image. Cracks were also observed to have originated from the TBC-VA interface. Low fracture toughness and high elastic modulus of the infiltrated region are primary causal factors for the generation of micro-cracks. For 10 cycles thermal shocking, the cracks appeared to be denser than the coating subjected to 5 cycles exposure and branched out, as they propagated across the coating from the topographical image in Fig. 23, crack coalescence with adjacent micro-cracks were evident in the cross-section. Krämer et al studied the effect of CMAS on TBC-bond coat system under thermal shocking condition, and a similar crack behavior was observed and categorized based on their presence in the sub-level CMAS-TBC interface. The increase in the monoclinic phase content was primarily responsible for the depletion of Yttria and destabilization of Zirconia, which led to the mechanical degradation of the coating. The thermal shock stress was evaluated by equation 6, considering the elastic modulus of the infiltrated region (E=  $262 \pm 4$  GPa),  $\Delta \alpha = 4 \times 10^{-6}$  K<sup>-1</sup>,  $\Delta T = 1275$  °C and  $\nu = 0.2$ , the thermal shock stress was estimated to be ~1.67 GPa. This is 12.74 times higher than the thermal stress generated in the infiltrated layer during isothermal exposure, and this aspect gives rise to a demanding emphasis on the mechanical properties of solidified VA melt during the quenching regime. The solidification of the VA melt and the emanation of cracks from it while cooling are crucial factors responsible for the mechanical degradation of the TBCs. Colombier et al. have estimated the value of thermal stresses in natural VA melt-water interaction to be 0.308 GPa, where the system was subjected to an extremely high cooling rate. High thermal stresses and rapid crack growth in VA glass during the thermal shock regime (~190 m/s) (van Otterloo, Cas, & Scutter, 2015).



Figure 24. Cross-section and topography SEM images of VA infiltrated 7YSZ TBCs post thermal shocking for 10 cycles.

It can be observed from topographical cracks in Fig. 24 that the crack spacing for the TBC subjected to 5 cycles of thermal shock exposure, increased from 6.4 - 20.7  $\mu$ m, as one progresses towards the coating. However, the crack pattern in the TBC exposed for 10 cycles revealed channeling of adjacent micro-cracks and an increase in the crack density compared to 5-cycle thermal exposure, as observed in figure 24.





Figure 25. Topographical SEM images of VA affected 7YSZ TBCs post thermal shocking for 5 cycles and10 cycles respectively.

This phenomenon has been observed for the case of glass slabs (Bahr et al., 1993) for an increased cooling rate, consistent with the idea that the crack might emanate due to melt solidification under extreme quench conditions, dependent on the cooling rate.

#### 2.3.4 Raman analysis

Raman spectral analysis was performed at the topographical corrosion ring of the thermally shocked TBCs, which had been formed as a result of the interaction between molten VA and TBC as shown in Fig. 25. Monoclinic phases were detected at 190 cm<sup>-1</sup>, which were absent in the as-sprayed TBCs, this indicates a rapid surficial deterioration of the TBC, as the VA melt spreads across the surface. As mentioned above, the increase  $(\Delta m = 14\%)$  in the monoclinic phase content plays a critical role in the mechanical deterioration of the TBCs.



Figure 26. Raman spectra obtained at points 1, 2 and 3 corresponding to the corrosion ring generated by the spreading of molten VA on the TBC surface

The destabilization of TBCs due to phase transformation  $(t \rightarrow m)$  leads to a subsequent volume change in the system, thereby leading to an impact on the residual stress. Raman spectra were obtained for as-sprayed TBCs prior to thermal shocking and the residual stress peak was identified at 640 cm<sup>-1</sup>, which is in good agreement with an earlier study on the residual stresses of TBCs subjected to thermal shocking (Chen, et al.,

2014) (Fig.26). Raman spectra were obtained at the cracked region of the TBCs (points 1,2,3 and 4), across the polished coatings post thermal shock of 5 cycles and 10 cycles respectively subjected to thermal shocking as shown in Fig. 27 a. Savitzky-Golay filter was utilized to eliminate the background noise and smoothen the obtained spectra at cracked regions (Fig. 27 b).



Figure 27.. Raman spectra of standard as-sprayed YSZ TBC specimen, and the residual stress peak at 640 cm<sup>-1</sup>.

It was observed from Fig. 27c that the difference in peak shift from the standard peak (640 cm<sup>-1</sup>), corresponding to the cracked region of the 5 cycles thermally shocked TBCs were higher than the TBCs subjected to thermal shock of 10 cycles. The difference in peak shift could be due to the residual stress relaxation, post crack generation in the TBCs. The presence of micro-cracks, as evidenced by the topographical and cross-sectional images of the TBC subjected to thermal shock of 10 cycles might be responsible for the relaxation of the residual stresses accumulated in the system. The friability of YSZ TBCs subjected to thermal shocking is dependent on an interplay among fundamental properties such as rapid wetting, surficial reaction, subsequent phase transformation to

monoclinic phase and the accumulation of residual stress. The rapid quench stress was estimated to be ~ 1.67 GPa, and the thermal expansion mismatch was  $4 \times 10^{-6}$ , the volumetric expansion induced by phase transformation are causal factors for the generation of micro-cracks in the TBCs. Additional work is under progress to understand the *in-situ* wetting nature of molten volcanic ash friability of TBCs in severe thermal cycling conditions.



Figure 28. (a) Cross-sectional SEM image of YSZ subjected to thermal shocking of 5 and cycles respectively (b) Raman spectra obtained in the cracked region at points 1,2,3 and 4 (c) Residual Raman peak shift in the cracked region at points 1,2,3 and 4.

# 2.4. Conclusions

The thermo-physico mechanical properties of the TBCs subjected to molten volcanic ash interaction was performed in-situ using state of the art optical dilatometry and indentation techniques. Micro-hardness of the infiltrated region, near the interface, was higher than the as-sprayed TBCs. The following conclusions can be drawn from the present study:

- In-situ wetting analysis of the morphological transition of molten VA, thermally shocked at 1300 °C indicated that the average spreading rate of the melt on TBC surface was 1.29 µm/sec. The contact angle also decreased rapidly from ~90° to 21.2°, during the first thermal shock cycle, this rapid wetting mechanism of molten VA on the TBCs was responsible for the thermo-mechanical as well as thermo-chemical degradation.
- The interaction between VA-TBC system destabilizes the Zirconia (due to depletion of Yttria) at a rapid rate, thereby leading to ~14% increase in monoclinic phase content which is detrimental to the mechanical properties of the TBC.
- Micro-hardness of the VA infiltrated layer implied an increase of 7 GPa, from the as-sprayed condition. Low fracture toughness (0.8 ± 0.1 MPa·m<sup>0.5</sup>), high elastic modulus (262 ± 4 GPa) of the infiltrated layer and thermal quench stress of 1.67 GPa are prime causal factors for the generation of micro-cracks in the TBCs.
- Surficial cracks generated post thermal shocking, revealed that the cracks potentially emanated from the VA melt during the quench regime. These findings offered a framework for further exploration of the properties of VA melt, which plays a seminal role in making the TBCs friable.
- The Raman spectra revealed peak shifts corresponding to the intensity of thermal shocking, which suggested presence of compressive residual stress. The increase in the micro-cracks after 10 cycles of thermal shocking led to a reduction in the residual stress.

• This study is limited to the effect of molten volcanic ash infiltration into freestanding YSZ TBCs. However, further research on the holistic topcoat-bond coat-TGO- super alloy substrate system, with an emphasis on the thermo mechanical aspect of VA melt nature is essential to understand the friability and crack propagation in the TBCs.



