

**Analysis of Service-Retrieved TBC-Coated Industrial Gas Turbine
Components**

By

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Declaration and Acknowledgements

I herewith certify that all material in this thesis which is not my own work has been properly acknowledged

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Abstract

Thermal barrier coatings (TBCs) have been widely used in gas turbine applications such as aerospace and power generation. TBC systems serve numerous purposes – the bond coat acts as a sacrificial layer for oxidation and the ceramic top coat works together with internal cooling systems to protect the superalloys from extreme temperature environments. With the rising demand for better fuel efficiency, the hot gas temperature within modern gas turbine engines has exceeded the working temperature of most advanced superalloys. The state-of-the-art TBCs have raised the high temperature capabilities of modern superalloys to a new level and have become an absolute necessity in modern gas turbine applications. While most research focus on the improvements of TBCs, the present study examines the environmental attacks which could lead to failures of TBCs. To be more exact, sand and dust particles often enter the mainstream hot gas flow path of gas turbines due to the powerful suction of its compressors, and internally generated particles, such as wear debris of the components, also could enter the mainstream hot gas flow path of the gas turbine. Once these particles (external and internal) pass through the combustion stage of the gas turbine engine, some of these particles become molten and adhere onto the surface of TBC-coated turbine components. These sand particles and debris gradually build-up in thickness and cause discoloration on the TBC surface. In some cases, the accumulated deposits could reduce the lifetime of TBCs. In other cases where particles carried by the mainstream hot gas flow path remain in solid state after passing through the hot combustion stage, such solid particles are very likely to impact the TBC coated turbine components, mainly the nozzle guide vanes and turbine blades right after the combustion chamber, damaging the TBCs. Since the gas stream inside the gas turbine engine travels at a high velocity, even micron size particles could build-up high kinetic energies. Upon striking the TBCs, these particles wear down the thickness of the TBCs, reducing its thermal insulation capability. Ex-service roll one (R1) turbine nozzle guide vanes and second stage turbine blades were retrieved from a land-based gas turbine for power generation and an aero-engine for transportation respectively, and the three nozzle guide vanes received were contaminated with surface deposits of various colours, while the turbine blades suffered from erosion and foreign

object damage. These turbine components were analyzed using laboratory techniques, primarily by scanning electron microscopy with energy dispersive X-ray analysis and X-ray diffraction. In addition, heat treatment tests are also conducted to study the effect of these environmental attacks on the performance and lifetime of TBCs to determine the response of the deposit to prolonged thermal exposure.

1. Literature Review

1.1. Thermal Barrier Coating System

The state-of-the-art thermal barrier coating system is a multi-layered system designed to reduce substrate metal temperatures, to resist high temperature oxidation and to protect against corrosive environments [1-4]. The TBC normally consists of three layers: the top coat, the bond coat, and the thermally grown oxide (TGO). The ceramic top coat is often produced by electron beam physical vapour deposition (EB-PVD) and plasma spray (PS) methods, both of which create a through thickness thermal gradient whilst in service. The very low coefficient of thermal conductivity commonly observed in top coat materials delays the time for the substrate metal to reach equilibrium with the external hot temperatures, allowing the internal cooling system to dissipate the heat by its cooling channels embedded within the internal structure of each turbine component. Immediately below the ceramic top coat lies a metallic bond coat which provides oxidation and corrosion resistance as well as improving the adherence of the top coat materials. The two main types of bond coats commonly used in high temperature gas turbine applications are platinum aluminide (PtAl) and MCrAlY type bond coats, where M refers to nickel, cobalt or combinations of nickel and cobalt. In addition, a layer known as the thermally grown oxide is located between the ceramic top coat and metallic bond coat which is a by product of the oxidation. Figure 1 shows a SEM cross-section of a typical TBC system where a temperature gradient (blue line) is created across the thickness of the top coat and the bond coat [1]. Internal cooling within the turbine blade (left side) constantly dissipates the heat from the hot gas environment, maintaining the temperature of the substrate material at a safe level (avoiding the loss of the substrate's mechanical properties).

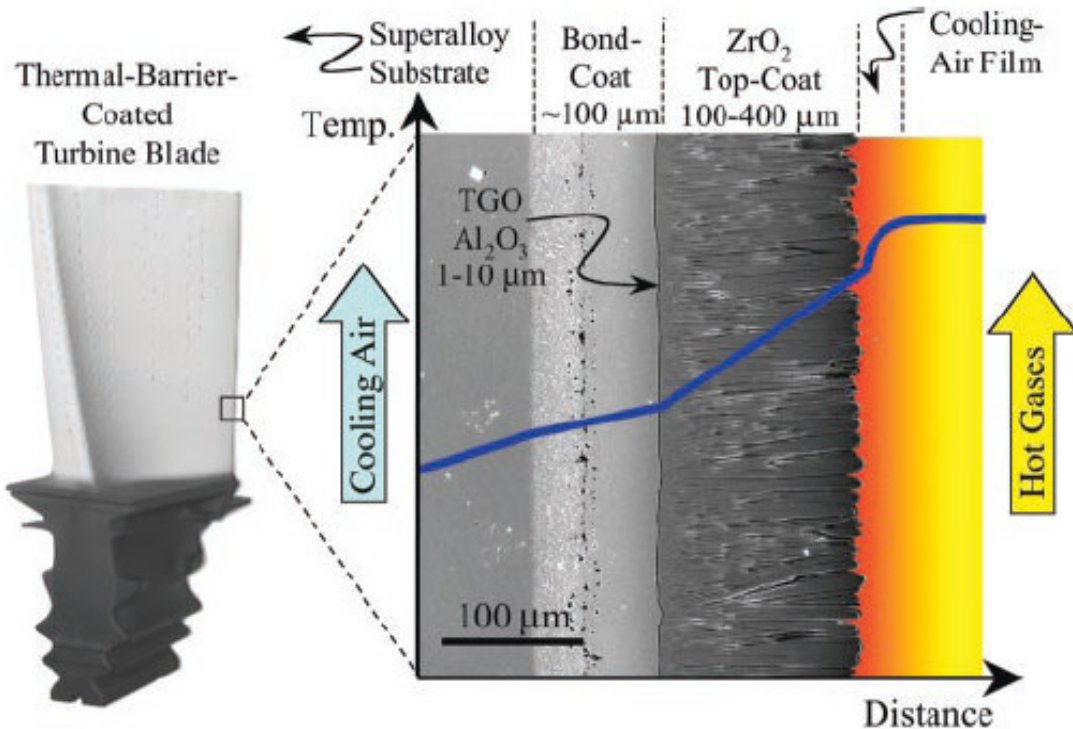


Figure 1 SEM cross section image of a typical TBC system, blue line indicates the change in temperature across the TBC [1] [figure by N. P. Padture et al.]

1.1.1. Top Coat

The top coat serves the purpose of producing a thermal gradient across its thickness. As such, the candidate materials for this application are required to have high melting points ($> 2000^{\circ}\text{C}$), low thermal conductivities (approx. $1\text{-}2\text{ W/mK}$) and similar thermal expansion coefficients to the common engine alloys ($8\text{-}16\text{ ppm/}^{\circ}\text{C}$) [5]. As TBCs are often placed in extreme temperature environments, the ability to accommodate the thermal expansion of the substrate materials is critical to the reliability of the top coat. Amongst all the candidate materials, zirconia (ZrO_2) is most suitable for this application. Despite its outstanding thermal insulating properties, the concern with zirconia lies in its tendency to undergo a phase transformation at high temperature; pure zirconia undergoes a tetragonal to monoclinic phase transformation at 1170°C , which is within the operating temperature range of gas turbines. The phase change induces a volume expansion, which creates a shear strain [6]. This phase transformation and consequent strain makes pure zirconia coatings vulnerable to spallation upon heating; therefore, a phase stabiliser is

required to suppress any possible phase transformations. Stabilizers such as CaO, MgO, Y_2O_3 , CeO_2 , Sc_2O_3 , and In_2O_3 which can inhibit the tetragonal to monoclinic transformation of zirconia and yttria (Y_2O_3) are commonly chosen. The phase diagram of the ZrO_2 - Y_2O_3 system [7] (Figure 2) illustrates the effect of Y_2O_3 addition on the tetragonal to monoclinic transformation in pure zirconia. The concentration of yttria required to stabilise the zirconia is further optimized to yield the longest cyclic service life. Stecura et al. have shown an optimal concentration of 6-8 wt % Yttria would result in the longest spallation lifetime of TBCs in cyclic heat treatment test environments [8] (Figure 3), and 6-8 wt % of Yttria addition is commonly used in practice.

The yttria stabilized zirconia (YSZ) top coat of TBCs are commonly coated by an EB-PVD or a PS coating method. EB-PVD coated TBCs have columnar grain structures, which offer better strain tolerance, and such columnar structures are ideal for the TBCs in aerospace turbine engines for its resistance against cyclic thermal environment, e.g. a landing and a take off for the aerospace gas turbine is considered as one rapid cooling and then rapid heating cycle. Plasma sprayed TBCs, on the other hand, have “splat-like” platelet morphologies with grain thicknesses ranging from 1 to 4 μm , and diameters ranging from 200 to 400 μm . Such microstructures are characterised by a high density of cracks and voids. These inter-splat cracks and voids lower the thermal conductivity of the material as heat transfer is slower by convection than conduction [9]. Plasma spraying, however, confers an absolute advantage in the cost of production and processes over EB-PVD as it is a faster coating method and incurs lower facility costs. The production of EB-PVD requires precisely controlled coating environments to maintain its characteristic uniform columnar structure. Slight modifications in process conditions, such as partial pressure of the coating chamber and substrate temperature, could significantly alter the microstructure of the coating [10].

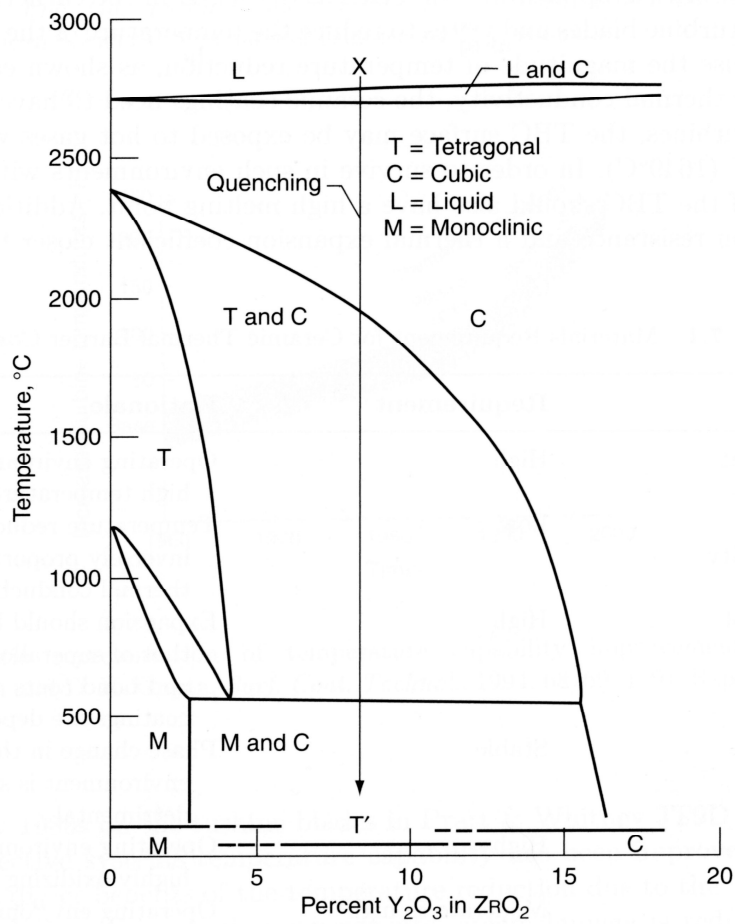


Figure 2 Phase diagram of ZrO_2 - Y_2O_3 system (wt %) [7] figure by Stecura et al.

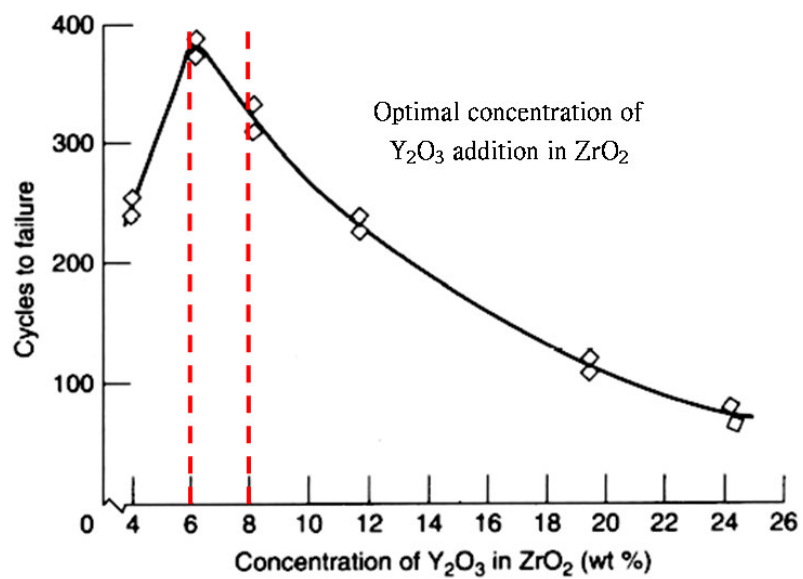


Figure 3 Cyclic lifetime of yttria stabilized zirconia vs. wt% of yttria addition [8] figure by Jones et al.

1.1.2 Bond Coat

The demand for higher gas turbine efficiency pushes the operating temperatures of modern superalloys to their limits. Alloying elements such as aluminium and chromium are maintained at the lowest possible levels in order to maintain a high melting temperature of the alloys. However, alloys with insufficient amounts of aluminium and chromium are prone to high temperature oxidation and corrosion attack as the aluminium and chromium resist oxidation by forming stable oxide phases. In other words, the aluminium and chromium contents are the sacrificial elements in the bond coat system. Bond coats are applied between the YSZ top coats and the metallic substrates to not only improve adherence of the YSZ to the substrate, but also provide aluminium and chromium reservoirs, increasing the oxidation and corrosion resistance. Commercial bond coats are classified into overlay coatings and diffusional coatings. An overlay coating is an additional layer on top of the substrate materials and is commonly applied using air plasma spray or EB-PVD methods. The overlay coating type of bond coat is often referred to as MCrAlX, where M stands for metal and X represents reactive elements. In practice, nickel or cobalt or combinations of both nickel and cobalt are referred to as M; whereas, X refers to reactive elements such as yttrium. Through extensive research, other alloying additions such as silicon, tantalum, hafnium, platinum, palladium, ruthenium, and rhenium were also found to improve the properties of bond coats, such as increased resistance to high temperature fatigue [11-13].

Diffusional type of bond coats consist of aluminides of nickel produced through diffusion-aluminizing or chemical-vapour deposition (CVD) methods. In the case of nickel-based superalloys, aluminum is deposited onto the alloy and heat treated to form nickel aluminides at the surface (β phase in the Ni-Al system). The rich aluminum content near the surface protects the metallic substrate against oxidation, providing a rich aluminum reservoir for forming an inert alumina (Al_2O_3) TGO layer. However, the diffusional type of bond coat does not provide an infinite aluminum reservoir and chemical failure would tend to occur upon aluminum depletion. Chemical failure occurs when thermodynamics of the alumina TGO layer become thermodynamically unstable such that the formation of TGO would no longer favour the formation of the inert Al_2O_3

oxide. Depending on the composition of the underlying substrate material, other oxides that are relatively more thermodynamically stable than Al_2O_3 would be formed [14]. In addition, for protection against hot corrosion, platinum additions to the aluminizing, chromizing, and siliconizing processes can also be employed to the superalloy substrate [15].

1.1.3. Thermally Grown Oxide (TGO)

The TGO layer lies in between the YSZ top coat and the metallic bond coat. The TGO is a product of oxidation, and the growth of the TGO layer is temperature and time dependent. The higher the operating temperatures, the faster the TGO growth. The most ideal bond coat materials are designed to promote the formation of $\alpha\text{-Al}_2\text{O}_3$ as the TGO. The low oxygen ionic diffusivity of $\alpha\text{-Al}_2\text{O}_3$ minimises the level of oxidation in the TGO layer [16]. In other words, the growth of TGO is controlled by both the inward diffusion of oxygen (from the outside gas stream) and the outward diffusion of aluminum (from the bond coat). The chemical reaction between oxygen and aluminum therefore occurs at the top coat / bond coat boundary, forming the TGO [17, 18].

In addition, each and every TBC system has a critical TGO thickness that leads to spallation. The critical thickness depends on the surface topography and the bond coat composition [5] of each individual TBC. Tolpygo et al. [19] have conducted research on EB-PVD YSZ on CVD coated $\beta\text{-Ni}$ (Pt, Al) bond coats, which determines the critical TGO thickness for spallation in a set of TBC systems. The experiments by Tolpygo et al. were carried out in cyclic conditions that are similar to the operating condition of aerospace gas turbine engines. (Note: under these conditions, the samples experienced cycles of heating and rapid cooling similar to repeated engine take-off and landing) The result of this research reveals the critical thickness of TGO for the particular system examined was approximately 6-7 μm . When the TGO thickness reached 6-7 μm , cracks would start propagating along the TGO / bond coat or the TGO / top coat interfaces which eventually lead to spallation of the top coat. However, it is to be noted that Tolpygo's research simulates an aerospace gas turbine environment, but not the land-based gas turbines. It is suspected that the average TGO critical thickness in the TBCs in

land-based gas turbine would be thicker than that of aerospace gas turbines due to the absence of cyclic thermal heating and cooling.

1.2. Environmental Attack on TBCs

In this section, environmental degradation of TBCs will be summarized. Common sources include chemical deposits, foreign object damage, and erosion damage and these will be discussed.