CHAPTER 3 THERMO-MECHANICAL DEGRADATION OF EB-PVD TBCS BY MOLTEN VOLCANIC ASH

# Chapter 3. Thermo-Mechanical degradation of EB-PVD TBCs by molten volcanic ash

# **3.1 Introduction**



Figure 29. Ash accumulation in the vanes of HPT blades (Venti. M, 2017)

As discussed in chapter 1, when volcanic ash is ingested into a modern jet engine, it will first erode the blades of the compressor, leading to a reduction in operational efficiency. The ash subsequently is entrained into the hottest zone of a jet engine, the combustion chamber; in this chamber, the peak flame temperature can be as high as 2000 °C, far in excess of the melting temperature of volcanic ash (~ 1100 °C). Consequently, entrained ash particles melt and may adhere to, and flow over (i.e., spreading and wetting) the surfaces of hot section components (e.g., nozzle guide vanes and high-pressure turbine blades- Fig.28) of the jet engine (Supplementary Figure 1). Previous research conducted by NASA Vehicle Integrated Propulsion research (VIPR) team attempted to introduce

volcanic ash in a stationary engine. The VIPR results provided an understanding on volcanic ash deposition on to the hot section of the stationary engine and clogging of cooling holes (Fig. 28) (Wesley, 2017). The columnar structure of EB-PVD coatings offer better mechanical resistance compared to APS coatings. However, the columnar structure is prone to molten volcanic ash infiltration readily compared to the lamellar structure. Studies dealing with the degradation of EB-PVD coatings by molten silicate , primarily focused on the infiltration kinetics and wetting aspect of the coating. There remains a paucity of experimental evidence on the in-situ tracking of molten volcanic ash infiltration, closer to the realistic deposition of molten volcanic ash on the TBCs. In this study, I experimentally simulate the impaction of molten volcanic ash on TBCs, by utilizing thermal spraying technique. *In-situ* high temperature optical dilatometry was employed, to determine the wetting and morphological transition of the impacted micro globules and determine the thermo-chemical and thermo-mechanical degradation of the EB-PVD YSZ coating.

#### **3.2. Experimental procedure**

#### 3.2.1 Volcanic ash characterization

As mentioned in chapter 2, fresh Eyjafjallajökull volcanic ash collected from the 23 May 2011 eruption, was re-melted. The natural ash samples tested contain both crystals and glass; re-melted ash samples however represent the glass formed by melting of natural assemblages. So, the bulk chemistry remains the same but the chemistry of the glass phase differs due to differentiation from melting and mixing of crystals with the original interstitial glass, thereby the ash samples were re-melted in order to eliminate the thermal history, present in them and obtain a homogenized molten state. X-ray diffraction pattern of the ash was performed to confirm the absence of crystals. The amorphous silica shoulder in the spectra represents the amorphous character of VA (Fig. 29). SEM image of VA also confirmed the absence of any crystals in the resultant VA (Fig. 11)



Figure 30. XRD spectra of Eyjafjallajökull volcanic glass

# **3.2.2 EB-PVD** coating fabrication

7YSZ coatings were prepared using a 150 KW EB-PVD system, fabricated at the German Aerospace Center (DLR, Köln). Coatings of thickness 450  $\pm$  20  $\mu$ m (Fig. 30a) were deposited onto alumina substrates of thickness 1mm. Surface roughness (R<sub>a</sub>) plays an important role in the wettability of coatings. R<sub>a</sub> of the EB-PVD coatings was  $3.54 \pm 20 \mu$ m (Fig. 30b), determined by 3d-confocal laser microscope of laser wavelength 405 nm (Keyence VK-X1000).







Figure 32. (b) Surface roughness of EB-PVD coating

# 3.2.3 Volcanic ash impaction

Molten VA micro globules were impacted on the surface of the EB-PVD coating, by employing atmospheric plasma spraying technology (Oerlikon metco 9MB spray), at Toyohashi university of technology, Japan. The thermal spraying was carried out using argon gas flow of 40 Lmin<sup>-1</sup>, an arc current of 800 Amp, arc voltage of 70 V, powder feed rate of 0.8 gmin<sup>-1</sup> and a constant spray distance of 100 mm (Fig. 31). Detailed specification of the in-flight parameters and spray particle diagnostics is available in our previous research (Song et al, 2019). The spray particulates are deposited as micro globules on the

surface of the EB-PVD coating, as seen in the Si elemental map in Fig. 31. Resultant EB-PVD coatings, used in this study were sectioned into dimensions of 3mm× 3mm by using a precision diamond wire saw (0.1 mm).



Figure 33. Schematic illustration of the impaction of volcanic ash on EB-PVD coating

#### 3.2.4 Micro-wettability measurement

In-situ observation of the micro-wetting was performed by employing the LINKAM TS 1500 hot stage installed on an OLYMPUS BX51M optical microscope. EB-PVD coating was placed in a ceramic sample insertion cup, heated from underneath and sides, at a temperature of 1300 °C and heating rate of 50 °C·min<sup>-1</sup>. Calibration of TS 1500 stage was performed with reference to the change in melting point of Au accordingly (temperature correction: -5 °C). Live imaging of molten VA microglobules on the surface of EB-PVD coating during the heating cycle, was recorded at 22 frames per second, using an inbuilt charge coupled camera. The change in contact angle of the VA micro globules (Fig. 32) was observed by recording the cross-section of the coating during the heating cycle, and the morphological change change of micro-globules was observed by recording the the shrinkage diameter of VA micro globules was determined by converting the real time photographs into binary form.

Drop-snake plugin in the imageJ software was utilized both global and local methodologies (as mentioned in chapter 2) to position the contours and evaluate the contact angle based on the global shape of the B-spline snake (Stalder, et al., 2006) (enclosing the active contour).



Figure 34. Contact angle of impacted micro globules, converted to binary form

#### **3.2.5 Characterization procedure**

The samples were embedded in epoxy and sectioned parallel to the rotation axis using a diamond coated lapidary saw blade at low speed. Standard metallographic techniques were employed to polish the samples and obtain a  $3\mu$ m finish and placed in a vacuum desiccator to avoid surficial contamination. The samples were subsequently investigated by scanning electron microscope (SEM Hitachi SU 5000) coupled with energy dispersive spectroscopy (EDS), to characterize the infiltration depth. Raman spectroscopic analysis was performed using a Horiba Jobin Yvonne (Xplora) system, mounted on an Olympus BX15 microscope, within a Raman shift range of 100–800 cm<sup>-1</sup>.

#### **3.2.6 Micro-hardness measurement**

Micro-hardness of the molten VA impacted EB-PVD coating was measured post heat treatment. Vickers micro indentation apparatus (VH-1202 Wilson), was used to indents on the polished cross-section of the coatings. A load of 500 gram-force was exerted, for a

hold time of 10 seconds. The Vickers micro-hardness  $(H_v)$  was evaluated by using equation 1.

# 3.3. Results and discussion

#### 3.3.1 Micro-wetting of molten VA micro globules

Molten VA post impaction onto the surface of EB-PVD coating are solidified in the form of globular structures, spatial characterization of the deposited dispersed micro-globules was characterized by elemental mapping of Si on the coating surface (Fig. 33).



Figure 35. Topographical BSE images and the corresponding Si elemental maps of volcanic microglobules on the surface of EB-PVD coatings

The distribution of the diameter of individual VA micro-globules on the surface of the coating was estimated by analyzing the elemental maps. Average diameter of the micro-globules was found to be  $33\pm1.6 \,\mu$ m (Fig. 34). Surface roughness plays an important role,

not only on the wetting, but also on the geometry of the impacted VA micro-globules as discussed in our previous publication (Song et al., 2019). In order to verify the melting range of VA, it was loaded into the heating stage at a temperature of 1250 °C and a heating rate of 5 °C·min<sup>-1</sup>. It was found that the melt softened at a temperature range of 1100–1175 °C (Fig. 35), this corresponded to the melting point 1164 °C (as mentioned in chapter 2).



Figure 36. Contact angle of impacted micro globules, converted to binary form

It was observed that the irregular ash coalesced into a regular molten blob at 1250 °C (Fig. 35), the morphological change in the structure is highly controlled by the transition in to highly viscous melt ( $\eta$ ~10<sup>3.42</sup> Pa.s). The average width of EB-PVD columns were estimated to be ~ 15 µm and the micro globules were dispersed on the coating such that, they encapsulated consequent columns. Earlier studies on the wetting of EB-PVD by molten silicates were limited to the geometrical changes of the spatial wetting and subsequent infiltration into the coatings.



Figure 37. Hot stage live images of the transition of irregular volcanic ash

However, in order to obtain a realistic picture of the wetting phenomena of VA on the TBCs, the EB-PVD coating was subjected to a temperature of 1300 °C to investigate the morphological changes of the impacted VA micro globules.



Figure 38. Change in contact angle of micro globule with respect to the temperature

Wetting of 1 mm VA pellet on the EB-PVD coating was also studied in order to compare the spreading behavior with that of VA micro globules, there was no visible transitions in the contact angle of VA until 750 °C, therefore the observation was carried out within the interval of 750–1300 °C. It was evinced that both VA micro globules and the molten VA pellet, completely spread the surface at 1300 °C. In the temperature range of 1070-1175 °C, a spike in the contact angle was observed for both the cases. However, the increase in the contact angle was more pronounced in the molten VA pellet (121 °) than the average contact angle of VA micro globules. The contact angle of the molten VA pellet later descended rapidly to 40°, where it was equivalent to the average contact angle of the VA micro globules. Comparing the cross-sectional change in the droplet and micro globules of both the scenarios, the average reduction rate of VA pellets (droplet) contact angle within the temperature range of 1070-1300 °C was 0.18 degrees per second and the average reduction rate of VA micro globules contact angle was 0.07 degrees per second. It can be interpreted that the rapid change in the contact angle of the molten VA ash pellet could lead to further spreading of molten VA on the coating, similar phenomenon was observed in the spreading of molten VA on APS coatings with an average spreading rate of 0.1 degrees per second.