1.2.1. Chemical Deposits

Gas turbine engines operating at elevated temperatures have increased susceptibility to chemical attack. The sources of chemical contamination include impurities such as sand and dust particles entering from the air intake and debris from internal wear. Once these particles pass through the hot combustion chamber, these contaminants could become molten and adhere onto the surfaces of the turbine components, especially in turbine sections directly after the exit from the combustion chamber. The relative compositions of the chemical deposits vary with the source; however, the main elements reported are very similar. Calcium-magnesium-alumino-silicate (CMAS) is the most common form of contaminant from air intake and it is substantially composed of CaO, MgO, Al₂O₃, and SiO₂. On the other hand, the contamination from internal engine wear is often found in the form of iron and nickel oxides [20, 21].

Air Intake Sources

Deposits resulting from air intake sources share some similarities. Toriz et al. [22] first reported the degradation of TBCs in jet engines in 1988. Their research found that molten debris adhering to the YSZ could induce stresses in the TBCs which eventually lead to delamination and spallation. However, this phenomenon was observed only when temperature of the hot section exceeded 1150°C, suggesting that the melting temperature of the contamination in this study was above 1150°C. Tests conducted at temperatures lower than 1150°C were found to have no or negligible amounts of deposits. Stott et al. [23] also studied the degradation of TBCs in aero engines. In Stott's investigation, calcium-magnesium silicate with a similar structure as diopside (CaMgSiO₃) was discovered on top of the TBCs from aero engine components operating in Middle East

routes. A similar study by Smialek et al. [24] investigated the sandy deposits found on Blackhawk helicopters' turbine hot sections that operated in the Persian Gulf. The sandy deposits observed were composed of calcium-aluminum silicates similar in composition to local desert sand. The melting point of this deposit was determined using laboratory tests and reported to be 1135°C.

Another study on environmental deposits was conducted by Borom et al [20], where contaminated turbine components from the Far East, Saudi Arabia and the south-western USA were analyzed and compared. In all three cases, microprobe analyses of various deposit types and locations were conducted. Table 1 summarizes the results from these analyses. The sources of contaminants were divided into internal engine components, external environment, and TBC materials. Minor amounts of iron and nickel oxides were suspected to be originated from internal engine wear; however, the exact natures of these oxides were not identified. Primary contaminants are CaO, MgO, Al₂O₃, and SiO₂, which come from the sandy operating environment. Interestingly, constituents of the contaminants can all be traced back to the composition of the earth's crust as listed in Table 2 [25].

Although several key aspects of these external contaminants were examined, the formation route of these chemical deposits remains unknown. For instance, the source of CMAS has been identified as sand and dust particles that enter the gas turbine from the air intake; however, it is not known how these sand and dust particles react with each other and result in the chemically stable deposit. These deposits can arise in two ways. In the first scenario, various sand and dust particles each with different elemental compositions become molten in the combustion chamber. Upon exiting the chamber, these particles remain molten then impact and adhere to the surface of turbine components. Various sand particles of different elemental composition agglomerate together and finally result in the form of CMAS. In the second scenario, each sand or dust particle is chemically composed of all the major elements of CMAS (calcium, magnesium, aluminum, and silicon) and the formation of CMAS is completed once these

particles become molten at the combustion stage. The literature on CMAS does not confirm the scenario and the formation mechanism of CMAS deposits remains unknown.

Table 1 Summary of microprobe analyses with the numbers corresponding to the relative ratio of each elemental composition [20]

Geographical location	Turbine hardware	Deposit type / location	Type of oxide	Source of oxides					
				Internal alloys		External environment		TBC materials	
				FeO + NiO	MgO + CaO	Al ₂ O ₃	SiO ₂	ZrO ₂	Y ₂ O ₃
Near East desert	Turboshaft shroud	Shroud	diopside	1	6	1	7	NA	NA
		Synthetic glass	diopside	1	6	1	7		
Far East	Power gen. combustor venturi	Group 3	di-calcium silicate	6	15	1	10	3.4	0.9
		Group 4	diopside	1	6	1	6	0.5	0.04
		Group 2	spinel	5	3	1			
SW USA	Turboprop shroud	CMAS-7	tri-calcium silicate	1	5	1	2	2	0.22
		CMAS-6	di-calcium silicate	2	6	1	4	2	0.35
		CMAS-1			3	1	2		
		CMAS-5	mono-calcium silicate	0.3	5	1	4	0.3	0.05
		CMAS-10			2	1	2	0.1	
		CMAS-11		0.2	6	1	6	0.4	
		CMAS-3			2	1	2	0.2	0.01
		CMAS-4			2	1	2	0.5	0.02
		CMAS-9			2	1	3	0.1	
		CMAS-2	calcium di-silicate		1	1	2	0.1	
		CMAS-8			1	1	2	0.1	
		YSZ						1	0.05

Table 2 Composition of earth's crust in volume % [23]

Elements	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	TiO ₂	Co ₂	P ₂ O ₃	other
Vol %	59.80%	14.90%	2.70%	3.40%	3.70%	4.80%	3.20%	3.00%	2.00%	0.80%	0.70%	0.30%	0.70%

Internal source of contaminants

In addition to external contaminants, there are a number of possible internal contaminants in a land-based gas turbine. Figure 4 is a schematic diagram of a commercial gas turbine engine that include turbine buckets, nozzles, combustors, turbine wheels, compressor blades, and turbine shafts, and Table 3 lists some common high temperature alloys used for these turbine components. The alloys used in these turbine components listed above are all possible sources of internal contaminants; however, it is to be noted that turbine buckets, nozzles, combustors are stationary and coated with TBCs or other types of oxidation resistant coatings. These coated turbine components are less likely to be potential sources of contamination.

On the other hand, compressor blades and the turbine shaft are rotating components and are suspected to introduce wear debris into the gas turbine system. Although some of

these turbine components are protected by the state-of-the-art TBCs, spallation of the TBC could still occur in some occasions which expose the metallic substrate surface. The exposed substrate surface would suffer from the hot erosion and the substrate metal would eventually become an internal contamination source. Unlike aerospace gas turbine applications, modern land-based gas turbines are equipped with advanced filtration systems that filter out most contaminants from the external environment. In the case of chemical deposits in a modern land-based gas turbine engine, internal wear debris is the primary source of contaminants.

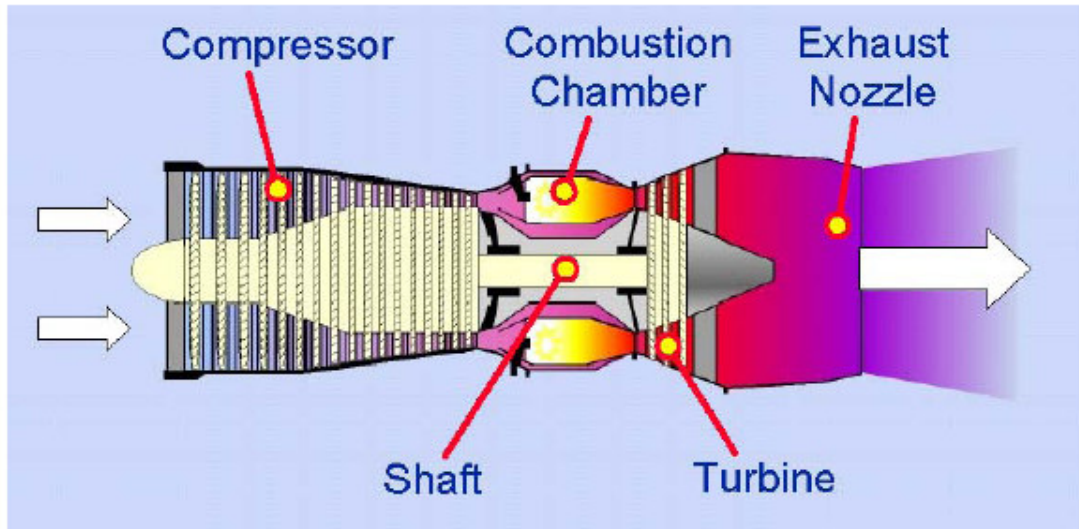


Figure 4 Commercial Gas Turbine Engine Layout [Figure by R.C. Reed] [26]

Table 3 High temperature alloys for gas turbine components in wt% [27]

Components	Cr	Ni	Co	Fe	W	Mo	Ti	Al	Cb	V	C	B	Ta
Buckets													
U500	18.5	Bal	18.5			4	3	3			0.07	0.01	
Rene 77	15	Bal	17			5.3	3.35	4.25			0.07	0.02	
In 738	16	Bal	8.3	0.2	2.6	1.75	3.4	3.4	0.9		0.1		1.75
GTD-111	14	Bal	9.5		3.8	1.5	4.9	3			0.1	0.01	2.8
Nozzles													
X40	25	10	Bal	1	8						0.5	0.01	
GTD-222	22.5	Bal	19		2	2.3	1.2	0.08		0.1	0.01	1	
Combustors													
SS309	23	13		Bal							0.1		
HA-188	22	22	Bal	1.5	14						0.05	0.01	
Turbine Wheels													
In 718	19	Bal		18.5		3	0.9	0.5	5.1		0.03		
A286	15	25		Bal		1.2	2	0.3		0.25	0.08	0.01	
Compressor Blades													
AISI 403	12			Bal							0.11		
GTD-450	15.5	6.3		Bal		0.8					0.03		
Turbine Shaft													
Cr-Mo-V	1	0.5		Bal		1.25				0.25	0.3		

Note: Nickel based superalloy - red highlight; Cobalt based superalloy –green highlight; Iron based alloy – blue highlight.

Contamination Induced TBC Delamination Mechanisms

Modern gas turbine blades and nozzle guide vanes are increasingly susceptible to chemical attack as operating temperatures increase. When the temperature of the TBC surface exceeds the melting point of the contaminants [20, 23, 24, 28], the wetting characteristic of the contaminants (deposits) would begin infiltrating the columnar structures of the TBC coated using the EB-PVD method. The depth of penetration depends on the temperature gradients across the TBCs as well as the particular service conditions. Mercer et al. [29] discovered that the depth of penetration is strictly temperature dependent for CMAS deposits. Figure 5 and Figure 6 present SEM images from the study of two contaminated sites of a turbine airfoil with the latter image taken at the suspected hot zone. Regions highlighted in red are CMAS deposits above the YSZ; whereas, regions highlighted in orange reveal the CMAS infiltrated YSZ. Regions highlighted in grey are uncontaminated YSZ. Note from the figures that the portion of YSZ with CMAS infiltrated shows fewer white areas, suggesting that the voids in between the columnar structures have been filled by molten CMAS. From these images, CMAS contaminant infiltrated $\sim 85\mu\text{m}$ deeper in the hot zone than in the relatively cooler region. Hence, the conclusion was drawn that the depth of penetration directly correlates with the level of temperature. As suggested by Mercer, CMAS infiltration can be used to determine the relative TBC surface temperatures.

A cold shock delamination mechanism for EB-PVD TBC was also characterized by Mercer et al. [29]. Figure 7 is a schematic diagram of a columnar TBC structure being infiltrated by molten CMAS resulting in horizontal TBC cracks and cold shock delamination. As the turbine cools, the infiltrated molten CMAS solidifies, thereby generating a near surface tensile stress which induces TBC delamination parallel to the surface. Repeated thermal cycling gradually extends the length of these cracks and eventually leads to extended areas of TBC spallation.

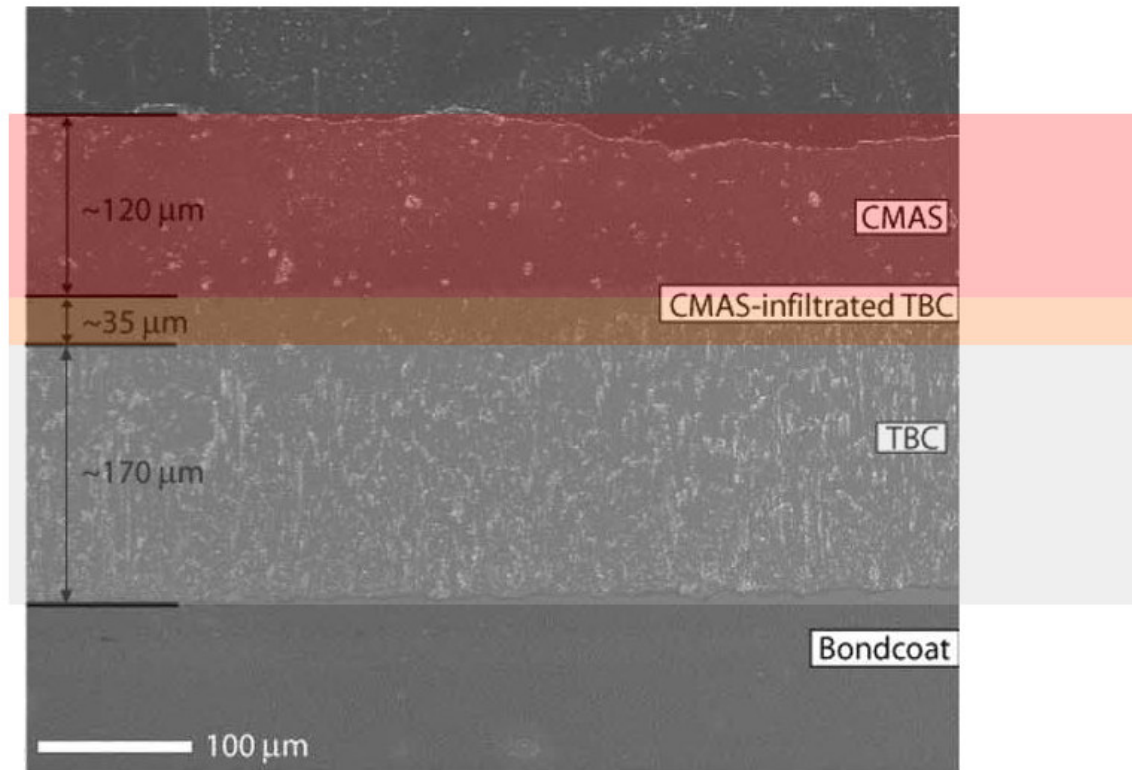


Figure 5 Region with thick CMAS deposits but shallow penetration depth (cool) [29]

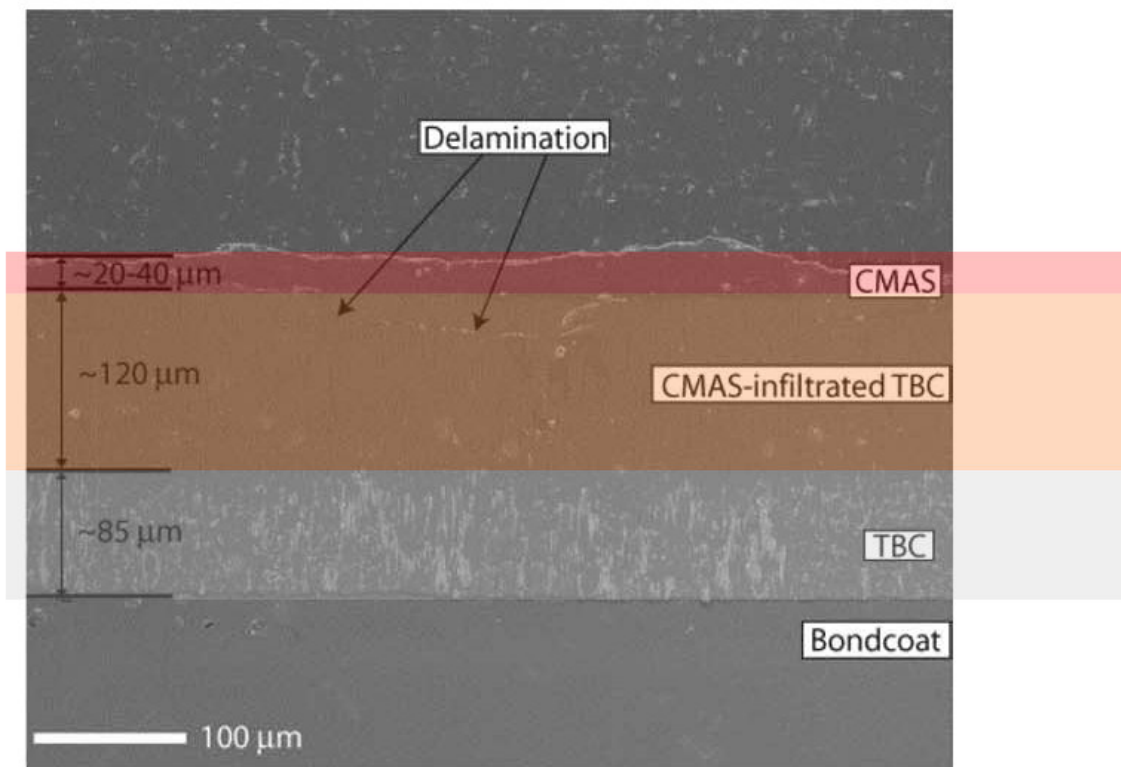


Figure 6 Region with thin CMAS deposits but deep penetration depth (hot) [29]

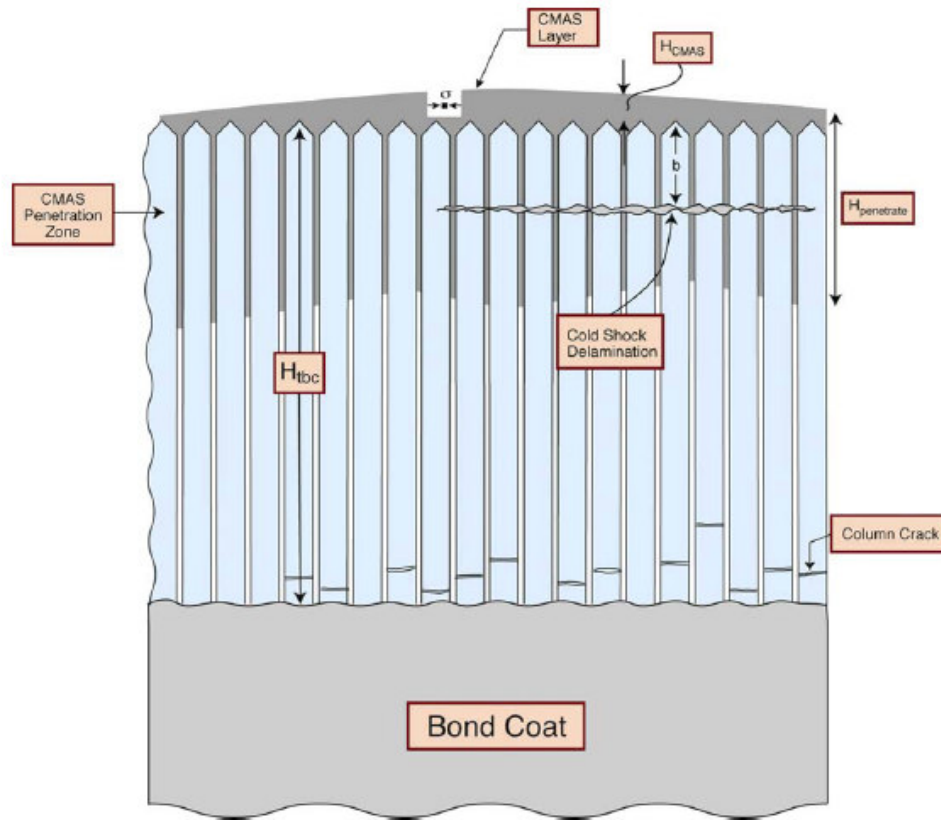


Figure 7 A schematic diagram of CMAS penetrating the EB-PVD coated TBC columnar structure [29]

Figure by Mercer et al.