Figure 39. Binary conversion of volcanic ash micro globules on the surface of EB-PVD coating

Topographical characterization of molten VA micro-globules was performed by tracking the shrinkage of the micro globule diameter (Fig. 37), during the heating cycle. VA micro globules of different diameters were selected to trace the behavior of shrinkage into the

EB-PVD columns. Micro globule of diameter 40  $\mu$ m (encapsulating two columns), showed no significant decrease in dimensions as the temperature is increased to 1050 °C. However, within the temperature range of 1070-1300 °C the globule shrinks to 3  $\mu$ m, and this could be attributed to the subsequent infiltration into the columns.



Figure 38. Change in the shrinkage diameter of micro globule with respect to the temperature

Micro globules of diameter above 80  $\mu$ m decreased rapidly within the temperature range of 1070-1300 °C, with an average shrinkage rate of 0.271  $\mu$ m·sec<sup>-1</sup>, whereas the shrinkage rate of 40  $\mu$ m micro-globule was 0.134  $\mu$ m·sec<sup>-1</sup> (Fig. 38). Previous studies on the wetting of molten CMAS on EB-PVD coatings also observed a similar reduction rate in the contact angle (Ravisankar Naraparaju et al., 2019).

# **3.3.2 Infiltration and long-term thermal aging**

The infiltration was characterized by subjecting the coatings to a hold-time of 10 seconds and 100 seconds respectively at 1300 °C. It was found that the maximum infiltration depth

of the coatings subjected to a hold time of 10 seconds was 33  $\mu$ m and it was further deeper as the hold time was increased to 100 seconds at 197  $\mu$ m (Fig. 39).



Figure 39. (a) Si elemental maps of EB-PVD coating held for 10 seconds and 100 seconds at 1300  $^{\circ}$ C (b) Penetration depth of the EB-PVD coatings with respect to heat treatment time

The infiltration time (t) of molten VA was estimated based on, the penetration depth (h), radius open for infiltration (r), surface tension of molten VA ( $\sigma$ ~0.36 N m<sup>-1</sup>, for

molten silicates), the contact angle of molten VA micro-globule ( $\theta$ ) and the permeability of molten VA (k) flow into the EB-PVD column was initially proposed by Zhao. et al., (2014) later modified by Naraparaju et al., (2017) based on the Darcy's law for unidirectional flow through porous medium, using the following equation:

$$t = \frac{\mu r h^2}{2\sigma k \cos \theta} \tag{7}$$

Permeability plays a pivotal role in predicting the infiltration depth, as it governs the infiltration of molten VA into the columnar coatings. In order to evaluate the permeability of the EB-PVD coatings, physical models (open-pipe model, concentric pipe model) were employed based on the impacted micro globules encapsulating the EB-PVD columns pipes (Fig. 42). Open-pipe model considers a hollow capillary tube, facilitating the infiltration, the permeability ( $k_0$ ) is calculated using the equation (Naraparaju et al., 2017):

$$k_0 = \frac{r^2 \phi^2}{8\tau (1-\phi)^2} \tag{8}$$

Where, r represents the radius of the columnar gap,  $\phi$  is the pore-fraction or porosity of the EB-PVD coating (determined by image analysis-13.9%) and  $\tau$  is the tortuosity factor (1–3) (Krämer, et al., 2006) of the coating evaluated as the ratio of columnar gap to the area of branched feather arm structures in the coating (Fig. 40)

The Concentric pipe model, considers the EB-PVD column with a kernel (Fig. 41), surrounded by a pipe for infiltration of molten VA. The permeability ( $k_c$ ) and radius ( $r_c$ ), are modified according to the considerations, using the following equation:

$$k_{c} = \frac{\phi}{8\tau} b^{2} \left[ 1 + \frac{a^{2}}{b^{2}} + \left( 1 - \frac{a^{2}}{b^{2}} \right) \cdot \frac{1}{\ln \frac{a}{b}} \right]$$
(9)

$$r_c = \sqrt{b^2 - a^2}$$

Where, a is the radius of the kernel and b is the radius of the pipe, considered as infiltration gap illustrated in figure 41. The infiltration depth of the micro globules into the coatings was evaluated by using equation (1), based on the permeabilities evaluated by equations (2) and (3). For short heat treatment time, the infiltration depth of VA micro globules evaluated by open pipe and concentric pipe models (Fig. 42) was not corresponding to the experimental infiltration depth, however at a prolonged duration of 100 seconds, the maximum experimental infiltration depth (197  $\mu$ m) corresponded to that of the open pipe model. Similar trend on the reliability of open pipe model for prolonged heat treatment time was represented in the case of molten silicate infiltration into EB-PVD coatings. Whereas the concentric pipe model fails in the accurate prediction of infiltration depth, presumably due to the preliminary geometrical considerations in the evaluation process. The pressure required driving the capillarity action of the infiltration of molten VA into the coating is evaluated by the following equation (Zhao et al., 2014):



$$\Delta p = \frac{2\sigma}{r} \cos \theta \tag{10}$$

Figure 40. (a) BSE image of VA micro-globule encapsulating EB-PVD columns (b) Schematic illustration of the columnar structure assumed to form a pipe like structure



Figure 41. BSE image of the EB-PVD columnar tip, in the form of a kernel

 $\Delta p$  is the pressure drop driving the molten VA micro globules into the coating, it was evaluated to be  $1.8 \times 10^6$  Pa or 18 atm. The capillary pressure of molten VA, as it impregnates into the feathery structure is higher than 18 atm., due to a constrained area. Reaction of molten VA with YSZ due to prolonged infiltration, was characterized by performing Raman analysis across the cross-section (Fig. 43). Mono- clinic phase (190 cm<sup>-1</sup>) was detected across the cross-section at 35 µm and 115 µm, in comparison to the as-sprayed EB-PVD TBC. It is evinced that a prolonged exposure of micro globules deposited on the surface could result in the monoclinic phase. This finding provides us a further insight in the durability aspect of TBCs, as the deposition of VA micro globules of average diameter 33±1.6 µm.


Figure 42. Change in the penetration depth with respect to time



Figure 43. Raman spectra of molten VA impacted and as-sprayed EB-PVD TBCs

The mechanical properties of the coating are greatly affected by the formation of monoclinic phase, which results in structural destabilization as discussed in the case of APS coatings in chapter 2. Molten VA impacted EB-PVD coatings were subjected to long term thermal aging of 100 hours at 1300 °C. BSE images of the cross section revealed that the EB-PVD columns sintered. From figure 44, the cross-sectional SEM image revealed that five adjacent columns sintered together as on single column of width 51  $\mu$ m, the

sintering of adjacent columns have opened wide gaps and cracks across the coating. From figure 45, it was evinced that an opening of 45  $\mu$ m was caused due to the sintering of adjacent columns. The thermal aging of the EB-PVD TBCs reveal the extent of damage by the deposition of VA microglobules of average diameter 33±1.6  $\mu$ m, which might potentially deteriorate the engine, when undetected by borescope inspection at low ash concentration levels.



Figure 44. BSE images of molten VA impacted EB-PVD TBCs subjected to a hold time of 100 hours



Figure 45. BSE images of molten VA impacted EB-PVD TBCs subjected to a hold time of 100 hours

#### 3.3.3 Mechanical characterization

The mechanical properties of the molten VA impacted EB-PVD TBCs was evaluated by Vickers micro hardness (Fig. 46). The EB-PVD coating was subjected to a temperature of 1300 °C, for a hold duration of 100 minutes. Indentation were placed across the cross-section of the coating at 50, 150, 250, 350 and 450  $\mu$ m. Due to the infiltration of molten VA micro globules and subsequent solidification, micro hardness of the coating at 50  $\mu$ m was found to be 10.9 ± 1.6 GPa and at 150  $\mu$ m was 10.8 ± 2.1 GPa. The infiltration depth from figure 39 justified the increase in micro hardness of the coating, the similar phenomenon was observed in the case of APS coatings, as discussed in chapter 2 (section 2.3.3). The micro hardness decreased to 6.7 ± 1.6 GPa, which represents the non-infiltrated region of the coating.



Figure 46. Hardness of VA impacted EB-PVD TBCs



Figure 47. BSE images of molten VA impacted EB-PVD TBCs subjected to thermal shocking In order to observe the generation of micro cracks due to the infiltration of molten VA impaction in a thermal shock condition, the EB-PVD TBC was subjected to thermal shocking (by following section 2.1.4) for five cycles and a hold-duration of five minutes

in the furnace. Presence of vertical crack emanating from the solidified VA melt, this was similar to the crack behavior of the APS coating shown in chapter 2

#### 3.4. Conclusion

- In-situ wetting analysis of the molten VA pellet and VA micro globules impacted on EB-PVD TBC was performed and the average reduction in the contact angle of the VA micro globule was lower than the Pellet, the encapsulation of the EB-PVD columns by VA micro globule was responsible for the constrained lateral spreading on the coating surface
- Surficial tracking of the micro globule shrinkage due to infiltration was observed and it was found that the micro globule was subjected to an average shrinkage rate of 0.271  $\mu$ m·sec<sup>-1</sup>
- Due to the columnar structure of EB-PVD, the infiltration of the VA micro globules infiltrated to 197  $\mu$ m, for a hold duration of 100 seconds. The infiltration depth of the coatings was estimated using open-pipe and concentric-pipe physical models. The open-pipe model was significantly successful in estimating the infiltration depth
- The capillary pressure of the micro globules penetrating into the coating was found to be 18 atm. The pressure of the VA micro globules could increase in the feathery structure, as the structures are constrained
- For a prolonged exposure at 1300 C for 100 minutes, the Raman spectra revealed the presence of monoclinic phase in the EB-PVD TBC. The coating was subjected to long term thermal aging for a hold duration of 100 hours and coalescence of adjacent columns were observed, leading to crack openings across he coating.
- The change in mechanical properties due to infiltration of VA micro globules, revealed that the micro hardness increased to  $10.9 \pm 1.6$  GPa in the infiltrated

region, and vertical crack was observed to emanate from the solidified VA micro globule during thermal shock condition.

• This study serves the purpose of understanding progressive degradation behavior of molten silicates, as they adhere to the surface of EB-PVD TBCs, and are usually undetected by visual means as the aircraft flies through low ash concentrations below the sensor limits (Davison & Rutke, 2013).



## CHAPTER 4. NOVEL TBCS WITH HEXAGONAL BORON NITRIDE ADDITIVES RESISTANT AGAINST MOLTEN VOLCANIC ASH WETTING

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### Chapter 4. Novel TBCs with Hexagonal Boron nitride additives resistant against molten volcanic ash wetting

#### **4.1 Introduction**

Efforts to constrain the impact of volcanic ash on jet engines grew substantially following the 2010 eruption of Eyjafjallajökull (Davison & Rutke, 2013). The range of such efforts has included the characterization of volcanic ash deposits in jet engines following natural encounters; understanding the rate of molten ash deposition, investigating the wetting of engine parts (Song et al., 2016); infiltration and chemical reaction of ash with TBCs (Levi et al., 2012); and simulation of engine operation air flow and temperature evolution in the presence of volcanic ash (Jiang et al., 2017). All such efforts are ultimately aimed at improving the durability of next-generation engines.

In the past ten years, it has been suggested that the most promising solution for mitigation of the infiltration of molten volcanic ash into TBCs might be achieved by Gadolinium zirconates ( $Gd_2Zr_2O_7$ ) and the addition of Al and Ti to YSZ (Drexler et al., 2011). This addition alters phase relations such that CMAS silicate melts crystallize an oxy-apatite phase upon reaction with the TBC, thereby limiting further silicate melt infiltration (Krämer, et al., 2008). In this solution, however, molten silicates remain in contact with the TBC, which further progressively deteriorates (Poerschke, et al., 2017). In this chapter, a more resilient and repellent TBC with novel properties is introduced which reduce silicate melt wettability, and thereby hem physical infiltration and degradation via chemical reaction. Here, design of a more resilient *h*-BN additives to YSZ with properties that reduce silicate melt wettability, and thereby inhibit physical infiltration and degradation via chemical reaction.

#### 4.2. Experimental Procedure

#### 4.2.1 Fresh volcanic ash characterization and homogenization

For this study, three fresh volcanic ash samples were utilized for this experiment: Eyjafjallajökull (Eyja), Soufriere Hills (SH), and Santa Maria (SM).Fresh volcanic ashes consist of groundmass glass and crystal content. In order to eliminate any weathering effect and thermal history present in the ashes, the crystal-bearing natural volcanic ash samples were heated in a platinum crucible to  $1650 \,^{\circ}$ C for 48 hours and were subsequently quenched in air. This treatment produces crystal-free glasses with the same thermal history. The glasses were then crushed and sieved to produce fine ash samples, the bulk chemical composition of the volcanic ash is presented in Fig. 48a. X-ray diffraction (XRD) pattern was measured for the re-melted ash samples using GE X-ray diffractometer (XRD 3003 TT) in Bragg-Brentano geometry using Cu-Ka1 radiation. The ashes were fully amorphous 2-theta ( $2\theta$ ) was in the range 20-80° (Fig. 48b), a Silica background holder of diameter 2.5mm was used to eliminate the background noise



Figure 48. Characterization of volcanic ashes. (a) Bulk chemical composition of volcanic ashes. (b) XRD spectra of the re-melted volcanic ashes showing only the amorphous silica shoulder, further confirming the amorphous character of the ash samples. (c) Viscosity of the ash samples

over the temperature range 1210 °C–1250 °C. (d) SEM images of re-melted Eyja, SF and SM ashes.

The viscosity of the molten volcanic ash as a function of temperature was estimated using multi-component viscosity evaluation model, developed by Giordano *et.al* (Giordano et al., 2008). Based on the viscosity model, the evolution of volcanic ash viscosities over known temperature ranges were calculated. The temperature dependence of viscosity ( $\eta$ ) is governed by the equation: log  $\eta$ = [A+B / (T(K)–C)], where A is the highest limit of log  $\eta$  for silicate melts, and B and C are factors which describe the compositional dependence. At a temperature of 1250 °C, the viscosity of the prepared samples were constrained at  $10^{2.85}$ - $10^{3.65}$  Pa s (Fig. 48c), using chemical composition as input parameter in the GRD model.

The re-melted volcanic ash samples were optically investigated using a scanning electron microscope (SEM) to determine the presence of crystals. A Schottky Field Emission Scanning Electron Microscope, Hitachi SU5000 was used for the SEM investigations (Fig. 48d), SEM and XRD results confirmed that the ash samples were homogenous. These re-melted/homogenized volcanic ashes (referred to as volcanic ash) have been employed for the following experiments carried out in this work. The melting point was estimated by using the rhyolite-melts software which is a modification of MELTS module (Gualda, et al., 2012), optimized for silica-rich magmatic systems (table 2). Although the current melts software is predominantly used for melt inclusion composition under highly pressurized conditions or water-saturated conditions, the liquidus temperature was estimated using the chemical composition of the volcanic ash using atmospheric pressure (1 bar) as the input parameter.

**Table 2**. Onset of melting of the volcanic ashes, estimated by rhyolitic melts software.

Characteristic	Eyjafjallajökull	Santa Maria	Soufriere	Hills
Temperature	(°C)	(°C)	(°C)	
Liquidus	1127	1159	1140	

#### 4.2.2 Wettability measurement

The re-melted volcanic ash was compacted into cylindrical pellets with radius and height of 1 mm by pressing the ash (applied pressure of  $1.5 \text{ N mm}^{-2}$ ) into a cylindrical die. The resulting cylindrical ash compact was ejected from the die onto the TBC substrate. The wettability of the ash on the TBCs was assessed by monitoring the silhouette transition of the volcanic ash pellet in a Dataphysics OCA 25-HTV 1800 optical dilatometer. The volcanic ash compact is subjected to high temperature exposure of 1250 °C, at a heating rate of 5 °Cmin<sup>-1</sup>. Wettability experiments were performed both in atmospheric conditions and *in-vacuo*, the latter using a turbomolecular pump to achieve a low pressure of  $< 10^{-5}$  Pa. Wettability was assessed using sessile drop method by monitoring silhouette transition of the specimen under high vacuum condition ( $<10^{-5}$  Pa). The furnace was calibrated with a gold shard on an alumina substrate and adjusted to according to the obtained temperature (1129 °C instead of 1064 °C, shift = -65 °C).