The degradation of plasma sprayed TBCs attacked by the CMAS has been studied by Stott et al. [23, 30, 31]. In their studies, sand samples from Dubai, Bahrain, and Doha were placed on the surface of plasma sprayed YSZ samples and annealed at temperatures from 1300 to 1600 °C to simulate the turbine environment. It was discovered that these sand samples have the capability of dissolving or extracting Y_2O_3 and ZrO_2 from the YSZ top coat of the thermal barrier coating system. Also, another interesting discovery from this research is the effect of calcium based mineral contents (CaO) of these sands. The CaO, although only less than 5 wt %, plays a key role in determining the ZrO_2 tetragonal to monoclinic phase transformation. Sands with low CaO contents (such as for Dubai sand and Bahrain sand at ~2wt% CaO) on a plasma sprayed YSZ in a stimulated gas turbine operating environment resulted in approximately 10 wt% reduction of Y_2O_3 in the YSZ after 20 hours at 1400°C. This gave rise to the formation of monoclinic ZrO_2 (the fine granular structures located at the upper portion of c and d of Figure 8). The newly

precipitated monoclinic phase zirconia with a fine granular structures generates a near-surface YSZ volume expansion upon cooling, ultimately leading to spallation of the entire top coat. Alternatively, in the case of high calcium content molten sand (such as Doha sand at ~4.5 wt% CaO), the rate of Y_2O_3 extraction from the YSZ was significantly delayed. Like Y_2O_3 , CaO also has the ability to stabilize ZrO_2 in the tetragonal phase. The molten Doha sand extracted only ~ 4 wt% Y_2O_3 from the YSZ and the presence of monoclinic ZrO_2 phase was limited, as shown in a and b of Figure 8.

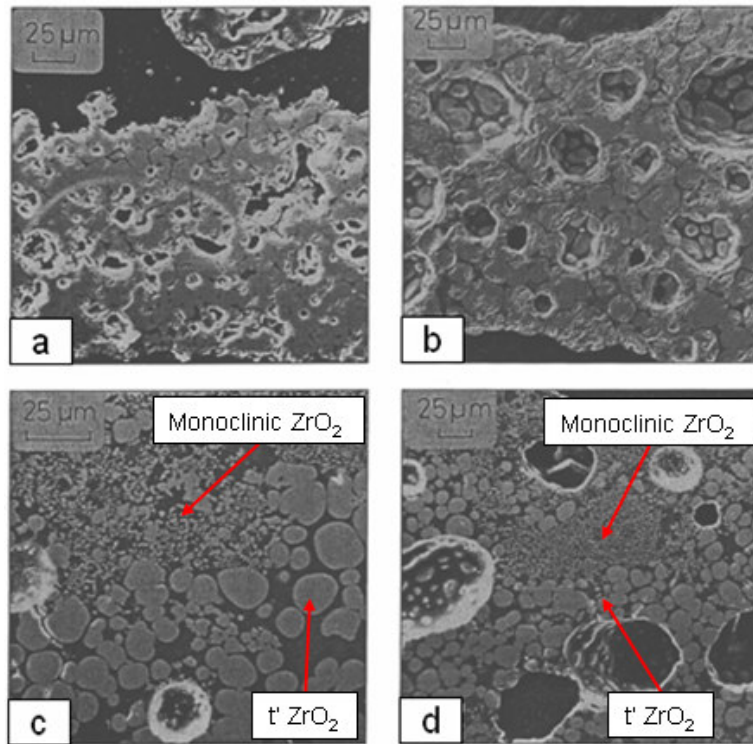


Figure 8 SEM images of plasma-sprayed TBCs attacked by a) Doha sand, 70 h at 1300°C, b) Doha sand, 20 h at 1400°C, c) Dubai sand, 20 h at 1400°C, and d) Bahrain sand, 20 h at 1400°C [31]

Protection of TBC Surfaces

The delamination of EB-PVD coated TBCs caused by chemical attack has drawn the attention of the end-users of gas turbines. Recent research aimed at the prevention of penetration of molten surface deposits can be categorized into physical barrier sealing and lanthanide series oxide doped TBCs.

Physical barrier sealing is an additional outer layer coated, typically alumina, on top of the YSZ, which physically stops contaminant infiltration. To effectively prevent molten infiltration, a physical barrier sealant is deposited onto the YSZ. Alumina-zirconia and tantalum oxide based physical barrier sealing overlayed on the ceramic YSZ coatings were invented by Nagaraj et al. [32, 33]. For CMAS based deposits, both the alumina-zirconia and tantalum oxide outer layers combine with the CMAS deposits to raise the melting temperature of the CMAS and to increase the viscosity of the molten CMAS infiltrating the EB-PVD coated YSZ. Turbine components coated with a physical barrier sealant are less prone to infiltration at elevated temperature. Since the deposition of physical barrier sealing requires no modification to existing TBCs, it is commonly used in practice.

Lanthanide series oxide doped TBCs, invented by Darolia et al. [34], modify the chemistry of the YSZ and delay the infiltration through chemical reaction with the molten CMAS, forming a reaction zone. These modified TBCs have two layers of top coat material. The outer layer of the top coat is zirconium oxide and hafnium oxide doped with sufficient amount of a lanthanum series oxide, while the inner layer is conventional YSZ. A schematic diagram of this multi-layer TBC is shown in Figure 9. When the TBC coated gas turbine component is suffering from high temperature CMAS attack at temperatures above the melting point of CMAS, the molten CMAS reacts with the rare earth elements, forming a densified reaction zone which delays infiltration. According to the patent by Darolia et al. [34], the amount of lanthanum series oxides necessary to effectively resist CMAS infiltration varies with the degree of environmental attack. Figure 10 shows an SEM image of a contaminated outer layer and the formation of the reaction zone. Regions in the “reaction zone” reveal white needle-like structures that are the by-product of the reaction. The outer layer of this system is zirconium oxide and hafnium oxide doped with lanthanum series oxides and not only provides resistance to CMAS, but also serves the purpose of thermal insulation. Spallation does occur in some cases as stress builds up in the “reaction zone” and cracks begin to form. Upon spallation of the outer layer, the inner YSZ layer would still be intact, maintaining the thermal barrier.

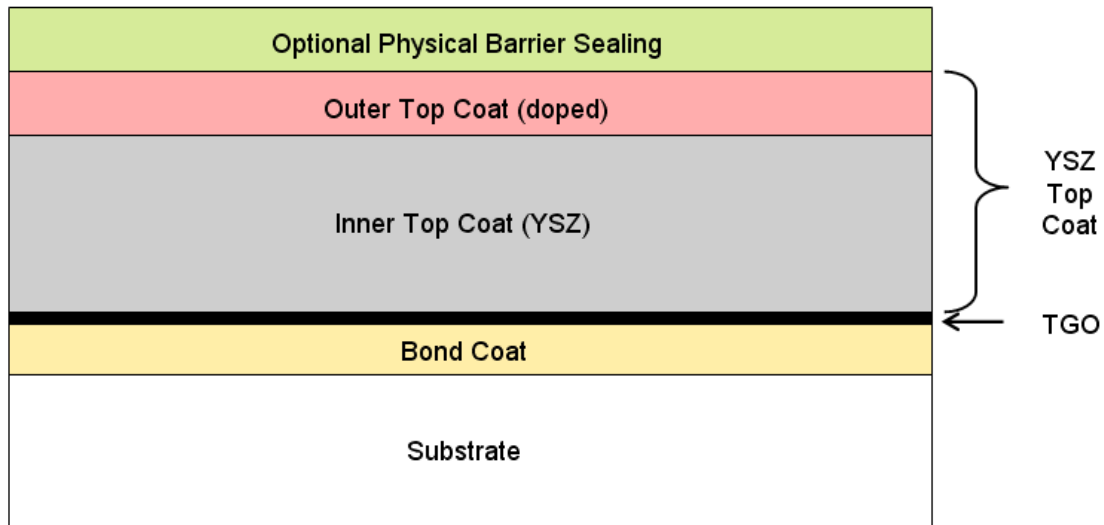


Figure 9 Schematic diagram of lanthanum series oxide doped TBC structure [34]

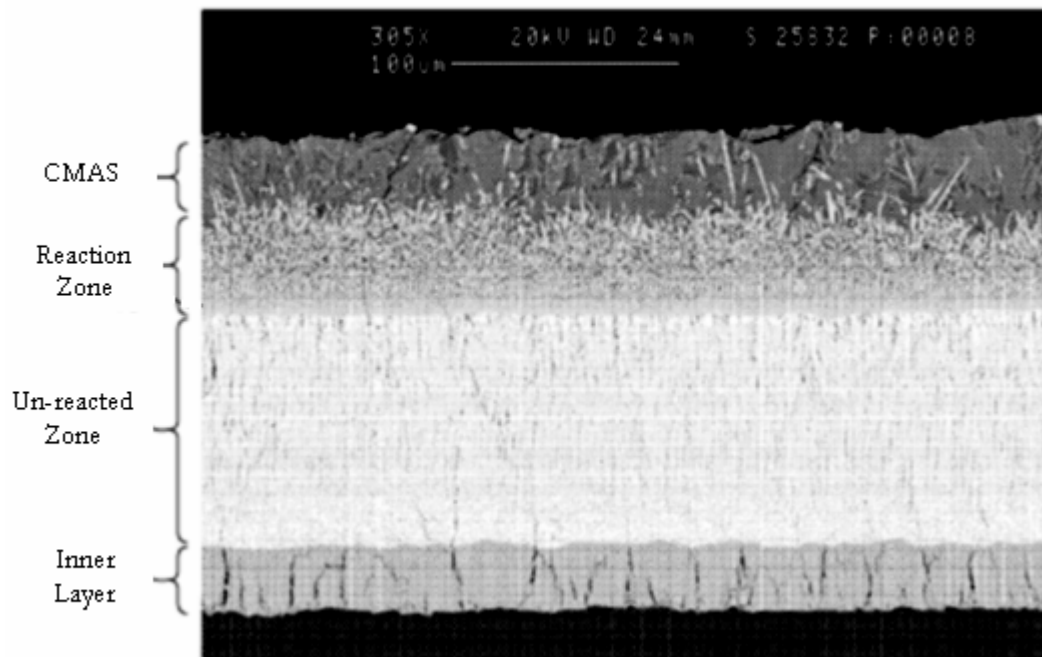


Figure 10 Cross-section of layered TBC exposed to CMAS at 1288 °C for an hour [34]

1.2.2. Foreign Object Damage

Foreign object damage (FOD) results from large particles ($>150\ \mu\text{m}$) impacting at low velocity or intermediate ($\sim 50\ \mu\text{m}$) and small ($>10\ \mu\text{m}$) particles striking at high velocity (up to 300 m/s [35]). In gas turbine applications, FOD-induced sudden spallation of the

YSZ top coat in TBC systems exposes the metallic bond coat to the hot gas environment. In rare extreme cases, even the bond coat can be removed, causing severe damage. Sources of FOD are typically sand particles and stones from external environment and metallic particles from internal wear. Cracking and plastic deformation are commonly observed in the case of FOD.

FOD Induced Cracking

When foreign objects strike the TBCs, the YSZ material near the surface is compressed, and the discrete columnar structures are destroyed. The compressive force generates circumferential cracks around a densification zone as shown in Figure 11. These cracks can elongate and cause delamination of the top coat [36]. These elongated cracks are known as “kink bands” and are often inclined at a 45° angle with respect to the TGO/YSZ interface. The amount of YSZ material removed during the impact of foreign object may not be significant to compromise the TBC system; however, the kink bands (45° cracks) often propagate toward the YSZ / TGO interface and can ultimately lead to spallation of a large area of YSZ. A noteworthy behaviour of kink bands is their relationship to temperature. Wellman et al. [37] discovered that formation of kink bands depends strongly on temperature; kink bands are frequently observed at higher temperatures and are less pronounced at lower temperatures. Figure 12 presents their experimental results showing the damage inflicted by FOD at four temperatures: 1200°C, 900°C, 800°C and room temperature. Kink bands and densification zones were clearly observed at 1200°C and 900°C, but not as clearly at 800°C and room temperature. It is suspected that ductility plays an important role in this behaviour suggesting that YSZ is more ductile at elevated temperature ($> 900^{\circ}\text{C}$) than at room temperature, avoiding the formation of the densification zone at high temperature. The results of these tests suggest that FOD could be a potential danger for YSZ delamination since most of TBC gas turbine components operate in excess of 900°C.

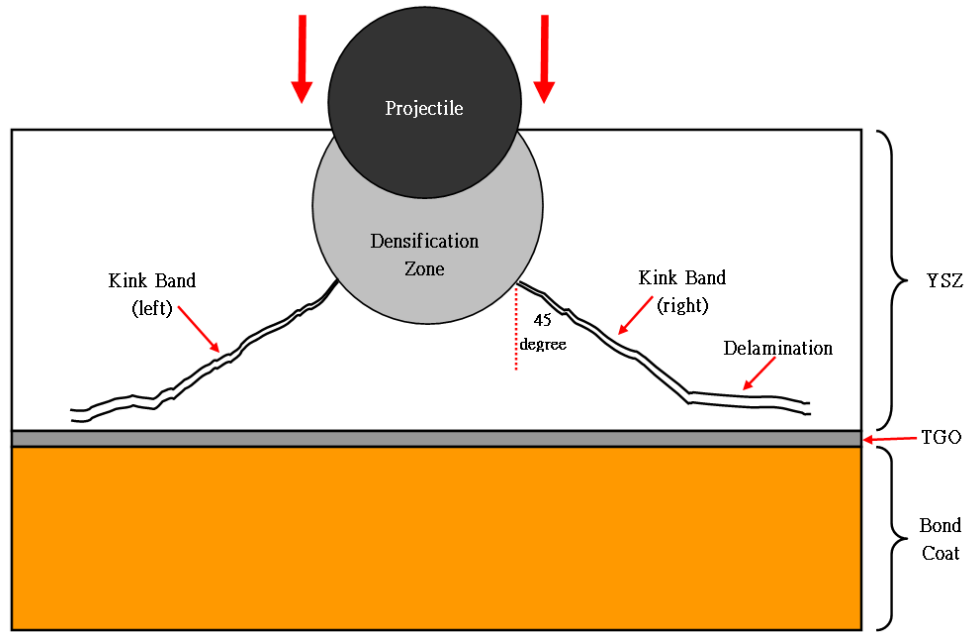


Figure 11 Schematic of various impact zones and cracking [36]

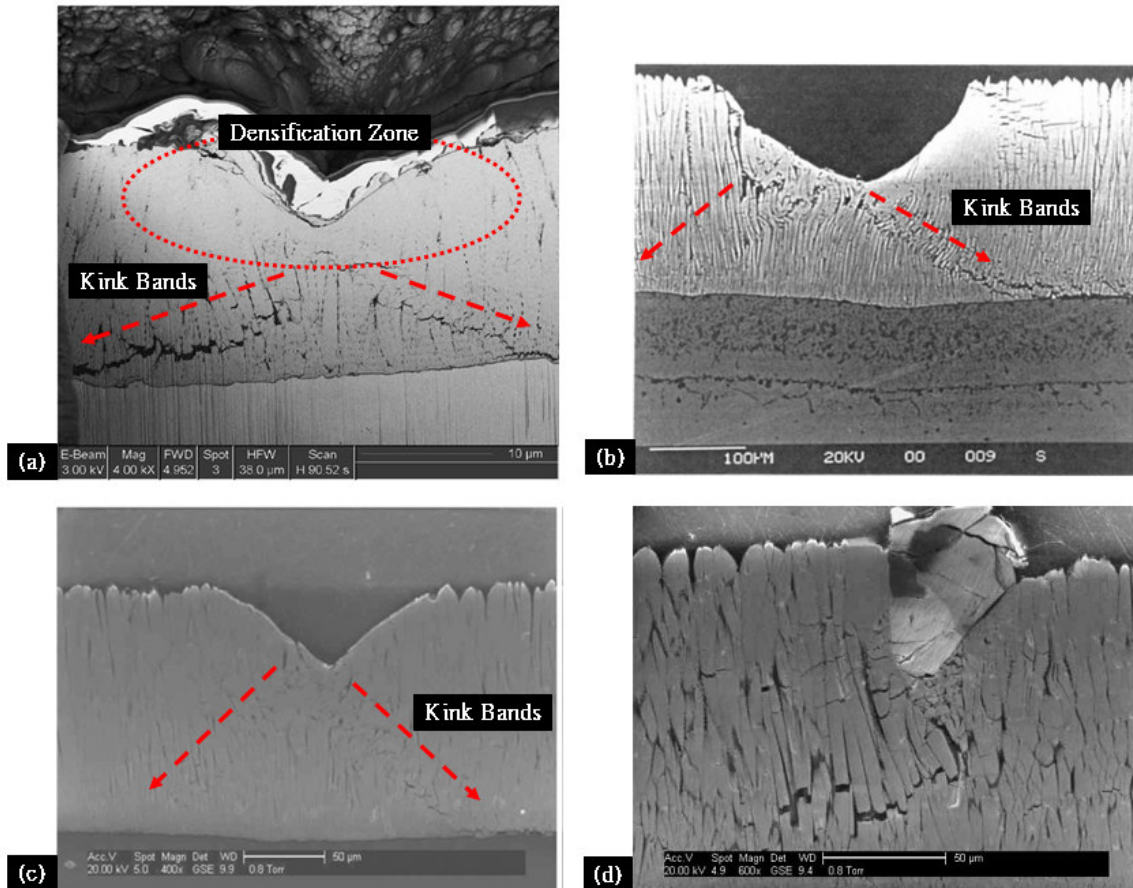


Figure 12 SEM micrographs comparing the effect of FOD at (a) 1200 °C [38, 39], (b) 900 °C [40], (c) 800 °C [38], and (d) room temperature [38]

FOD Induced Plastic Deformation

Plastic deformation of EB-PVD YSZ induced by FOD was recently observed and reported by Wellman et al. and Steenbakker et al. [38, 41]. From their research, it is suggested that TBC materials with rare earth doping exhibit rather different properties than the conventional YSZ due to compositional and process modifications. Their research observed plastic deformation of YSZ in a FOD stimulation of an EB-PVD TBC specimen in a simulated FOD environment between room temperature and 900°C. The deformed YSZ columns did not undergo any cracking and the extent of the densification zone was limited. The plastic deformation of the YSZ absorbed much of the impact energy such that the formation of kink bands and cracking were not present (Figure 13). In the FOD study by Steenbakker et al. [41], a 2 mol% Gd_2O_3 doped YSZ sample was tested in a simulated FOD environment at 800°C and the result was compared with other standard YSZ samples. The doped YSZ top coat exhibits much finer columns than the un-doped YSZ; however, these fine columns were prone to buckling as shown in Figure 14. As mentioned earlier, literature has reported that Gd_2O_3 doping increases resistance to CMAS infiltration as well as reducing the thermal conductivity of the YSZ; however, the doping also modified the predicted properties of the YSZ. Detailed studies on the FOD and erosion resistances of rare earth doped TBCs have not yet been reported and the plastic deformation of YSZ was only been observed in laboratory experiments.