The images were captured at 60 frames per second (fps), using a charge coupled camera device. The contact angle was determined, to quantify the wettability of molten volcanic ash on TBCs. Binary images were generated from the real time images of the molten drop at 1250°C. A local methodology of choosing contours is more accurate than the global choice of contours. The drop-snake plugin in ImageJ utilizes both global and local methodologies, which allows us to position the contours and evaluate the equilibrium contact angle- $\theta_c$  based on the global shape of the B-spline snake (enclosing the active contour) (Stalder et al., 2006)

#### 4.2.3 Non-wetting behavior of molten volcanic ash on *h*-BN substrate

The wetting mechanism on a substrate is mainly governed by the substrate microstructure and chemical reactivity of the substrate and molten volcanic ash droplet. Hexagonal boron nitride (*h*-BN) is currently regarded (to best of our knowledge) as the sole refractory ceramic material exhibiting a non-wettability of molten Si inferred to be due to its covalently-bonded structure, involving honeycomb-structured sheets bound by weak ionic inter-planar attractions (Drevet, et al., 2009). Here, I tested its performance at impeding molten volcanic ash wetting at high temperature. To evaluate the wettability of *h*-BN with molten volcanic ash, a single Eyjafjallajökull glass shard was loaded onto *h*-BN substrate (dimension:  $12 \times 12$  mm) and the sample assembly was heated to  $1250 \,^{\circ}$ C at a rate of 5  $^{\circ}$ C min<sup>-1</sup> in the optical dilatometer under high vacuum conditions. Profile imaging was used to monitor the morphological evolution of the shard (Fig. 49a)with increasing temperature and time (Fig. 49c); The initial angular shape of the shard, starts to soften (i.e., the edges round) around 1170-1200 °C and a near spherical-shaped bead is achieved exhibiting an equilibrium contact angle of  $120^{\circ}$  upon reaching  $1250 \,^{\circ}$ C (Fig. 49b), (confirming the non-wetting properties of the coating).



Figure 49. Non-wetting behavior of hexagonal-boron nitride (*h*-BN) thin film substrate. (a) Quenched Eyjafjallajökull melt shard before thermal treatment on *h*-BN thin film substrate ( $12 \times 12 \text{ mm}$ ) at 25 °C. (b) Real time photograph of the geometrically transitioned spherical melt at 1250 °C, in-vacuo condition (<10-5 Pa). (c) Sequential In-situ silhouette morphological transition of the irregular shard to a sphere from 25 °C to 1250 °C. (d) Macroscopic images showing the non-wetting behavior (left) and non-adhesion property (right) of solidified melt on the surface of *h*-BN substrate.

Once cooled to ambient room temperature, it was observed that the solidified silicate did not stick to the coating (Fig. 49d); thereby, confirming h-BN coatings exhibit non-wetting, non-sticking properties that need to be understood in terms of their potential exploitation

in future coating designs. The non-wetting of molten Eyjafjallajökull ash on the *h*-BN substrate could be attributed to surficial reaction process, by the formation of  $Si_3N_4$  layer (Fig. 50).



Figure 50. (a) The topography of *h*-BN substrate (b) SEM image of the substrate topography (c) Magnified BSE image indicates high contrast globules on the topography (d) Topographical EDS maps of Si and N

#### 4.2.4 Fabrication and Characterization of the TBCs

We employed APS method to produce novel coatings consisting of *h*-BN (20 wt.%) and 7YSZ (80 wt.%) (referred to as *h*-BN YSZ) onto an alumina substrate (Al<sub>2</sub>O<sub>3</sub> > 96%). 7 wt. %YSZ powder with a particle size of less than 63  $\mu$ m (Fujimi) and boron nitride powder with a particle size of less than 45  $\mu$ m (Alfa Aesar) were used as feedstock. Alumina substrates were chosen in this work instead of traditional superalloy substrates to facilitate isothermal heat treatment of the system above 1200 °C. Conventional YSZ coatings were fabricated by thermal spraying (Table 3), for comparative tests *versus h*-BN YSZs with same spray conditions (referred to as YSZ). The coatings were

ultrasonically cleaned using de-ionized water post fabrication, and stored in a desiccator in order to avoid any surficial contamination.

Arc Voltage	Carrier gas	Arc current	Spray distance	Powder feed
(V)	$(Ar, L \cdot min^{-1})$	(A)	(mm)	rate
				$(g \cdot \min^{-1})$
70	40	800	100	0.8

 Table 3. Plasma spray parameters.

Inspired by the dual non-wetting, non-sticking properties of h-BN with respect to molten volcanic ash, and in order to explore further the potential benefits of h-BN as an additive in conventional TBCs, atmospheric plasma spraying method (APS) was utilized (Table 3) to produce novel coatings consisting of h-BN (20 wt.%) and 7YSZ (80 wt.%) (referred to as *h*-BN YSZ TBCs) onto an alumina substrate (Al<sub>2</sub>O<sub>3</sub> > 96%). 7 wt. % YSZ powder with a particle size of less than 63 µm was obtained from Fujimi, while boron nitride powder with a particle size of less than 45 µm was obtained from Alfa Aesar. Conventional 7YSZ TBCs were fabricated by thermal spraying, for comparative tests *versus* h-BN YSZ TBCs with same spray conditions (referred to as APS YSZ TBCs). The TBCs were ultrasonically cleaned using de-ionized water and stored in a desiccator under vacuum, in order to avoid any surficial contamination. For surface characterization of TBCs, the surface roughness (S<sub>a</sub>) was evaluated using a Keyence VK-X1000 3D-laser scanning microscope with a vertical resolution of 0.02 µm, laser wavelength of 405 nm and a scan speed of 4 µm s<sup>-1</sup> on a surface area spanning  $700 \times 700 \,\mu m^2$ . For microstructural characterization of TBCs, the samples were initially embedded in epoxy and sectioned parallel to the rotation axis using a diamond coated lapidary saw bladed coating at low speed. Standard metallographic techniques were employed to polish the samples to obtain a 3µm finish. The samples were subsequently investigated by SEM and electron dispersive spectroscopic (EDS) analysis.

#### 4.2.5 Heat treatments of TBCs

Thermal aging and thermal shock heat treatment processes were performed using EM301 Hesse Instruments furnace. Eyjafjallajökull ash pellets with radius and height of 1 mm were loaded onto the geometrical centre of the TBCs, and they were thermally aged at 1250°C with a heating rate of 10 °C min<sup>-1</sup> for hold durations of 3-48 hours and cooled at 10 °C min<sup>-1</sup>. The furnace was calibrated with a gold shard on an alumina substrate and adjusted to according to the obtained temperature (1074 °C instead of 1064 °C, shift = +10 °C) The extent of spreading of molten volcanic ash on the TBCs post thermal aging was evaluated by the spreading area, which was determined by capturing images of the surface of TBCs using a Canon Eos 80D camera, with a lens of 65mm focal length. The captured RGB image was converted into a binary form using ImageJ. The resultant spreading area and diameter of the binary image was evaluated using ImageJ software. Thermal shocking was performed by traversing the TBCs into the furnace kept constant at 1250°C, the samples were placed in the furnace for hold times of 1 and 3 hours respectively. The TBCs were subsequently removed and rapidly quenched in air (as described in chapter 2). The TBCs were molded into epoxy resin and sectioned post-heat treatment, to examine the presence of cracks post thermal shock across the sample cross section. To characterize the infiltration of molten volcanic ash into the TBCs across the cross-section, the samples were initially molded in epoxy and sectioned parallel to the rotation axis using a diamond lapidary saw bladed coating at low speed. Standard ceramographic techniques were employed to polish the samples and obtain a 3µm finish, prior to the SEM and EDS analysis. The average porosity of the TBCs was determined using ImageJ software.

#### 4.2.6 Micro-hardness measurement

The microhardness of the coatings was measured using Vickers micro-indentation technique (Wilsson VH-1202). The coatings were sectioned across the cross-section and standard metallographic techniques were employed to polish the samples, for Vickers indentation and characterization of the infiltration depth of molten volcanic ash into the coatings. 6 micro-indents were placed across the cross-section of the coatings, at different

depths (50, 75, 100 and 150  $\mu$ m), with a load of 300 gf. and a hold-time of 10 seconds. The Vickers micro-hardness (H<sub>v</sub>) was evaluated by using the following equation:

$$H_{v} = 0 \cdot 102 \frac{F}{S}$$

where F is the indentation load (N) and S is the indented surface area (mm<sup>2</sup>).