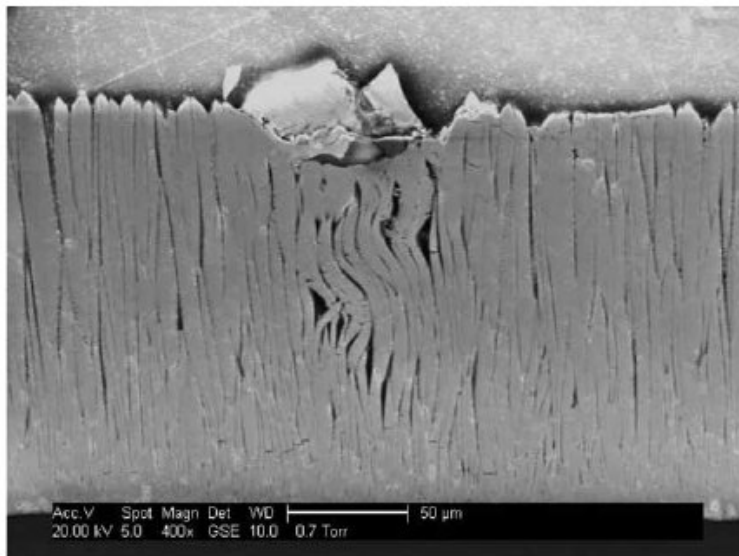


Figure 13 Plastically deformed YSZ material after impact by larger particle [38]

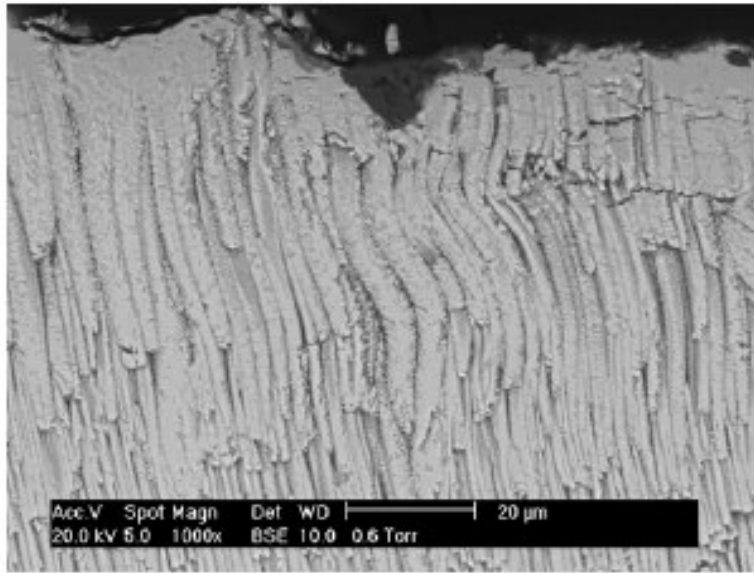


Figure 14 Buckling behaviour of 2 mol % Gd_2O_3 doped YSZ [41]

1.2.3. Erosion

Similar to FOD, erosion is another type of environmental attack that is more mechanical than chemical. In the case of erosion, the YSZ of the TBC system is gradually removed, causing localised temperature increases at the metal substrate. Several studies aimed at assessing the lifetime of TBCs have discovered that erosion is a major life-limiting factor in both land-based [42] and aerospace TBC coated turbine components [43, 44]. Factors affecting the erosion rate of TBCs are coating methods, particle sizes, particle velocity, and impact angle.

Erosion on PS and EB-PVD coated TBCs

Figure 15 and Figure 16 present SEM images comparing the microstructures of EB-PVD and PS coated TBCs [45]. The PS YSZ exhibits a ‘splat-like’ microstructure containing 10-15 % porosity and micro-cracks. Although these porosity and micro-cracks are benign in terms of accommodating thermal stress and reducing the thermal conductivity, voids and micro-cracks are detrimental to erosion. Nicholls et al. have conducted several key studies [45-47] on the erosion rate of bulk zirconia, PS zirconia, EV-PVD zirconia, and bond coats under the same test conditions. Their experimental results (Figure 17) indicate that EB-PVD YSZ performs 10 times better than PS YSZ in erosion tests carried

at both high temperature and room temperature. Bulk zirconia and bond coat materials are more resistant to erosion when there are no pre-existing internal cracks or voids that promote crack networking. Their findings are also in agreement with Tabakoff [48], who have conducted similar tests at 540°C.

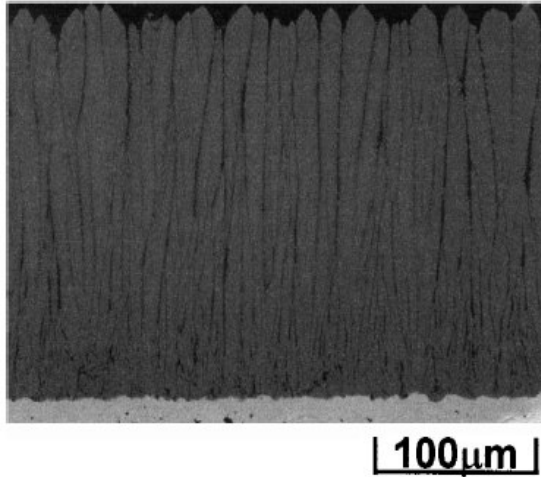


Figure 15 Columnar EB-PVD Coated TBCs [45]

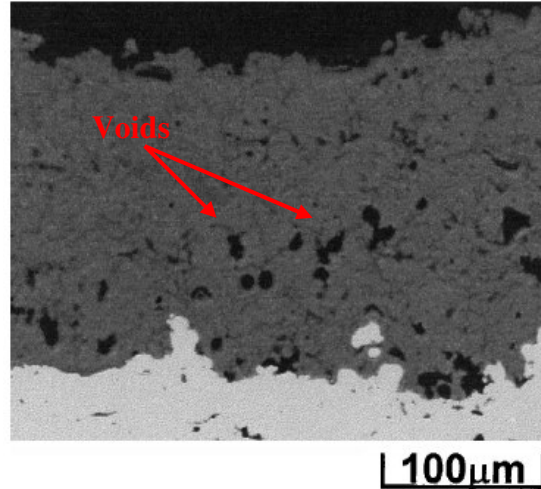


Figure 16 PS Coated TBCs with voids and cracks [45]

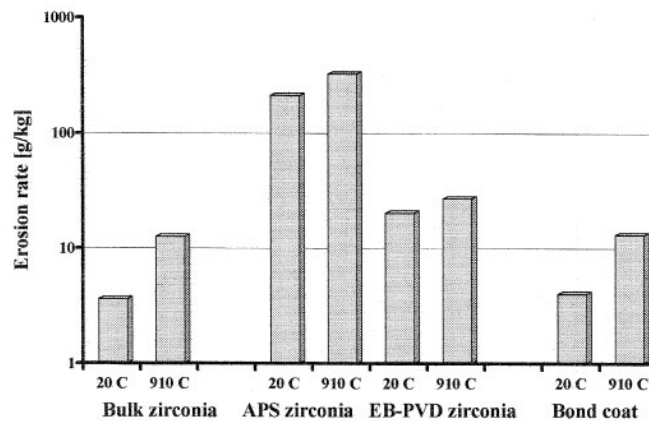


Figure 17 Erosion rate comparison chart between bulk zirconia, APS zirconia, EB-PVD zirconia, and bond coat materials [45]

Effect of Particulates on Erosion Rate

The rate of erosion of the YSZ varies with the impacting material, particulate size, and impact velocity. In Bruce's study on erosion and impact testing of TBCs [49], the effects of impact material, size of particulate, and mass of the particulates are discussed.

Literature reports that particulates as large as 2000 μm can be sucked into aircraft engines during landing and takeoff [50-52]. Once in the engines, particulates are chopped by the fans of the compressors and their sizes are reduced to the order of hundreds of microns or smaller [50-52]. The tests by Bruce fed alumina, silica, and zirconia particulates of various sizes into a burner rig combustor. According to the test results, alumina particulates result in the highest erosion rate whereas zirconia results in the lowest. Large particulates (180 μm alumina) do not contribute as much damage as 50 μm and 10 μm alumina particles since large particulates travel at slower velocities. In terms of the damage to the YSZ surface, striking with 10 μm particulates polishes the surface while striking with 50 μm particulates induces lateral cracks.

The effect of particulate velocity was studied by Nicholls et al. [46, 47, 53], Toriz et al. [54], and Tabakoff et al. [48]. These studies conclude that erosion rate increases with particulate velocity; the faster the air velocity, the more impact energy carried by each particle. Erosion tests with particulate velocities up to 300 m/s were conducted [53] and the results are shown in Figure 18. Both air plasma spray (APS) and EB-PVD TBC coated samples showed increases in erosion rates at higher impact velocity; however, the effect of test temperature was not taken into account in these experiments.

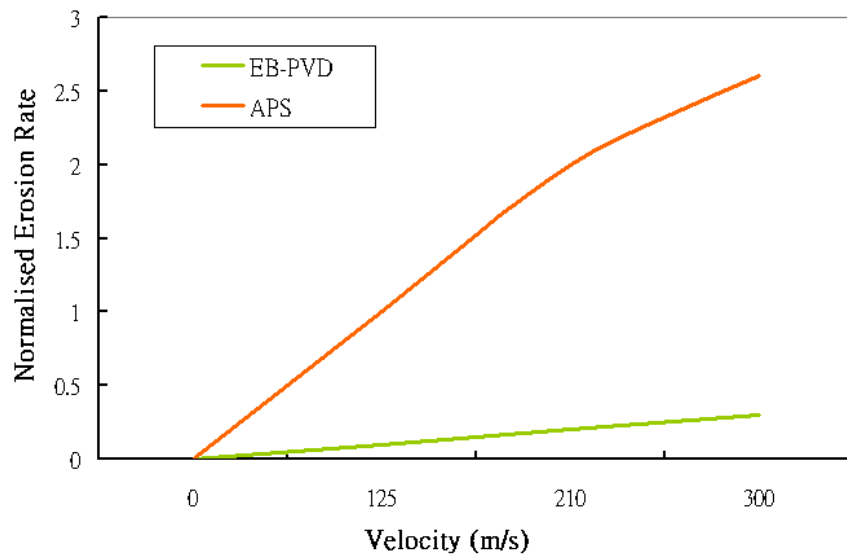


Figure 18 Erosion of EB-PVD and PS TBCs with respect to particulate velocities [53]

Effect of Impact Angle on Erosion Rate

Wellman et al. characterised the effect of impact angle on erosion rate and found that the rate of erosion is most severe at a 90° angle of impact (Figure 19) [38]. His experimental conclusion is also in agreement with others [22, 48, 55, 56]. However, most of these erosion studies were conducted at temperatures where the physical properties of the erodent do not affect the test results. Nicholls et al. conducted high temperature erosion testing at 910 °C using silica [45]. In this study, the high test temperature caused the silica particulates to become partially molten and softened. As a result, maximum rate of erosion did not peak at 90°; but instead, a 30° impact angle resulted in the highest erosion rate. It was suggested that at 90° impact angle, the partially molten silica heals the fractured TBCs reducing the crack propagation, whereas at 30° impact angle, the crack healing effect was least pronounced.

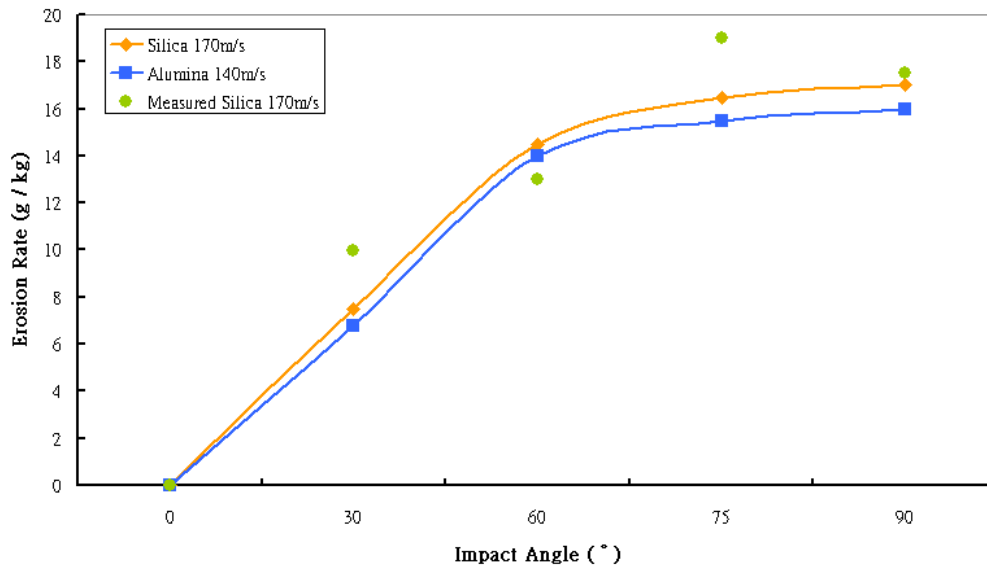


Figure 19 Erosion rate as a function of impact angle [38]

The goal of the research described in this thesis was to provide insight into the environmental degradation of coatings on turbine components. The approach was two-fold. In the first part, presented in Chapter 2, the discoloration on vanes from a commercial combined cycle generator was evaluated and attempts were made to correlate the in-service temperature profile in the blades by combining information obtained from

analysis of the discoloration with γ' size variations and the thickness of the thermally grown oxide.

The second part of the research, presented in Chapter 3, evaluated the erosion characteristics of several 2nd stage turbine blades service-retrieved from a PW4000 series to determine the potential cause of early TBC spallation. These studies provide insight into the nature of thermal barrier coating degradation in industrially relevant situations rather than laboratory control experiments.

2. Analysis of Surface Contamination

The author would like to state that a part of the work in this chapter was published in the International Symposium on Superalloys (11th: 2008: Champion, Pa.) and the published work is attached in Appendix A of this thesis.

A major aim of the project was to characterise the surface deposits on commercial combined gas cycle turbine vanes. The approaches to this characterisation required insight into the position of the blades in the turbine in order to assist in identification of the source of contamination. The following sections describe the approaches and results.

2.1. Background

Since the particular land-base CCGT has an advanced air filter system, the contaminants were mostly debris from internal sources such as compressor blades. Chemical deposits were most pronounced on the row one (R1) vanes which revealed various bands of color on the surface of the TBCs along the length of the vane. Three service-retrieved R1 nozzle guide vanes were examined. These vanes exhibited various levels of TBC surface discoloration. Additionally, there are notable differences from one vane to another suggesting that each vane had experienced a slightly different exposure to the deposit or a temperature or oxygen partial pressure (PO_2) profile whilst in service, as illustrated in Figure 20.

2.2. Experimental Procedures

A modern combined cycle gas turbine (CCGT) power plant reported heavy surface contamination on the TBC coated nozzle guide vanes and blades. Three ex-service row one (R1) vanes have been examined. The three R1 vanes were removed from a Siemens V94.3 gas turbine after ~ 14,000 equivalent operating hours. This particular turbine consists of silo combustors feeding into the R1 vanes with a turbine inlet temperature of ~1160 °C. Since the gas enters the R1 vanes in a swirl, some vanes experience hotter gas temperatures than others. The amount of discolouration on the vanes varies, and three vanes were selected showing marked differences in their surface discolouration. Dense black colour deposits were observed on the pressure side leading edge and trailing edge,

whereas red and brown deposits were present on other pressure side surfaces. Vane A, B, and C (Figure 20) were chosen to represent the variation of possible temperature profiles based on their geometric arrangement in-plane. In addition, in some cases the distribution and variation of these coloured deposits show marked differences along cooling channels on a single vane indicating that the deposit (or the deposition process) is strongly affected by temperature.

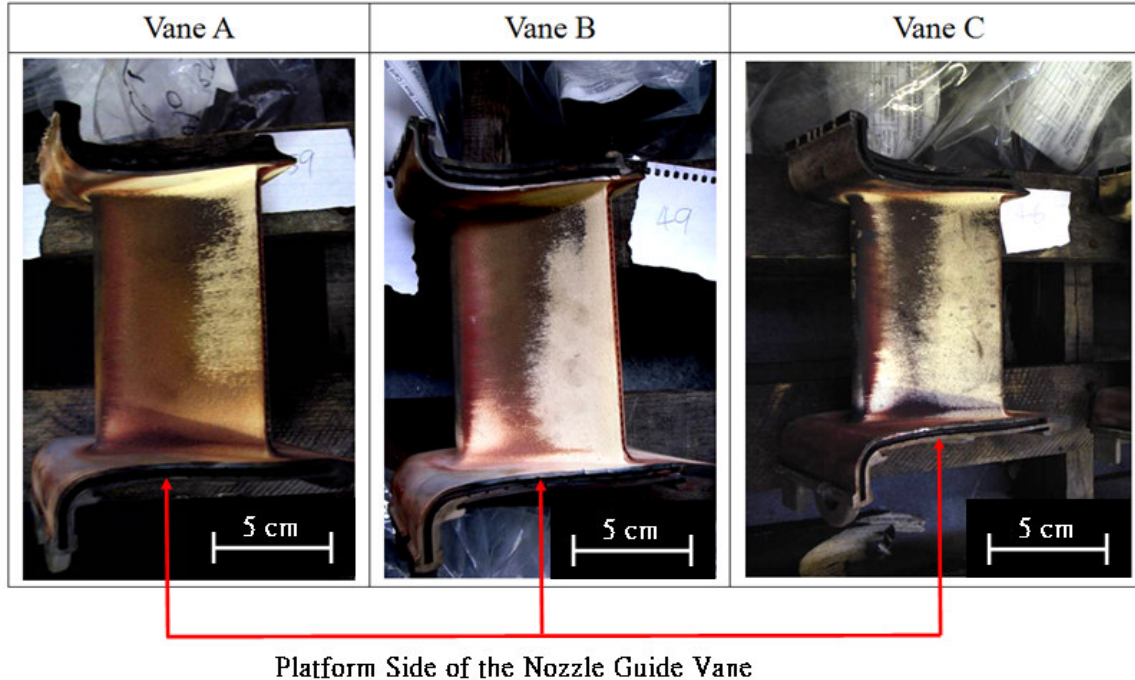


Figure 20 Images of Vane A, B, and C with the pressure sides facing upward

2.2.1. Sample Cutting and Preparation

Service-retrieved turbine components received from RWE nPower were sectioned using an industrial cut-off wheel at RWE Swindon's laboratory after initial visual observations. For the cutting, the vane was positioned using two C-clamps to prevent slipping as shown in Figure 21. The two platforms were the first to be sectioned. The body of the vane was then sectioned into 5 pieces approximately equal in length. Disassembled vane parts from Vane B are shown in Figure 22. Sectioned body pieces were brought back to Imperial College's laboratory for further sectioning. A Beuhler IsoMet 2000 Precision Saw with alumina blades was used for the finer sectioning jobs. Figure 23 shows the smaller sectioned pieces from Vane B after fine sectioning with the IsoMet 2000.

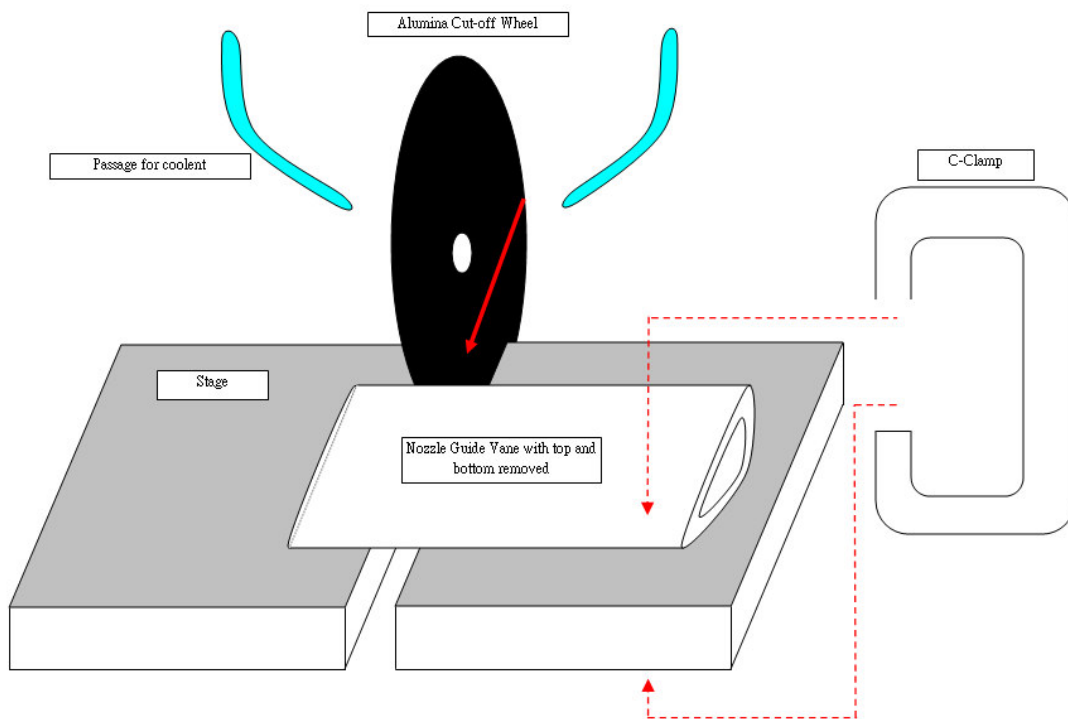


Figure 21 A schematic diagram describing the setup of a cut-off wheel using a C-clamp

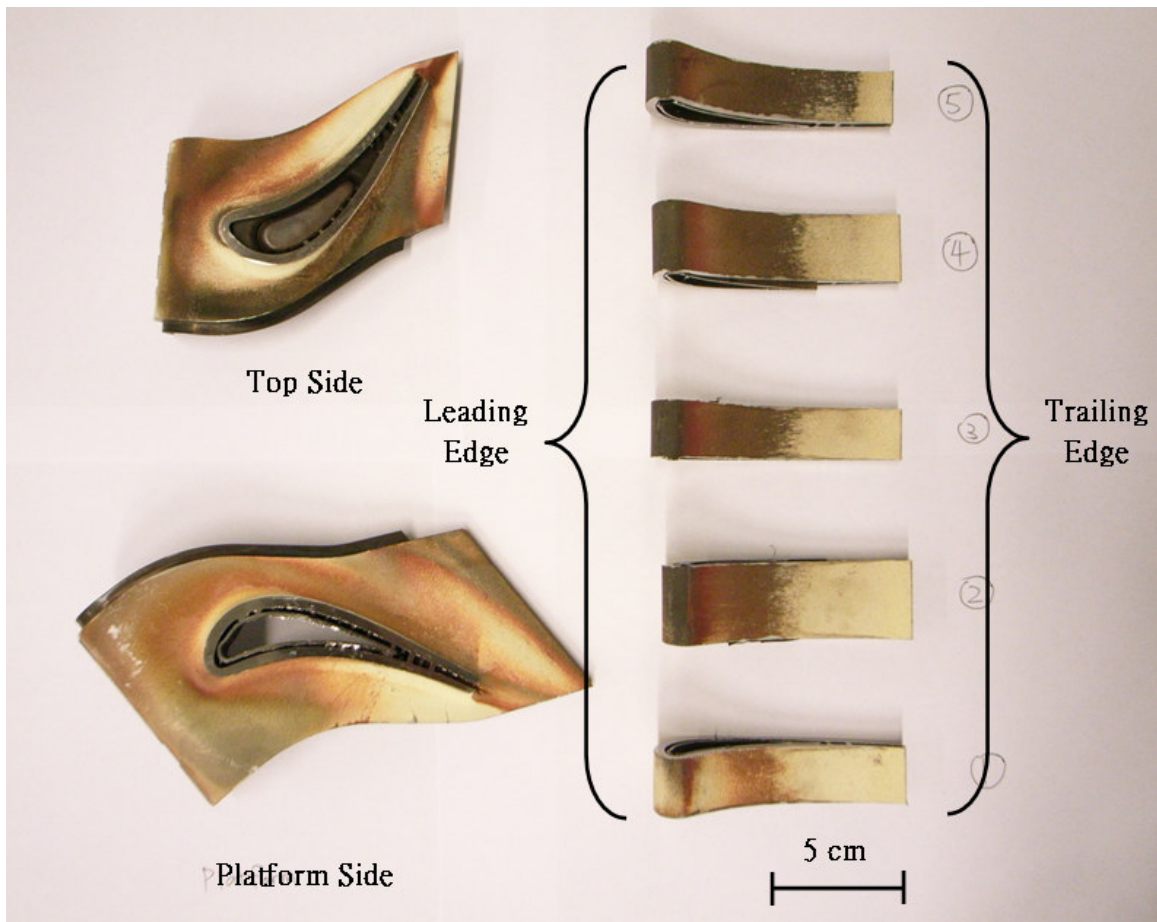


Figure 22 Blade pieces sectioned by the cut-off wheel

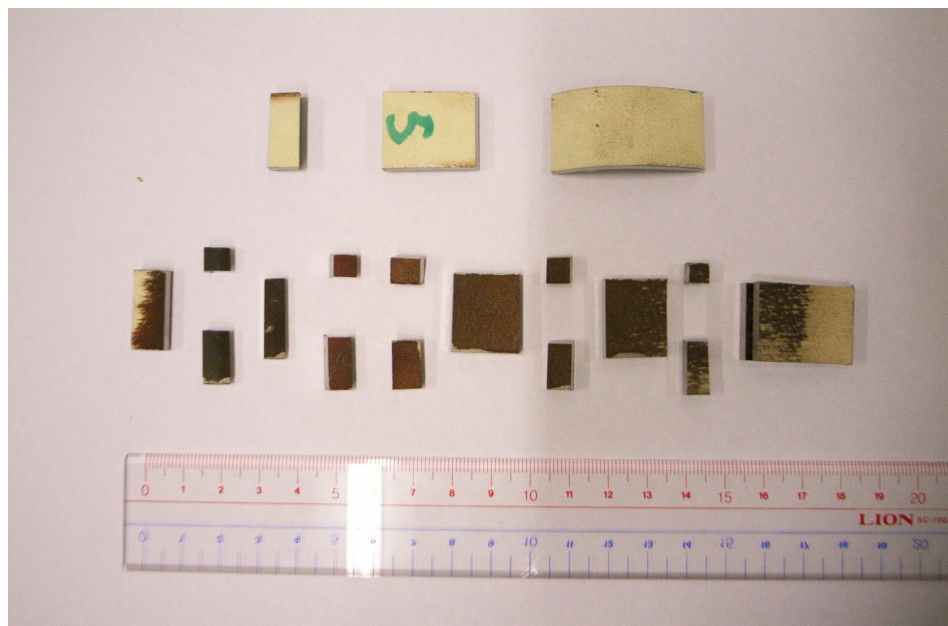


Figure 23 Smaller sectioned pieces by IsoMet 2000 Precision Saw

2.2.2. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDS)

In order to better understand the deposit chemistry and morphology, a range of analysis techniques were used. Surface and cross-sectional scanning electron microscopy (SEM) were conducted on five selected positions across the pressure side of the discoloured nozzle guide vane. Figure 24 illustrates position 1 to 5 on a sectioned body piece from Vane B. This particular specimen has 4 different colours of deposits across the pressure side: black (position 1 and 5), light brown (position 3), dark brown (position 2), and red (position 4). SEM examinations were performed using a field-emission-gun scanning electron microscope (FEGSEM; LEO Gemini). The in lens secondary electron mode was employed to reveal the surface morphology of these deposits. Images were generated with an accelerated voltage of 5 kV with a working distance of 7 mm. For cross-sectional images of the deposits, backscattered electron mode (BSE) was selected to show the atomic number contrast within the deposit layer. Oxford Instruments ISIS EDS was used to perform surface and cross-sectional mapping to determine the elemental composition and distribution within the deposits.

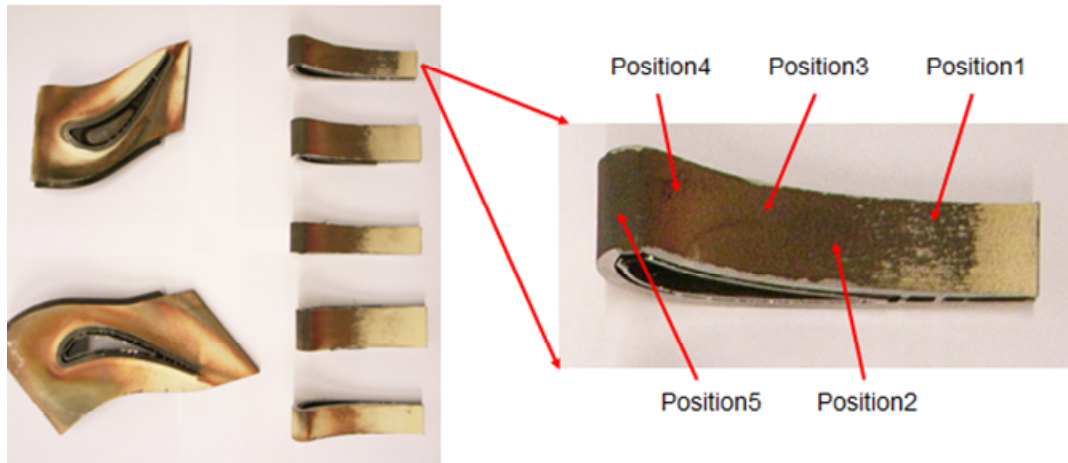


Figure 24 Areas selected for SEM examinations

2.2.3. X-Ray Diffraction

X-ray diffraction (XRD) was conducted on discoloured TBC surfaces using a Philips PW 1710 diffractometer with Ni filtered Cu K α radiation. The primary goal for conducting XRD is to identify the correct phases of the substances within the deposits, supported by

the chemical analysis given by EDX. Due to the curvature of the vane, specimens for XRD were cut down to the smallest possible size (approximately 5 mm x 5 mm size) in order to minimize the effect of curvature on the results. These XRD specimens were positioned using blue clay and levelled. Step size for the scan was set at 0.04° and a scan step time of 30 second per step size was set constant for every scan with an X-ray scanning angle set from 20° to 80° .

2.3. Results and Discussion

The results obtained from visual inspection, scanning electron microscopy / EDS and XRD provide complementary information. The results are presented and discussed, allowing the sources of contamination to be identified and mechanisms for deposition to be proposed.

2.3.1. Visual Inspection

Pressure side images of Vanes A, B, and C are shown in Figure 20. The TBC surface discoloration as observed by visual inspection varies dramatically between the vanes: Vane A had most of its surface covered (approx 75 % surface area) by the deposit, Vane B 50% and Vane C had the least (approx 35 %). The discoloured areas reveal dark / light brown, red and black deposits on all three vanes. Dark / light brown deposits tend to cover most of the area on the pressure side. Red deposits can only be seen near the pressure side leading edge. Lastly, black deposits are observed on both the pressure side leading edge and trailing edge. By looking vertically, fewer deposits appear to be accumulated near the platform side. Vane C, which reveals the highest ratio of black deposit, has TBC coating spallation observed at its pressure side leading edge, as shown in Figure 25.

The vane platforms were also examined and have a notable discoloration pattern. One of the most interesting observations is that the distribution of red deposits tends to align with the path of cooling air from the trailing edge as shown in Figure 26. Unlike the hot gas exits from the combustor, this internal cooling air contains much higher oxygen content (close to atmospheric PO_2).



Figure 25 Spallation of Vane C on the pressure side leading edge

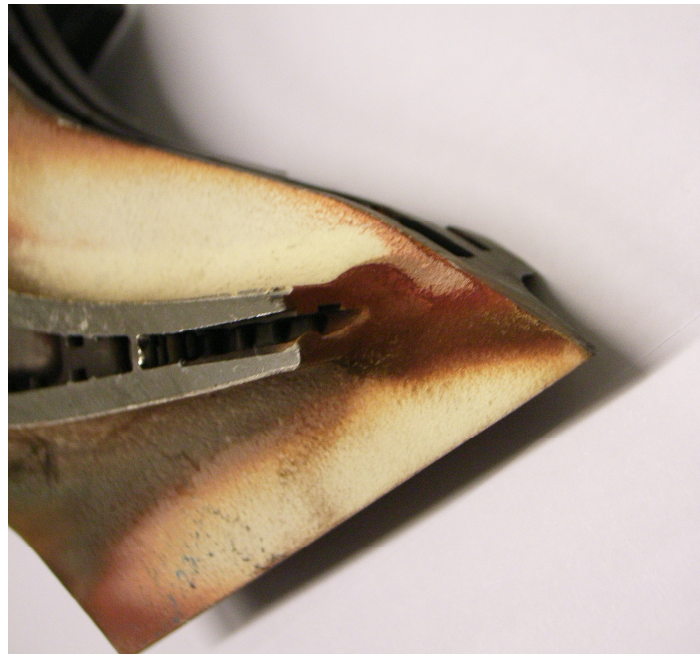


Figure 26 Red deposit near the cooling duct

2.3.2. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDS)

Surface Analysis

Surface SEM imaging on the deposit has revealed several surface morphologies. The most commonly observed surface structures were granular and flagstone-like plates (Figure 27 and Figure 28). The size of the granular particles was relatively uniform, ranging from 2 to 4 μm . The flagstone-like plates, on the other hand, had much more variation in size with typical plate sizes ranging from 3 to 10 μm . For the larger plates, a horizontal ridged surface was also observed. Consolidated regions (Figure 29) and needle-like structures (Figure 30) were also observed; however, these microstructural features occupied only a minor fraction of the total surface area analyzed.