#### **4.2.7 Characterization Procedures**

Standard metallographic techniques were employed to polish the samples and observe the cross-section. Surface roughness ( $R_a$ ) of the coatings was evaluated using a Keyence VK-X1000 3D-laser scanning microscope. Raman spectroscopic analysis was performed using a (Horiba Xplora) system, with a wavelength of 532 nm. The samples were subsequently investigated by SEM and energy dispersive spectroscopic (EDS) analysis to measure the maximum infiltration depth. The average porosity was estimated across the cross section of infiltrated samples by utilizing ImageJ software.

#### 4.3. Results and Discussion

#### 4.3.1 TBC Characterization

As-sprayed YSZ and *h*-BN YSZ coatings consist of a lamellar structure formed by coarse splat like microstructure (Fig. 51). The average porosity of *h*-BN YSZ is ~29%, which is slightly higher than that of YSZ coatings (~22 %). Surface roughness (R<sub>a</sub>) values of *h*-BN YSZ and YSZ coatings are  $7.3 \pm 1.02 \mu m$  and  $6.8 \pm 0.18 \mu m$ , respectively (See Fig. 51c and 51f).

The quality of the *h*-BN additives in the *h*-BN YSZ coatings might be compromised by oxidization in air at high temperatures (~1100°C) (Jacobson, Farmer, Moore, & Sayir, 1999). Thus, particular attention was paid to characterizing any potential oxidation. Coating mapping using electron dispersive spectroscopy identified a small fraction of nitrogen (N), scattered onto and within the coating, suggesting minor oxidation (Figs. 52a and 52b).



Figure 51. Properties of *h*-BN YSZ and conventional APS YSZ coatings. (a) Photograph of *h*-BNYSZ coating ( $6 \times 3$  mm) fabricated by thermal spay deposition on an alumina substrate. (b) Cross-sectional SEM image of *h*-BN YSZ coating (thickness: ~ 200µm). (c) Surface roughness profile of *h*-BN YSZ coating topography evaluated by confocal laser microscopy. (d) Photograph of conventional APS YSZ coating ( $6 \times 3$  mm) on an alumina substrate. (e) Cross-sectional SEM image of APS YSZ coating (thickness: ~ 400µm) (f) Surface roughness profile of APS YSZ coating topography evaluated by confocal laser microscopy.



Figure 52. Characterization of *h*-BN YSZ. (a) SEM image of *h*-BN YSZ coating surface and the corresponding distribution of nitrogen obtained by EDS. (b) Cross-sectional SEM image of *h*-BN YSZ coating and the corresponding nitrogen distribution obtained by EDS. (c) Raman spectra acquired at the cross-section of YSZ, *h*-BN YSZ coating and cross-section of *h*-BN substrate.



Figure 52. Characterization of *h*-BN YSZ. (d) X-ray diffraction pattern of the *h*-BN YSZ TBC indicates the presence of *h*-BN and t-YSZ, as compared to standard *h*-BN (crystallography open database (COD): 2016170) and t-YSZ (COD: 1521477) XRD profile data.

Raman spectral mapping of the coating revealed a peak at 1365 cm<sup>-1</sup> (Fig. 52c) and XRD providing unambiguous evidence for the presence of pure (non-oxidized) *h*-BN particulates in the coating. XRD of the coating further indicates the presence of both *h*-BN (peak: 27°) and tetragonal YSZ (*t*-YSZ) (peak range: 34.6–35.8°), as expected in a well fabricated *h*-BN YSZ TBC (Fig. 52d). Hence, it must be concluded that the oxidation of h-BN in the coating remains minor during the experiments.



Figure 53. Surface profile across *h*-BN YSZ and APS YSZ coatings.

 $R_a$  of TBCs play an important role in the wetting of molten volcanic ash (Huh & Mason, 1977), as observed from previous chapters and it was ensured that  $R_a$  was uniform across the surface (Fig. 53).

#### 4.3.2 Wetting resistance of *h*-BN YSZ against molten volcanic ash

To evaluate the wettability of *h*-BN YSZ coating with molten volcanic ash, preliminary wetting experiments were performed under vacuum, for a duration of 1 hour. It was found that the three volcanic ash samples evolved to form non-wetting, near-spherical molten droplets with high contact angles  $\theta_c \sim 110^\circ$  when resting on the *h*-BN YSZ, whereas they significantly wetted the surface of YSZ coating, evidenced by low contact angles  $\theta_c \sim 40-55^\circ$  (Figs. 54a and 54c).

The results demonstrate that *h*-BN YSZ coating exhibit non-wettability to molten volcanic ash under vacuum. Bearing in mind the potential oxidation of *h*-BN, I further determined the wetting properties of the coatings with Eyjafjallajökull (hereafter referred to as Eyja) ash under oxidizing atmospheric conditions. Eyja was chosen due to the lowest melting point and lowest viscosity at 1250 °C compared with the other volcanic ash samples. Here, 1-hour hold-time tests were performed and *in-situ* images at 1250 °C reveal that the melt completely spread onto the surface of YSZ coating ( $\theta_c = 14.7^\circ$ ). Spreading of molten Eyja ash on *h*-BN YSZ (Figs. 54b and 54c) was much more limited, exhibiting a contact angle  $\theta_c = 55.34^\circ$ , more than thrice that of conventional YSZ coating (Fig.54c). These results demonstrate that the novel *h*-BN YSZ coatings have an increased resilience to wetting by molten volcanic ash compared to YSZ coatings, under atmospheric conditions.



Figure 54. Wettability of volcanic ash on conventional YSZ and novel *h*-BN YSZ coatings. (a) Photographs of the three volcanic ash droplets with variable wetting degrees on the surface of *h*-BN YSZ and YSZ coatings in-vacuo at 1250 °C. (b) Photographs of molten Eyja ash droplets on the *h*-BN YSZ and YSZ coatings at 1250 °C, in oxidizing condition. (c) Comparison of the contact angles resultant from the wetting of molten volcanic ash onto *h*-BN YSZ and conventional YSZ coatings in vacuum and atmospheric oxidizing conditions at 1250 °C.

In order to examine the influence of  $R_a$  on the wetting, *h*-BN YSZ of  $Ra= 3.43 \pm 0.37 \mu m$  was fabricated (Figs. 55) and  $\theta_c$  was found to be 51.5°, post wetting of molten Eyja ash for a soak-time of 1 hour. Thereby, it was inferred that the variation in  $R_a$  of *h*-BN YSZ coating did not influence the degree of wetting on the surface.

![](_page_93_Figure_0.jpeg)

Figure 55. Influence of R<sub>a</sub> on wetting (a) R<sub>a</sub> value of *h*-BN YSZ (b) spreading behavior.

To resolve the extent to which molten volcanic ash spreads onto the TBCs, the spreading area of the melt was evaluated. We note that the onset of color fading was observed by the formation of a faint-brown ring/ corrosion ring (Fig. 56) (Hodaj, et al., 2007) The corrosion ring formed post 3 hrs for the YSZ coating, whereas it was observed post 12 hrs for the *h*-BN YSZ coating, that is 4 times longer. Surficial reaction as a result of complete wetting of the molten Eyja ash ( $\theta_c$ ~0), is evident from the formation of the corrosion ring, which is visible for a soak time of 3 hours on YSZ coating, in contrast to 12 hrs long term exposure of *h*-BN YSZ coatings.

![](_page_93_Figure_3.jpeg)

Figure 56. Extent of Spreading of Eyja ash on the coatings under atmospheric condition. (a) Spreading of molten ash on the surface of *h*-BN YSZ (upper row) and conventional APS TBCs (lower row) at 1250  $^{\circ}$ C

![](_page_94_Figure_0.jpeg)

Figure 56. Extent of Spreading of Eyja ash on the coatings under atmospheric condition. (b) Comparison of the extent of spreading on the coatings.

#### 4.3.3 Infiltration resistance of *h*-BN YSZ against molten volcanic ash

The infiltration of molten Eyja in the coatings after thermal aging was determined by the elemental distribution of Si, mapped across the cross-section of the coatings.  $\theta_c$  made by molten Eyja on the surface of *h*-BN YSZ was 43° during a soak time of 3 hrs and 16° during a soak time of 6 hrs at 1250 °C (See Fig. 57).

![](_page_94_Figure_4.jpeg)

![](_page_94_Figure_5.jpeg)

Molten Eyja thoroughly wetted the surface of YSZ coatings for a soak-time of 3 hrs at 1250 °C (See Fig. 58).  $\theta_c$  of thermally soaked *h*-BN YSZ was higher than conventional YSZ, this was related to its minimal infiltration as seen in Fig 57a. Previous studies on the modifications of the microstructure of TBCs suggested that a minor difference in  $\theta_c$ , had a significant impact on the infiltration depth of molten CMAS into TBCs (R Naraparaju et al., 2017).

![](_page_95_Figure_1.jpeg)

Figure 58. BSE images-Contact angle of molten Eyja ash on APS YSZ post thermal soak time of 1 and 3 hours

For a soak-time of 12 hrs, the maximum infiltration depth of *h*-BN YSZ (86  $\mu$ m) was twice the infiltration depth of 6hrs thermally aged *h*-BN YSZ (43  $\mu$ m) (Figs. 59a and 59b).

![](_page_95_Figure_4.jpeg)

Figure 59. Infiltration of molten of Eyja ash into the coatings at atmospheric condition. (a) Maximum infiltration depth ( $\mu$ m) of molten volcanic ash into each TBC

![](_page_96_Figure_0.jpeg)

Figure 59. Infiltration of molten of Eyja ash into the coatings at atmospheric condition. (b) Si-Elemental maps (by EDS mapping) of *h*-BN YSZ and YSZ coating (BSE images) for soak-time of 12 hrs at 1250 °C. (c) Average porosity (%) of as-sprayed coatings and coatings infiltrated by molten volcanic ash.

Previous research on Alumina doped YSZ has also documented shallow penetration of molten CMAS into a highly porous coating. Here, the lower wetting propensity of molten ash was observed on *h*-BN YSZ versus YSZ coating had a significant impact on the infiltration depth, presumably owing to the reactive wetting of *h*-BN and molten silicate. The inter-relationship between thermal aging and variation in contact angle was observed as the molten volcanic ash completely wetted the surface of 12 hrs thermally aged *h*-BN YSZ coating from 16 ° of 6 hrs thermally aged *h*-BN YSZ coating. However, the lower sub-region of the 12 hrs thermally aged *h*-BN YSZ coating was unaffected by infiltration and the influence of oxidation could be minor (Fig. 59b), due to the presence of N in the underlying unaffected layer (Fig. 60). The minimal effect of oxidation could be attributed to the thermal insulation by YSZ constituents, which traditionally offer a temperature reduction of 170 °C to protect the underlying substrate (as discussed in chapter 1)

![](_page_97_Figure_0.jpeg)

Figure 60. EDS elemental maps of 12hrs thermally soaked *h*-BN YSZ coating.

The coatings were further subjected to thermal aging for 48 hours, and it was observed that there was no residual glass present on the surface of the coatings and molten Eyja completely reacted with the coatings (Fig. 61). It was evident that the conventional YSZ coatings completely reacted with molten Eyja. Whereas h-BN YSZ coating was prone to the reaction in an uneven manner, with an increase in density of globular Si-based reaction products. The reason behind this phenomenon is still unclear and the future work will be directed to produce uniform layered h-BN YSZ coating structure, in order to investigate this behavior.

![](_page_97_Figure_3.jpeg)

Figure 61. BSE images and corresponding EDS Si elemental maps of 48hrs thermally soaked *h*-BN YSZ and conventional YSZ coatings.

#### **4.3.4 Mechanical properties**

Micro-hardness values of the coatings subjected to infiltration by molten Eyja, for a soak time of three hours was evaluated. The average micro-hardness values of as-sprayed conventional YSZ ( $6.55 \pm 1.2$  GPa) and *h*-BN YSZ coatings ( $6.52 \pm 0.5$  GPa) were nearly the same. The micro-hardness of molten Eyja infiltrated coatings was measured across the cross-section, tracking the infiltration depths at 50, 75, 100 and 150 µm respectively. At an infiltration depth of 50 µm (example: Fig. 62a and 62b), it was evident that both conventional YSZ ( $9.23 \pm 0.89$  GPa) and *h*-BN YSZ ( $8.51 \pm 0.72$  GPa) coatings exhibited high micro-hardness values (Fig. 62c), due to the infiltration of molten Eyja. At 75 µm, conventional YSZ coating ( $9.06 \pm 0.44$  GPa) exhibited higher micro-hardness values than *h*-BN YSZ coating ( $6.76 \pm 0.56$  GPa), this corresponds to the presence of molten Eyja in conventional YSZ coating.

![](_page_98_Figure_2.jpeg)

Figure 62. Micro-hardness of the coatings. (a) Microscopic image of the indent impression of h-BN YSZ coating. (b) Depth of indent impression on h-BN YSZ coating.

![](_page_99_Figure_0.jpeg)

Figure 62. Micro-hardness of the coatings. (c) Change in the micro-hardness corresponding to the measurement depth

The infiltration of molten Eyja into the coating and further solidification led to the increase in micro-hardness value (accompanied by stiffening), which results in the mechanical degradation of the coating (as discussed in chapter 2). *H*-BN YSZ coatings exhibit better stiffening resistance than the conventional YSZ coatings, as wetting of the coatings play a governing role in the infiltration of molten volcanic ash thereby influencing the micro-hardness value.

#### 4.3.5 Thermal shock resistance

Infiltration of molten volcanic ash into the TBCs due to rapid thermal shocking generate cracks, due to localized stresses and quenching of the melt in the inter lamellar region. Mechanical properties of h-BN additives are of great interest and possess high thermal shock resistance and are proven to increase the thermal shock resistivity in composites (Kovalčíková, et al., 2014).

![](_page_100_Figure_0.jpeg)

Figure 63. Thermal shocking resistance of *h*-BN YSZ TBCs. (a) Optical microscopic image of crack-free *h*-BN YSZ TBCs post thermal shocking at 1250 °C for 1 hr. (b) Optical microscopic image of APS YSZ TBCs with vertical cracks post thermal shocking at 1250 °C for 1 hr, marked in the red enclosure. (c) Optical microscopic image of crack-free *h*-BN YSZ TBCs post thermal shocking at 1250 °C for 3 hrs. (d) Optical microscopic image of APS YSZ TBCs with vertical cracks post thermal shocking at 1250 °C for 3 hrs. (d) Optical microscopic image of APS YSZ TBCs with vertical cracks post thermal shocking at 1250 °C for 3 hrs. (d) Optical microscopic image of APS YSZ TBCs with vertical cracks post thermal shocking at 1250 °C for 3 hrs, marked in the red enclosure. (e) Change in porosity of the TBCs post thermal shocking.

APS YSZ TBCs are prone to thermal shocking as they are vulnerable to cracking which progressively extend from the splat boundaries. Silicate melt infiltration into the pores of coatings is likely to impart some losses in strain tolerance relative to uncontaminated coatings. To test this, I subjected the coatings to rapid thermal shocks. These tests indicate that *h*-BN YSZ TBC does not crack when subjected to such rapid thermal fluctuations (Figs. 61a and 61c), indicating its higher capacity to resist thermal shocks; in contrast, cracks developed in the APS YSZ TBCs in response to thermal shock (Figs. 63b and 63d).

Porosities of the TBCs play a major role in thermal shocking (Vaßen, et al., 2004), the change in porosity post thermal aging was higher for the conventional APS YSZ TBCs than h-BN YSZ TBCs (Fig. 63e). Deeper Infiltration by molten ash into APS YSZ TBCs at lower hold time durations compared to h-BN YSZ TBCs accompanied by higher spreading velocities as discussed earlier, are responsible for faster penetration of ash into APS YSZ TBCs. The crack generation in the APS YSZ TBCs could be due to solidification of the melt, when subjected to rapid atmospheric quenching. Hence it was observed that h-BN 4SZ TBCs under extreme thermal shock resistance of YSZ TBCs and the potential of h-BN YSZ TBCs under extreme thermal cycling will be analyzed in future studies.

#### 4.3.6 Exploring the wetting properties of carbon additives

In order to explore other candidate materials resistant to the wetting of molten silicates. carbon was found to offer properties similar to *h*-BN, and is also structurally similar to *h*-BN. Eyja glass shard was placed on C substrate, and was loaded into the optical dilatometer isothermally heated to 1250 °C under controlled conditions, following the similar steps employed in section 4.2.4.

![](_page_101_Picture_3.jpeg)

Figure 64. In situ photograph of spherical Eyja volcanic ash globule on C substrate at 1250 °C

![](_page_102_Picture_0.jpeg)

Figure 65. Non-sticking of solidified Eyja glass shard on C substrate

As seen in the insitu photograph in figure 64, C substrate exhibit non-wetting by molten Eyja and post heat-treatment. From Fig. 65, the glass shard was observed to completely detach from the surface of the substrate. Based on the properties exhibited by C substrate, C-YSZ coating was prepared by APS method, using similar conditions employed in section 4.2.5.