In general, regions with brighter surface deposits (light brown, bright red) tend to have uniform granular microstructures. Regions with darker surface deposits (dark brown, black) reveal flagstone-like plates. The black deposits, in particular, have almost the complete surface dominated by large plates, whereas dark brown deposits have mixtures of granular and plate surfaces.

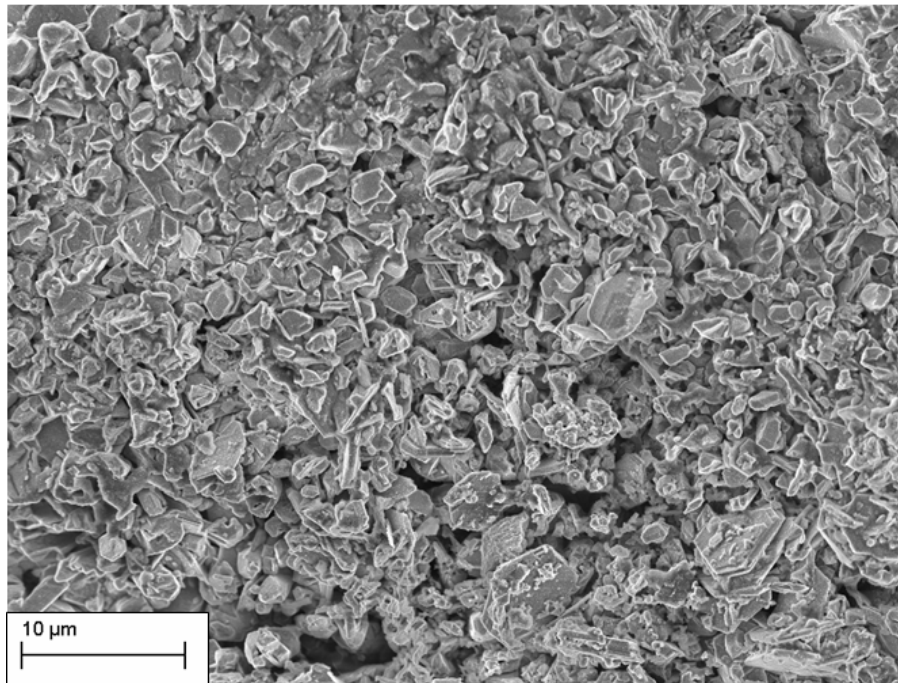


Figure 27 Granular structures on the commonly observed on the lighter colour deposit surface on the pressure side; SE image

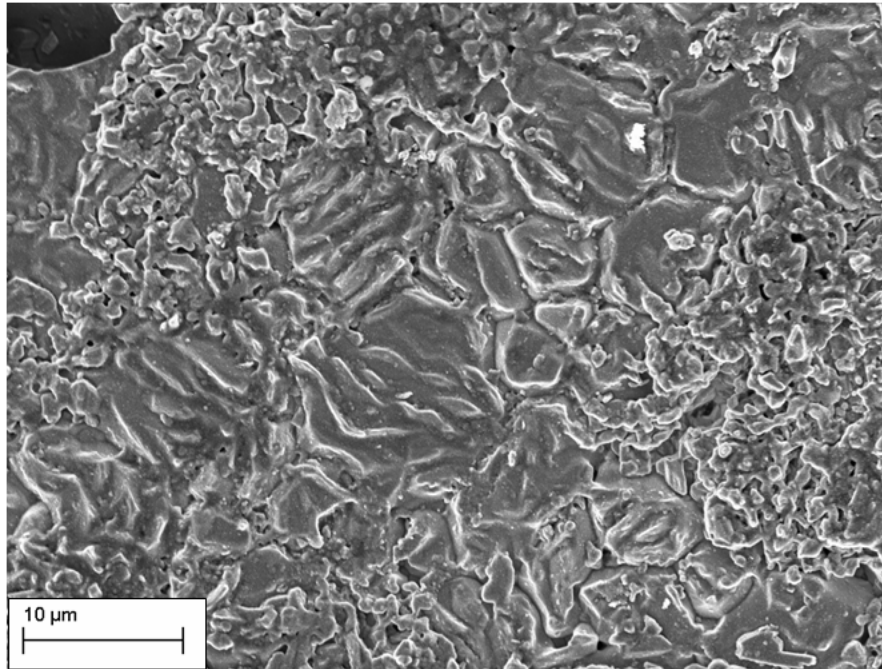


Figure 28 Flagstone-like plates commonly observed on darker deposit surface SE image

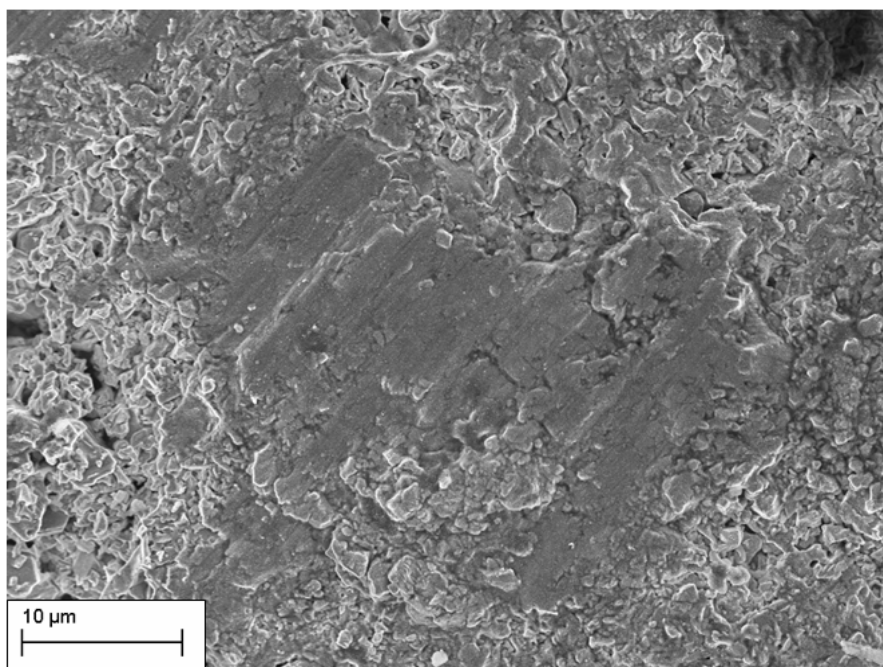


Figure 29 Large area of consolidated region on top of granular layer: SE image

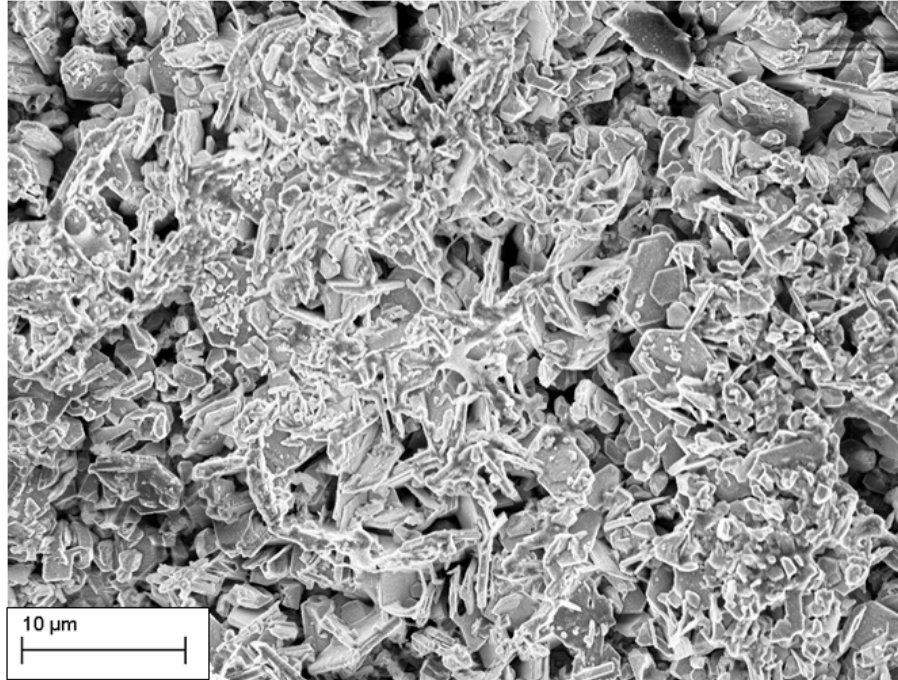


Figure 30 Needle-like structure surface observed in lighter colour deposits: SE image

As for chemical composition, surface EDS mappings have detected iron with traces of calcium (~5 atomic %), magnesium (~1 atomic %), aluminium (~5 atomic %), and silicon (~1 atomic %). The calcium, magnesium, aluminium, and silicon sources are primarily sand and dust particles which pass through the filter system from outside. It was first suspected that these elements form the CMAS (calcium-magnesium-alumino-silicate), which is commonly reported in aerospace and most land-based gas turbine applications [2, 3]; however, the EDS results from Figure 31 and Figure 32 do not provide enough evidence for this assumption due to the trace amounts of Mg and Si. This particular CCGT avoids environmental attack by CMAS through the use of efficient air filters which block most external impurities.

Figure 31 shows the EDS mapping of a granular surface from a light brown coloured surface. Results indicate the presence of calcium, magnesium, aluminium, and silicon in combination with much larger iron signals. On the other hand, mappings of the black deposits covered by flagstone surface structure are shown in Figure 32. Figure 32 reveals high intensity of iron as well as some calcium and aluminium contents. The calcium, and

aluminium contents observed from Figure 32 are corresponding to the gaps and openings between the flagstone-like plates.

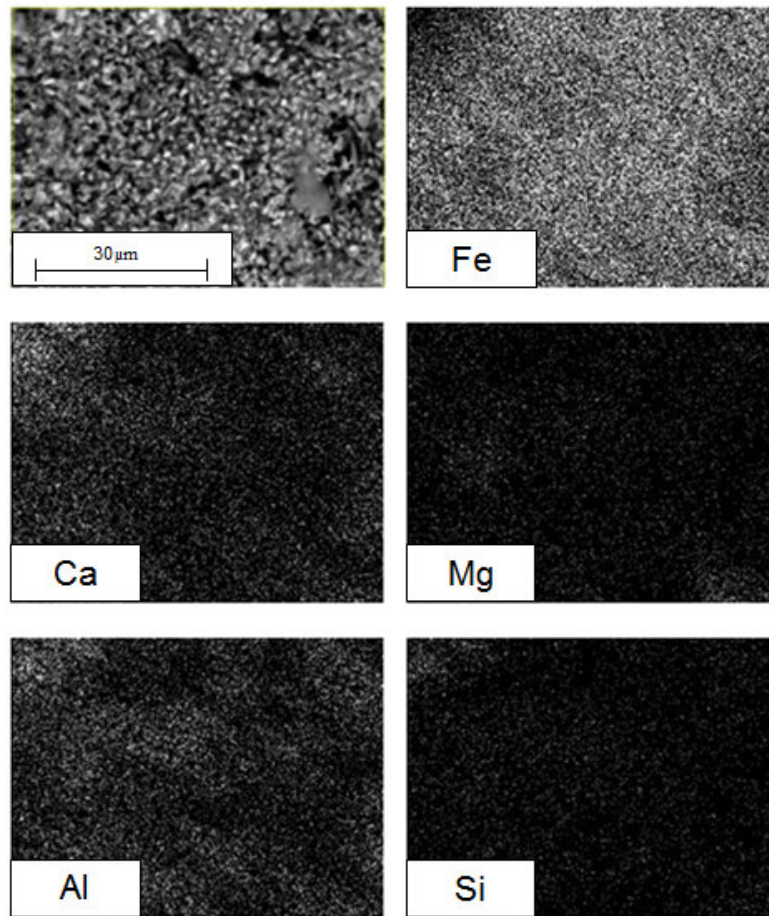


Figure 31 EDS Mapping on granular surface reveals the chemical composition and distribution of Fe, Ca, Mg, Al, and Si, the top left presents an SE image of the mapped area

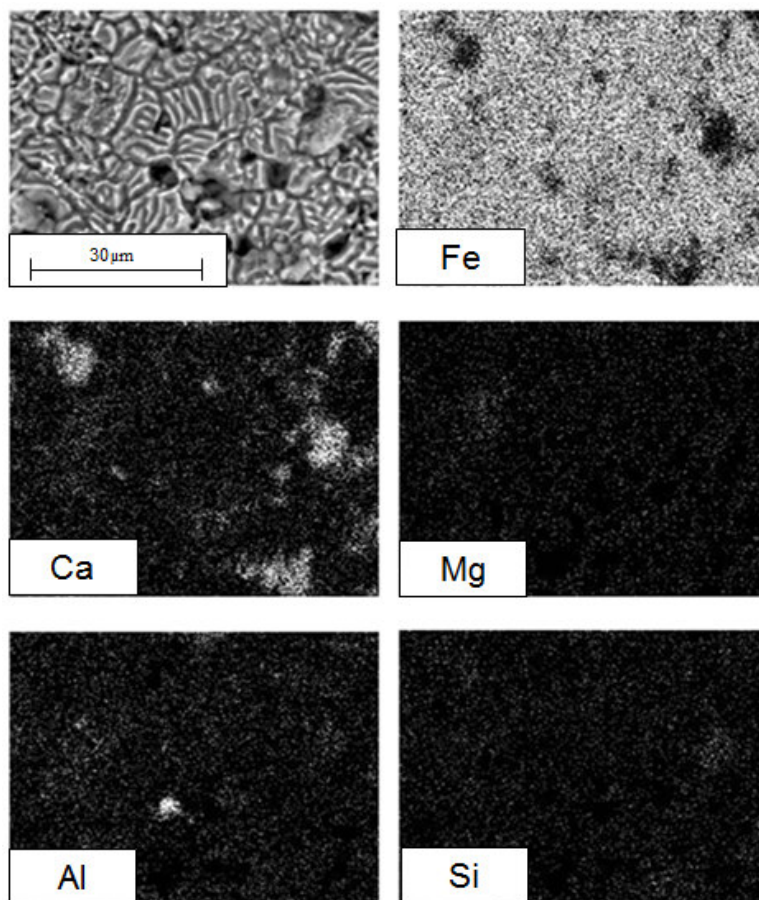


Figure 32 EDS Mapping on Flagstone plate surface reveals mostly iron on the surface, the top left presents an SE image of the mapped area

Cross-sectional SEM Analyses:

Cross-sectional analyses have been conducted on the various deposits. Figure 33 and Figure 34 show areas with light brown and red deposits, respectively. A large number of voids (the black contrast within the deposit layer) were observed within these deposits. The back scattered electron mode (BSE) images also revealed multiple phases within the deposit layer. A dense, darkly imaging layer exists at the most outer layer of the deposit (indicated by the red arrows), follow by another layer of bulk lighter contrast phase (indicated by green arrows). This outer layer is not uniform in thickness and contains granular or needle-like structures. This is consistent with observations from the surface using SE imaging that granular structure dominates the surfaces of lighter colour deposits (light brown and red). These cross-sectional images revealed that the granular layer is only a thin layer on the surface while a compact layer lies underneath. The granular layer

shows lower BSE - contrast, indicating the presence of low atomic number elements. At this stage, the structure of the inner layer is still unknown as the surface SEM could only reveal the outer layer, but the layer will contain elements of higher atomic number than the outermost layer.