![](_page_102_Figure_3.jpeg)

Figure 66. Raman spectra of C-YSZ coating

Raman analysis was utilized to detect the presence of carbon, and the presence of distinguished peak at 1580 cm<sup>-1</sup> (Fig. 66), corresponded to C and thereby it was concluded that C was not oxidized during the fabrication of C-YSZ coating. In order to verify the

potential of CYSZ coatings subjected to the wetting of molten Eyja ash, thermal aging experiment was performed using the optical dilatometer under atmospheric condition. It was evinced that the insitu images were unable to be recorded, due to the rapid volatilization of C distributed on the surface of C-YSZ, which caused the silhouette of the Eyja ash pellet to destabilize from 900 °C. In figure 67, post heat treatment, the surface of C-YSZ was observed, and the surface coarsened presumably due to the volatilization of C from the surface and faint brown patches could be attributed to the reaction of molten Eyja and C-YSZ. The corrosion ring, suggests that Eyja melt completely spread and reacted with the remnant C-YSZ does not qualify as an additive to provide resistance against molten volcanic ash wetting.

![](_page_103_Picture_1.jpeg)

Figure 67. Volatilization of carbon from the surface of CYSZ coating

#### 4.4. Conclusion

In order to counteract the propensity of ingested, molten volcanic ash droplets to wet and infiltrate TBCs and cause damage to jet engines, novel *h*-BN YSZ coatings was developed and tested which exhibit enhanced resistant behavior against molten volcanic ash wetting. Employing controlled laboratory testing, I first demonstrated that pure *h*-BN substrates have silica-phobic properties under vacuum conditions at 1250 °C. Further, I have fabricated novel coatings containing 80 wt.% YSZ and 20 wt.% *h*-BN, and tested their ability to resist molten volcanic ash droplets, compared to conventional YSZ coating.

Under vacuum conditions, this new coating repelled volcanic ash droplets, preventing infiltration of the substrate, unlike the conventional coating. Under oxidizing conditions, h-BN YSZ coating appeared more resilient as it was found that molten ash only partially wets the substrate *i.e.* the molten ash spread less and more slowly on *h*-BN YSZ versus conventional TBCs. H-BN YSZ coating exhibited better stiffening resistance than conventional YSZ coating, due to their resilience against rapid wetting and infiltration of molten volcanic ash. Finally, it was found that the new coating is more resilient to thermal shocks than the conventional YSZ coating. The thermo-mechanical aspect of degradation and potential challenges like the prevalence of water vapor in a gas-turbine environment on h-BN YSZ, will be discussed in the future. This work extends the scope for physicochemically resilient "silica-phobic" TBCs with h-BN additives, which possess the potential for mitigating risks associated with volcanic ash ingestion into jet engines. Further investigations employing such TBC solutions against other atmospheric contaminants, as well as testing of its performance under severe thermal cycling conditions are underway. It should be noted that, though carbon is structurally similar to h-BN and was resistant to molten silicates under controlled conditions, it failed to offer resilience against molten silicate wetting in atmospheric conditions due to the rapid volatilization of carbon in the coatings.

# 

CHAPTER 5 CONCLUSION

#### **Chapter 5. Outlook**

In this study, the thermo-mechanical aspect of molten volcanic ash wetting on the surface of APS TBCs and EB-PVD TBCs was investigated, novel h-BN YSZ coating was fabricated to resist the wetting of molten volcanic ash and thereby inhibit the infiltration of the melt. Of course, in the realistic case, the thermo-mechanical degradation of the TBCs undergo microstructural changes with respect to segmented crack formation, which might originate from the TGO or bond coat layer. This phenomenon is further enhanced in long term operational cycles, this dissertation provides an insight on the preliminary aspect of wetting induced origin of cracks and the first-time observation of spreading kinetics of molten volcanic ash on TBCs, subjected to thermal shocking. In order to improve the understanding of the failure mechanism associated with the infiltration of molten silicates, the wetting aspect of the coating investigated in this dissertation play a key role as it is the preliminary step initiating surficial degradation. Complete understanding of the degradation aspect (the study of the mechanism of wetting, followed by infiltration, leading to the thermo-chemical interaction between molten volcanic ash and YSZ ultimately resulting in the thermo-mechanical failure) by molten volcanic ash, gives raise to the development of novel TBCs to counteract the degradation caused by molten volcanic ash infiltration. Hexagonal boron nitride was chosen as an additive to YSZ in this study and have been tested to exhibit resilience against molten volcanic ash wetting and it was also demonstrated that not all candidate additives (eg. carbon) possess the ability to mitigate molten volcanic ash wetting under atmospheric conditions. This study is a preliminary step towards the direction of considering non-traditional additives to conventional YSZ, which offer resilience against molten silicate wetting. To determine the vulnerability of TBCs affected by two extreme contrast type of molten volcanic ash, in terms of total alkali silica content; basaltic and rhyolitic ashes. Finally, I present the results of an ongoing study to track the micro-cracks generated by basaltic and rhyolitic ashes:

# 5.1 Vulnerability of APS TBCs subjected to infiltration by basaltic and rhyolitic volcanic ashes

In the beginning of chapter 2, the mechanical properties of basaltic, trachy-andesitic and rhyolitic volcanic ashes was determined. From the micro hardness results, it was observed that there was no significant difference in the Knoop micro-hardness. However, no previous study has investigated the origin of micro-cracks in TBCs, due to the wetting and infiltration of basaltic and rhyolitic volcanic ashes. In order to investigate the onset of micro-cracks generated in the APS TBCs due to the infiltration of basaltic (Kilauea volcano) and rhyolitic (Cordon Caulle volcano) ashes, the thermal shock experiment was performed for one cycle at a temperature of 1300 °C.

#### **Micro-computed tomography**

The micro-computed tomography scans of the coatings affected by molten Eyja ash was conducted at the Zoologische Staatssammlung München (Munich, Germany) using a phoenix nanotom m cone beam  $\mu$ CT scanner with down to 1.25  $\mu$ m voxel size. To obtain higher resolution, 1mm of APS TBC was used with the following parameters: source voltage of 100 KV, 170  $\mu$ A source current, 0.1 mm Al filter, 1.25 isotropic voxel resolution and 1000 projections over 360 with three averaged images recorded per each rotation position.

#### Tracking micro cracks generated in the APS TBC

Post thermal shocking, it was observed that molten Kilauean ash spread completely on the APS TBC and also appeared to enclose the corners of the surface. This aspect could be attributed to the least viscosity at 1300 °C ( $10^{2.1}$  Pa·s) among the other two volcanic ashes.

![](_page_107_Figure_6.jpeg)


Figure 68. In situ wetting and spreading area of volcanic ashes on APS TBCs

Molten Eyja ash covered 2.6 mm of the coating and the extent of spreading by Cordon Caulle volcanic ash was 1.7 mm on the APS TBC, as shown in figure 68.



Figure 69. Tomographic images- Crack length tracking in Kilauea volcanic ash affected APS TBC The micro cracks generated in the APS TBCs due to thermal shocking by the influence of molten volcanic ash wetting was observed by micro computed tomography, and it was evinced that micro cracks were evident in Kilauea affected APS TBCs whereas there were no crack generated in the Cordon Caulle and Eyja ash affected APS TBCs. Crack behavior was tracked across the cross-section of the coating and the crack spread horizontally across the APS TBCs, crack coalescence was also observed (Figure 69). From cross-sectional SEM image shown in Fig. 70, it was evinced that there were no micro cracks

present in the Cordon Caulle ash affected APS TBC. The cracks in Kilauea ash affected APS TBC was observed to emanate from the side of the coating, as the ash encapsulated entire coating surface.



## Figure 70. BSE images of the origin of micro crack in APS TBCs

These findings demonstrate that the basaltic volcanic ash cause more damage to the TBCs. It should be noted that the mechanical properties of the volcanic ashes chosen for this study was not significantly different from each other, however the damage caused by the volcanic ash depends on the viscous nature of the ash and the extent of spreading on the surface of TBCs. In order to conclude on the vulnerability aspect of different types of volcanic ashes, not only the mechanical properties but also the thermo-physical properties (dynamic viscosity, thermal expansivity) play a crucial role in the degradation of the TBCs.

All such information on the wetting aspect of the molten volcanic ash, its implications on thermo-mechanical degradation and the understanding of the damage imparted by different type of volcanic ashes would contribute to a greater picture of mitigating molten silicate infiltration into the TBCs and also aid the development of novel

coating combinations. This dissertation sheds light on the unexplored aspect of molten volcanic ash micro globule wetting, that progressively deteriorates the longevity of the coatings, when the ash particulates are undetected or lower than the sensor limit.

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