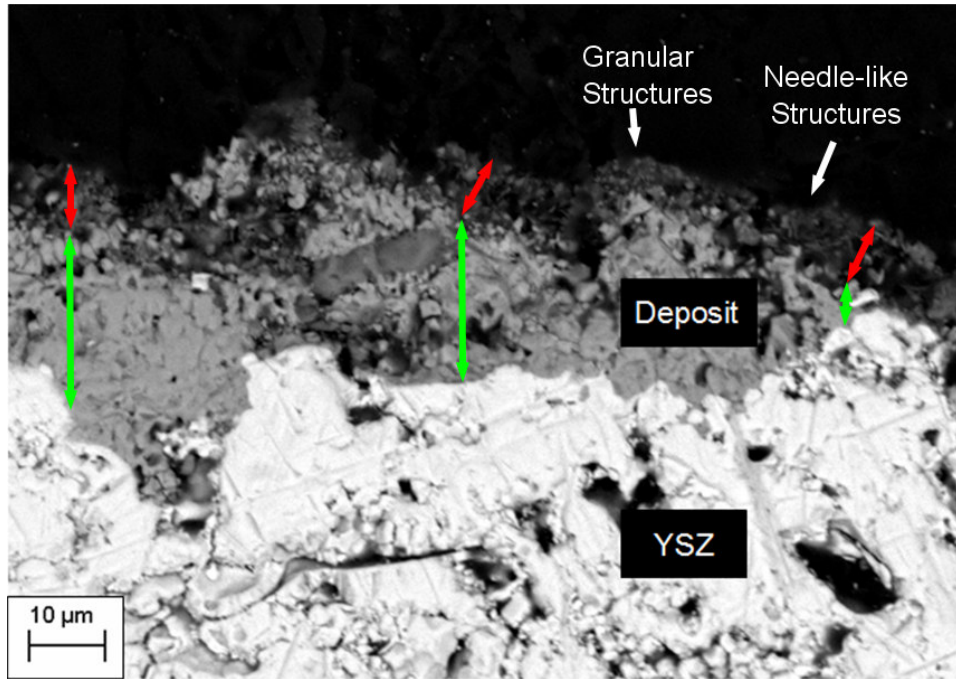


Figure 33 Cross-sectional SEM of light brown deposit; BSE image

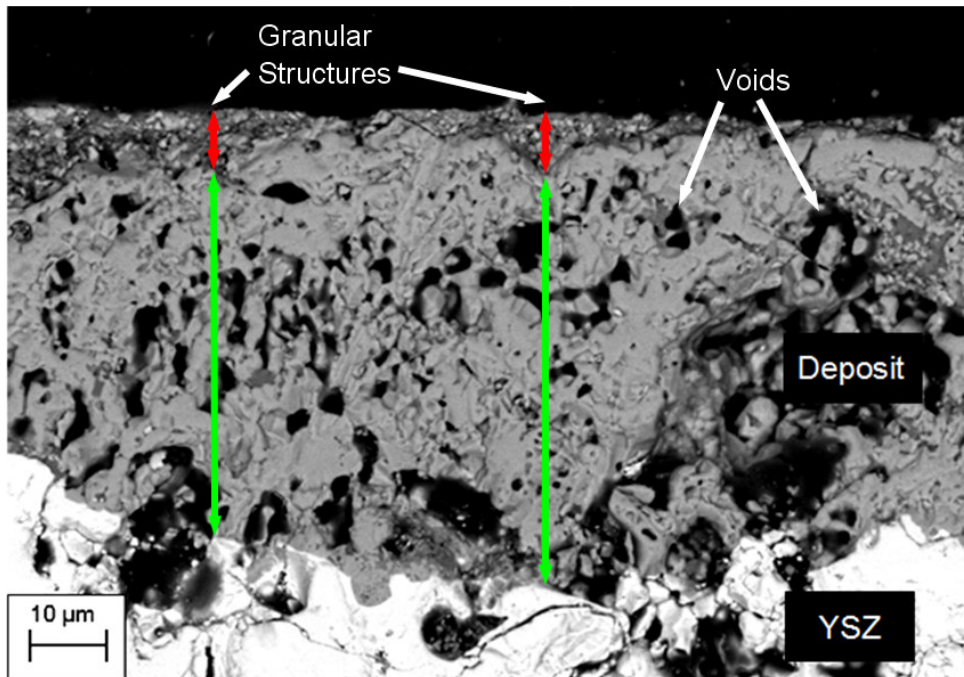


Figure 34 Cross-sectional SEM of red deposit; BSE image

Figure 35 and Figure 36 are cross-section SEM images of the black and dark brown deposits (darker colours) from Vane B. These darker colour deposits are more consolidated with lower fractions of porosity as well as thicker than the lighter colour deposits (more accumulation of deposits). Most of the observed porosities are larger than that observed in the red and light brown deposits. This suggests a sintering effect may have taken place in the darker deposits during the CCGT operation. It is suspected that small porosities were initially present during the accumulation of the deposit, and as the accumulation continues, these small porosities agglomerate into larger voids. Multiple layers in the deposit are also identified from the images below; a dense layer present at or near the surface as indicated in the Figures with a lighter contrast layer occupying the rest of the deposit thickness. From these cross-sectional SEM images of the deposit, it can be seen that the high density phase often exists in a form of narrow layer parallel to the surface. Recalling from surface SEM analysis on these sites, the surfaces of these deposits are mostly covered by flag-stone like plate structures with a minor fraction of granular structure below the plate structures. EDS mapping of the surface (Figure 32) reveals calcium and aluminium signals from the regions beneath the plates.

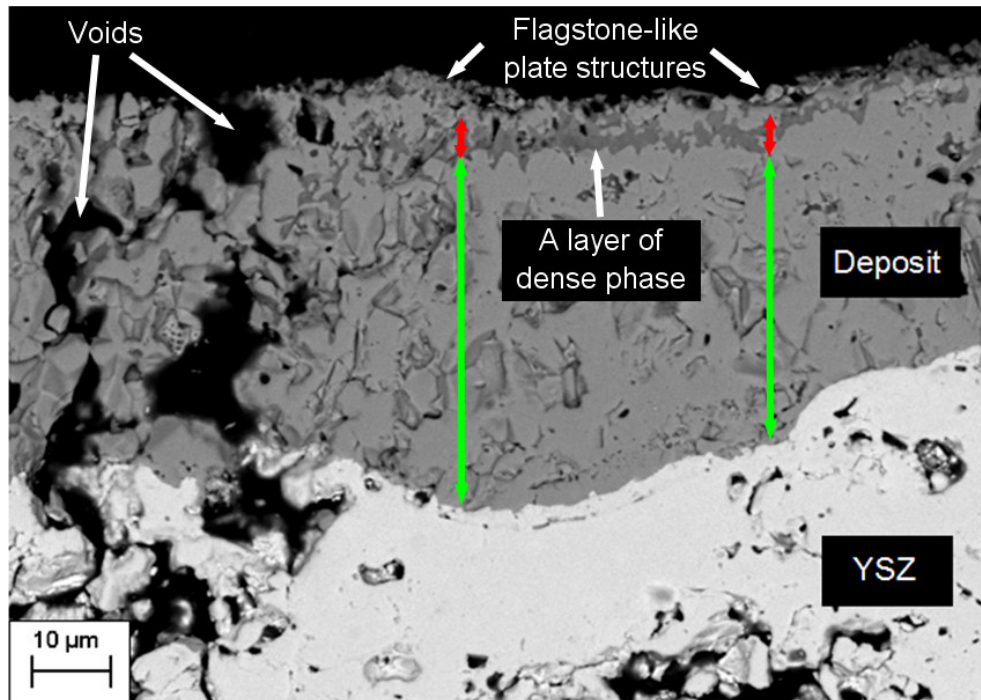


Figure 35 Cross-sectional SEM of black deposit revealing a dense layer near the surface: BSE image

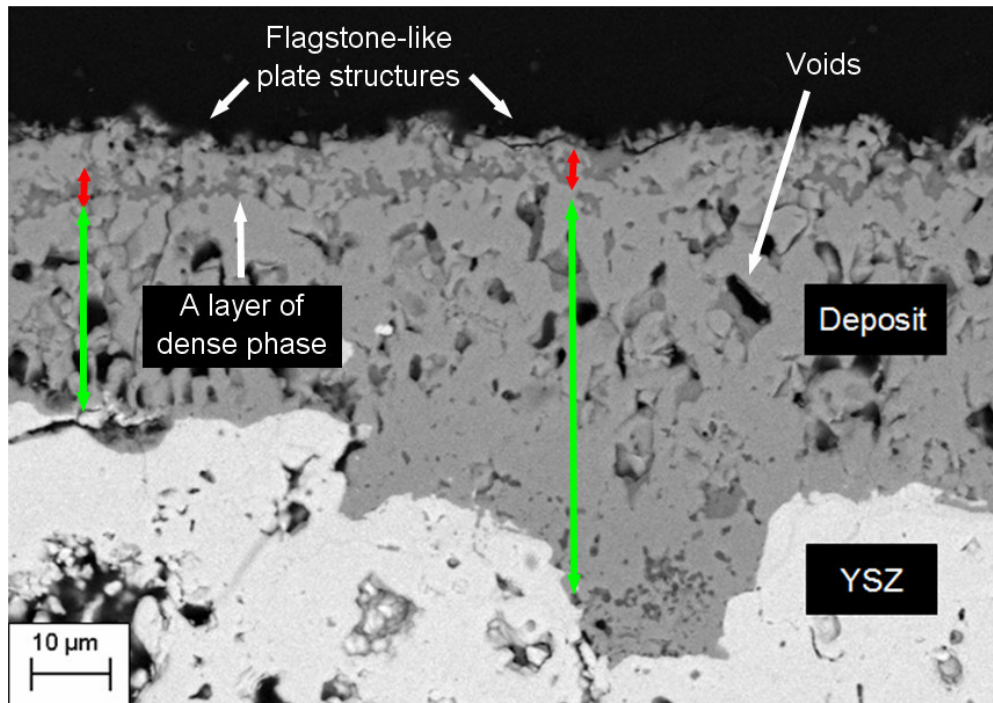


Figure 36 Cross-sectional SEM of dark brown deposit revealing a dense layer near the surface: BSE image

Additionally, the extent of formation of the thermally grown oxide (TGO) can also be observed from the cross-sectional SEM images. In the BSE images presented below (Figure 37 and Figure 38), the TGO is the dense layer that grows between the YSZ and bond coat. The morphology of the TGO can vary substantially; they can be thin uniform layers (approximately 1 to 10 μm). However, in other cases, the TGOs can be very rough and irregular, making it difficult to measure the thickness. The thickness of the TGO layer under the black deposit surface (Figure 39) is considerably thicker than that of light brown deposit site (Figure 40). The growth rate of the TGO between a TBC and a MCrAlY bond coat depends upon temperature [8, 9]. Formation of the TGO therefore provides evidence about the relative temperature experienced at these two sites, *i.e.* these data imply that the black deposit covered area had experienced a relatively higher temperature than the region with light brown deposit. Further analytical work will be performed to quantify this.

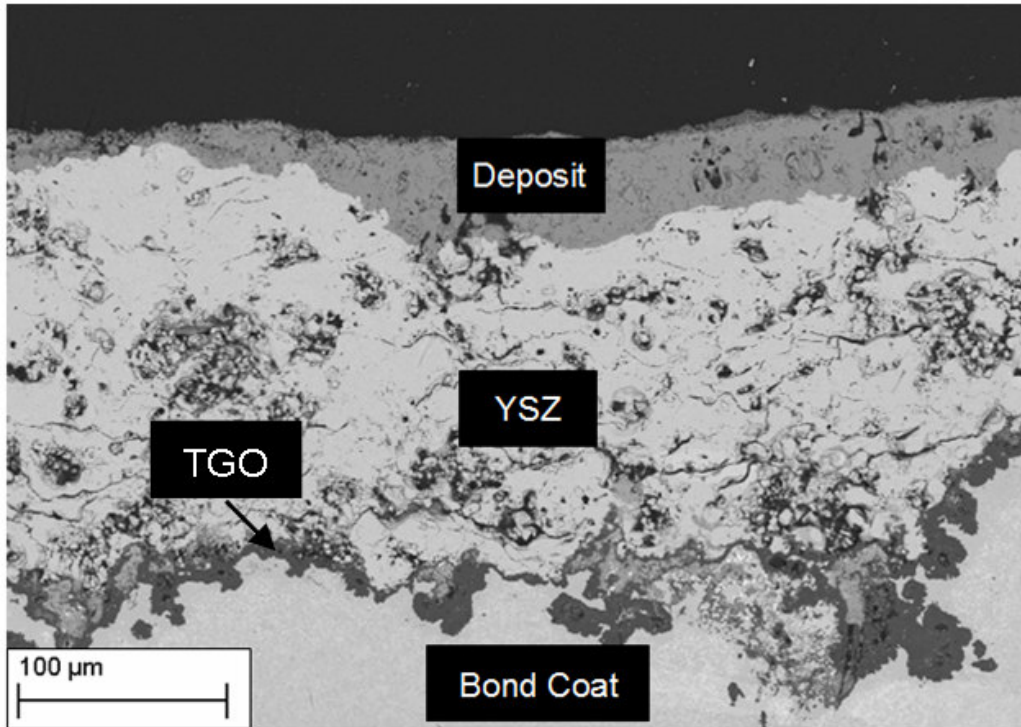


Figure 39 Cross-section SEM image of black deposit, revealing a thick and irregular TGO layer in between the YSZ and bond coat

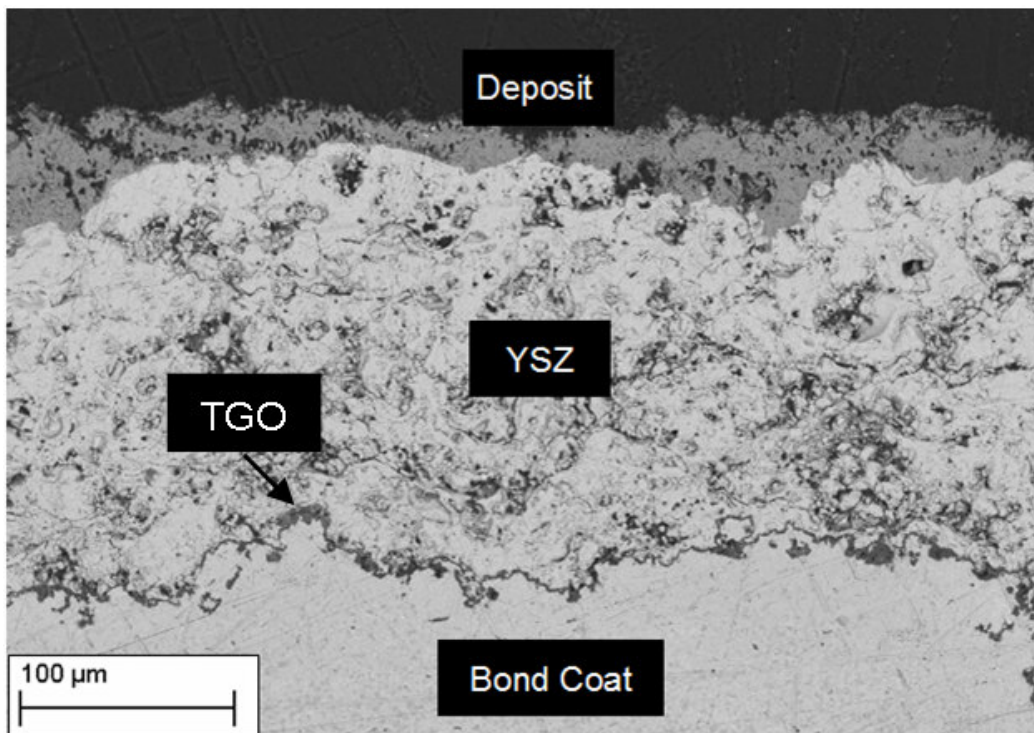


Figure 40 Cross-section SEM image of light brown deposit, revealing a thin and relatively uniform TGO layer in between the YSZ and bond coat

Cross-sectional EDS analysis examined the chemical composition and distribution of the contamination deposit. EDS mapping again reveals high iron content (~ 30 at%) with a minor trace of calcium (~ 2 at%) and aluminium (~ 5 at%). Figure 41 shows the EDS mapping of a light brown deposit site. Calcium and aluminium were observed near the surface and the deposit / YSZ interface, whereas the bulk of the deposit is primarily iron oxides. The calcium and aluminium appear to be inhomogeneous, suggesting the existence of two different compounds. For comparison, an EDS map of a dark brown deposit is shown in Figure 42. Minor calcium and aluminium signals were again detected from these dense regions. In the study of other environmental degradation, yttria extraction was reported. Stott et al have shown that in the case of CMAS attack, yttria content could be reduced in the YSZ top coat [17, 23, 31]. However, for these particular iron oxide deposits, EDS mapping reveals no sign of yttria extraction within the sensitivity of the measurements.

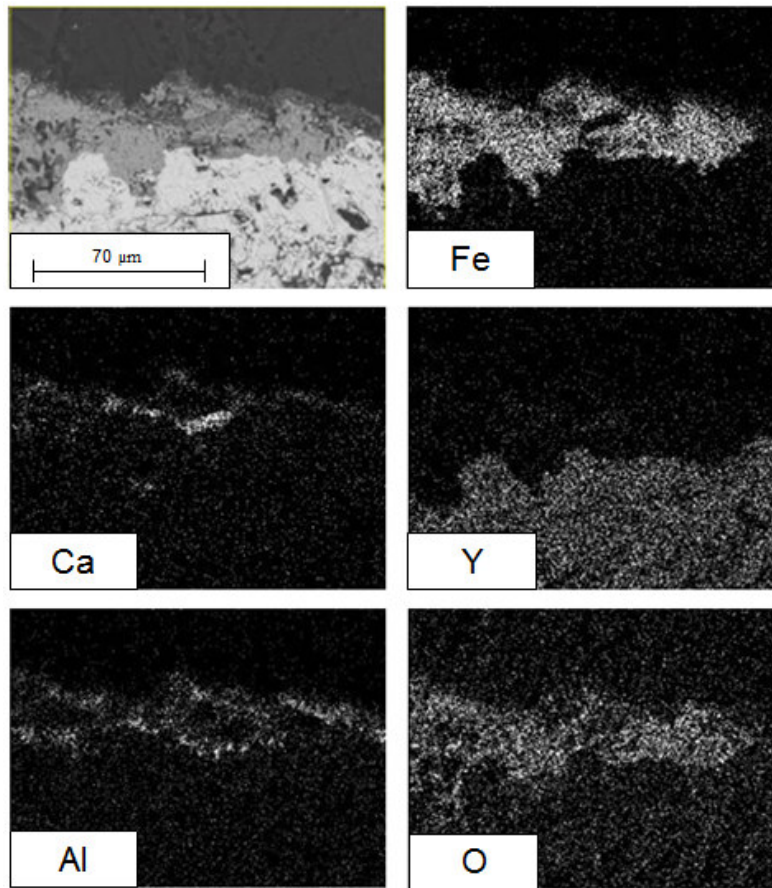


Figure 41 EDS mapping on the cross-section of light brown colour deposit site

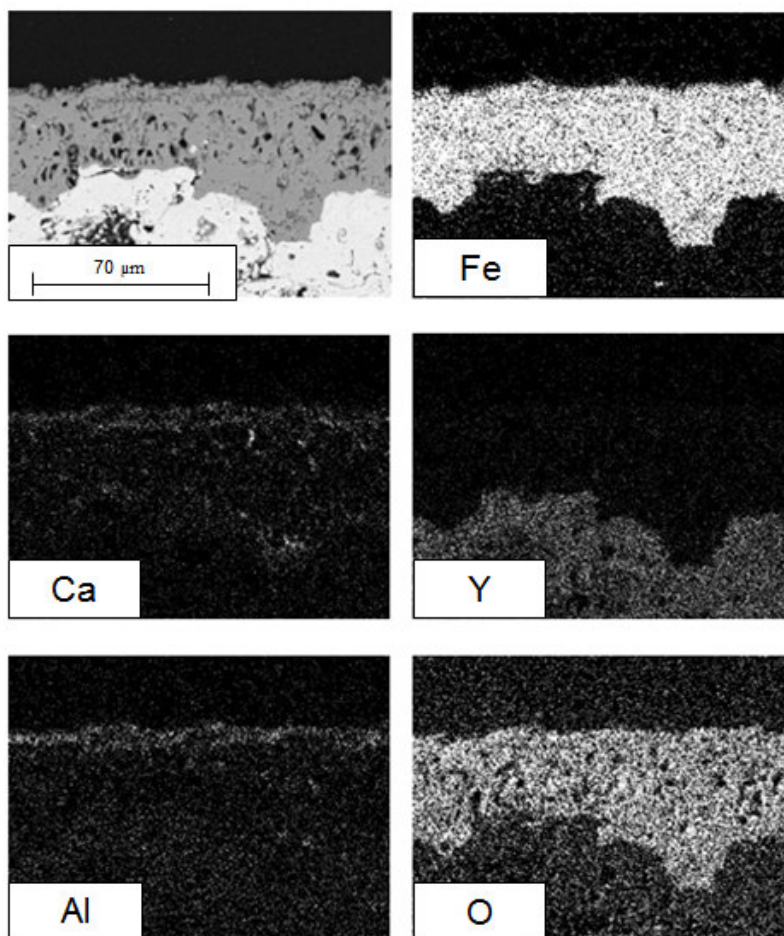


Figure 42 EDS mapping on the cross-section of dark brown colour deposit site

2.3.3. X-Ray Diffraction (XRD)

Identifying the contaminants on the surface of the TBCs has been one of the major objectives of this study and while EDS analysis has indicated the elements present, further characterisation is required to identify the phases. XRD analyses were performed on material from five discoloured sites of the EB-PVD coated vane piece. According to the cross-sectional EDS, multiple oxide phases were suspected. Sites chosen were based on the 5 different colours on the vane piece: green, black, brown, and red, and individual XRD diffractograms are illustrated in Figure 43 to Figure 47. Since the deposits layers are generally thick (greater than 30 μm in most surfaces), the XRD could only reveal the phases near the surface. A mixture of hematite (Fe_2O_3) and magnetite (Fe_3O_4) phases have been identified as the major contaminants for each deposit. Phases identified in

each specimen are summarized in Table 4. Identified minority phases include yttrium zirconium oxide ($\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$), alumina (corundum, Al_2O_3), and nickel cobalt oxide (NiCo_2O_4) as well as the majority hematite (Fe_2O_3) and magnetite (Fe_3O_4). The yttrium zirconium oxide and alumina were probably introduced as contaminants in powder collection step for the analysis from the TBC

The iron oxide previously identified by EDS has been identified as hematite and magnetite and accounts for the red, brown, and blackish discolouration [57]. Magnetite is present for all discoloured surface deposits; however, hematite was only observed for red and black deposits. Reddish discolouration was mostly observed near the pressure side trailing edge and some near the leading edge. Blackish deposits were observed only at the pressure side leading edge. The brownish deposits observed at the centre of pressure side contain only magnetite. Nickel cobalt oxide is only detected in the greenish deposit and is responsible for their colour. The greenish discoloured site was only found at the TBC spallation site where the nickel superalloy substrate was exposed. The exposed metal surface was unable to sustain the high temperature and nickel oxide was deposited in the nearby regions (refer to the green deposit). Lastly, regions with no discoloration (white surface) showed no sign of any contaminants and were consistent with the TBC material.

Table 4 Summary of XRD Results

Surface Colour	Oxide Phases Identified
Green	$\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$, Al_2O_3 , NiCo_2O_4 , and Fe_3O_4
Black	$\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$, Al_2O_3 , Fe_2O_3 , and Fe_3O_4
Brown	$\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$, Al_2O_3 , and Fe_3O_4
Red	$\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$, Al_2O_3 , Fe_2O_3 , and Fe_3O_4
White	$\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$, and Al_2O_3

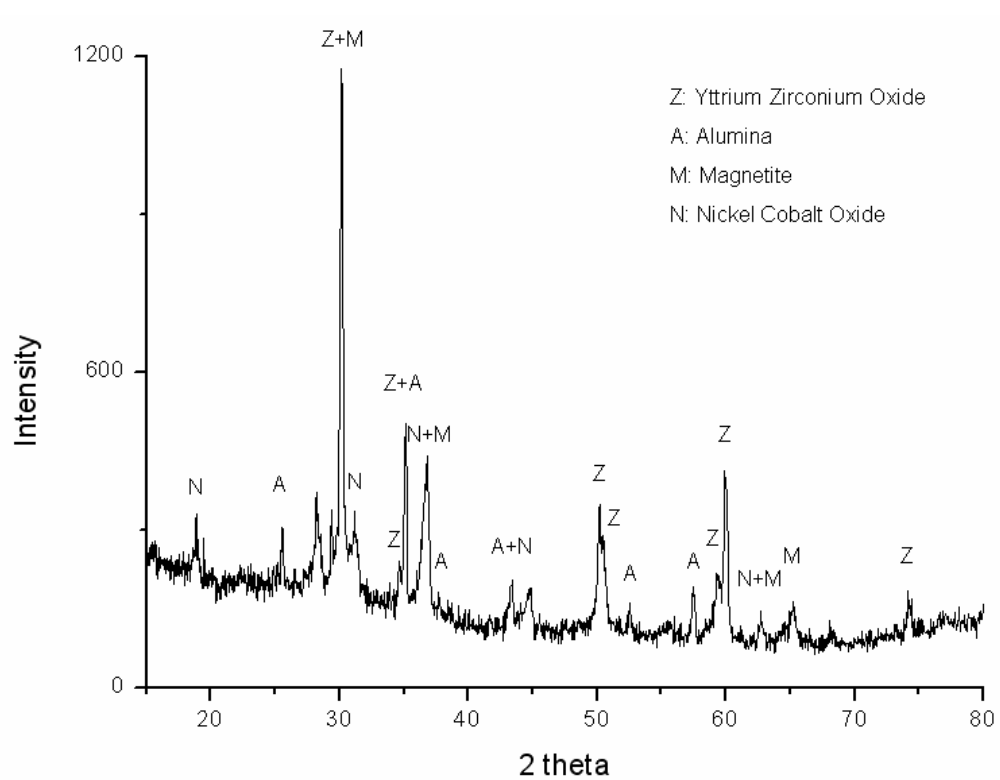


Figure 43: XRD peak profile for green deposit

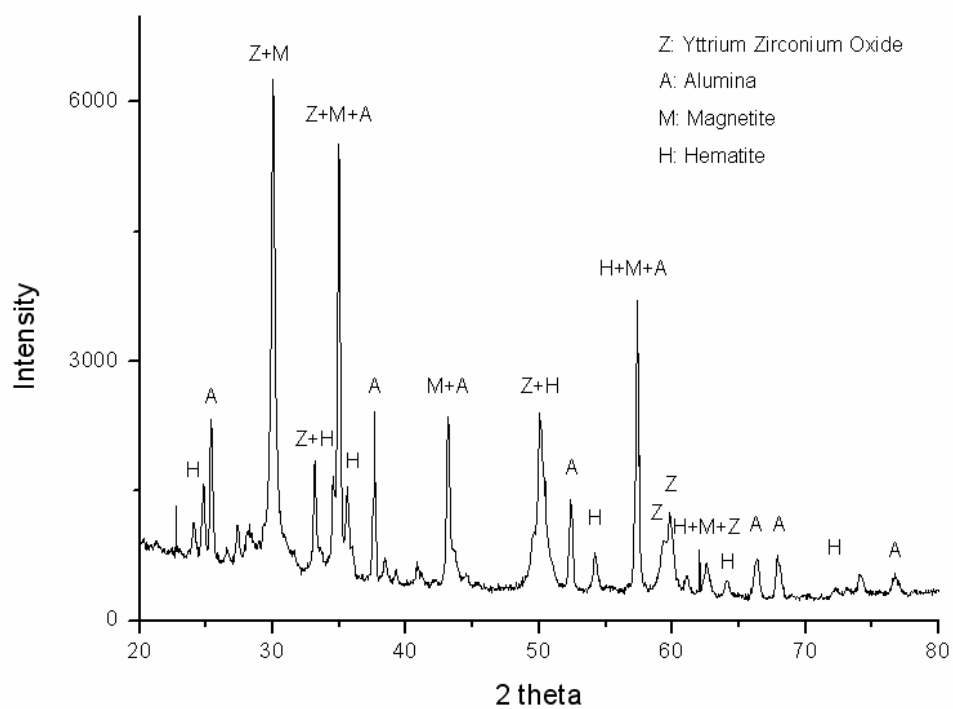
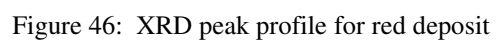
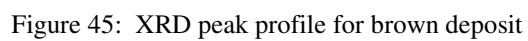


Figure 44: XRD peak profile for black deposit



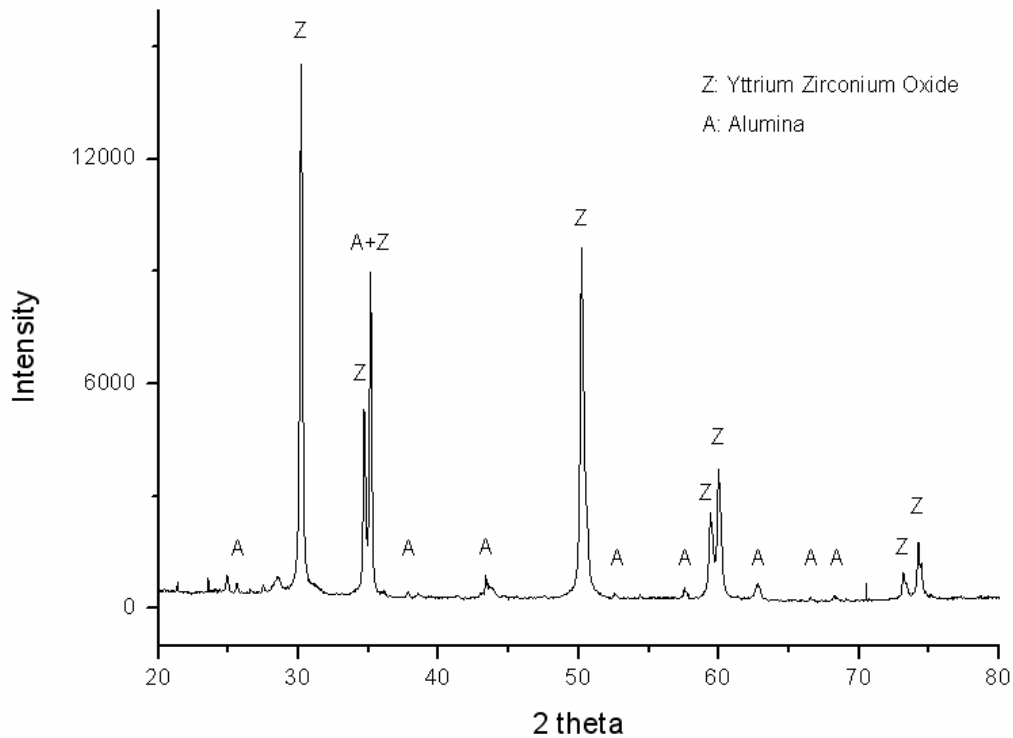


Figure 47: XRD peak profile for un-contaminated white surface

By using EDS and XRD techniques, hematite (Fe_2O_3) and magnetite (Fe_3O_4) were found as the primary chemical deposits on the vane surface. The significant amounts of iron deposit are suspected to come from internal sources such as metallic wear debris from the compressor stages and turbine shaft both of which are steel.

In order to understand the formation of these phases, it is necessary to consider the thermodynamic stability of the various iron oxide phases, specifically with respect to temperature and oxygen partial pressure. The air stream inside the combustion chamber experiences temperatures over 1600 °C and at these temperatures, the iron containing wear debris from the compressor stages would exist in a liquid phase. Once the hot gas stream exits the combustion chamber, it is then cooled to approximately 1160 °C just before entering the first turbine stage. The combustion gas is then mixed with internal cooling air guided from compressor stages, and therefore the oxygen partial pressure at the first turbine stage is assumed to be at 0.21 atm which is the same as air. The $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ pressure-temperature phase diagram [58] (Figure 48) can be used to track the

phase changes of the iron oxides. Through following the cooling curve indicated on the figure (marked in red), at a constant oxygen partial pressure of air, magnetite is the first phase to fully solidify at $\sim 1590^{\circ}\text{C}$. Then at $\sim 1365^{\circ}\text{C}$, the hematite phase solidifies and co-exists with magnetite.

Cross-sectional and surface SEM analyses on the deposits reveal their microscopic features. At this point, the surface discolouration can be categorized into darker colour and lighter colour deposit groups. Darker deposits include black and dark brown whereas lighter deposits include red and light brown colours. These groups have explicit microstructural features. Flagstone-like plates were only observed on the darker deposit surfaces whereas granular surfaces were mostly observed for lighter deposits. Densification possibly by sintering is observed in the darker deposit layers but not on the lighter deposits suggesting that the darker colour deposit covered regions experience higher temperatures for longer. This is in agreement with the observations of TGO thicknesses.

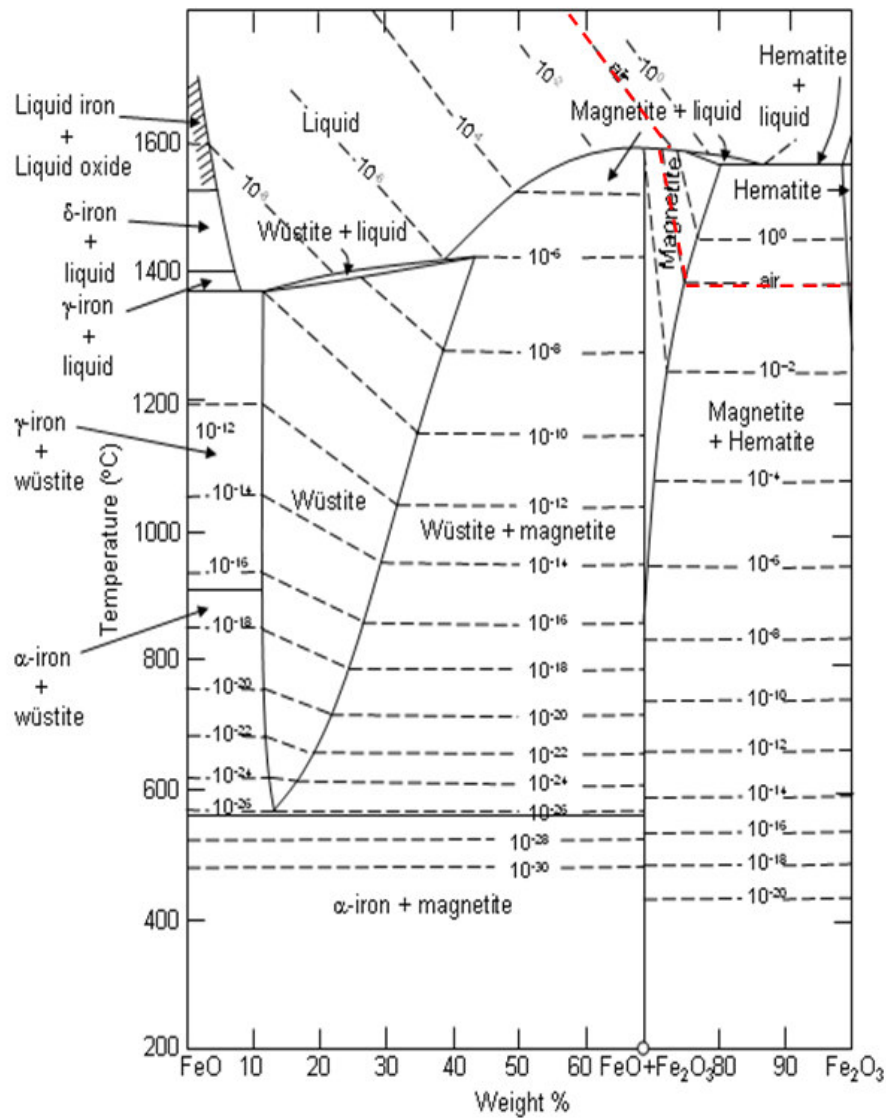


Figure 48 FeO/Fe₂O₃ pressure-temperature phase diagram [58]

2.3.4. Gamma Prime Coarsening Analysis

Vane A and C were selected for analyses of gamma prime size. This was done in an attempt to use gamma prime size to assess the relative temperature experienced by the vanes. To compare the relative substrate or TBC surface temperatures, gamma prime particles at a number of corresponding positions on these two vanes were measured and recorded. Since both Vane A and C experienced the same service hours, it is expected that regions with larger gamma prime particles will have been exposed to higher

temperatures during operation. The purpose of this study is to monitor the change of gamma prime size and therefore extrapolate the relative temperature profile experienced by these nozzle guide vanes under discoloured TBCs. Critically it is also part of the scope of this project to determine relationships between surface TBC colours and temperature in order to assess if the coloration can act as a guide for plant engineers.

Background:

Gamma prime precipitates are the cuboidal phase found in the gamma matrix and are the most important microscopic feature of superalloys. The gamma prime precipitates provide the precipitation hardening effect to the superalloy which enhances its strength at high temperature [59-61]. The size, shape, and morphology of gamma prime precipitates respond to operating conditions such as temperature, service hours, loading stresses, and gas environment [62, 63]. The gamma prime coarsening with respect to temperature conditions will be used to assess the relative operating temperatures for the vanes. It is known from the literature that gamma prime precipitates grow with respect to temperature on a logarithmic scale.

Experimental Procedure:

Sample Cutting and Preparation:

Service-retrieved nozzle guide vanes, Vane A and Vane C, were first sectioned using an industrial size cut-off wheel at RWE nPower facility; followed by a Beuhler IsoMet 2000 precision saw with an alumina blade. Eight specimen pieces have been selected and cut with four pieces from each vane. Figure 49 outlines the positions and labels for these 8 specimens. A, B, C, and D are four corresponding positions of the 4 corners on the pressure side. Sectioned specimens were mounted in cold-setting epoxy resin and their cross-sections were polished to 1 μm . All specimens had been etched under 4% KCl of deionised water solution for 4 seconds at 3V.

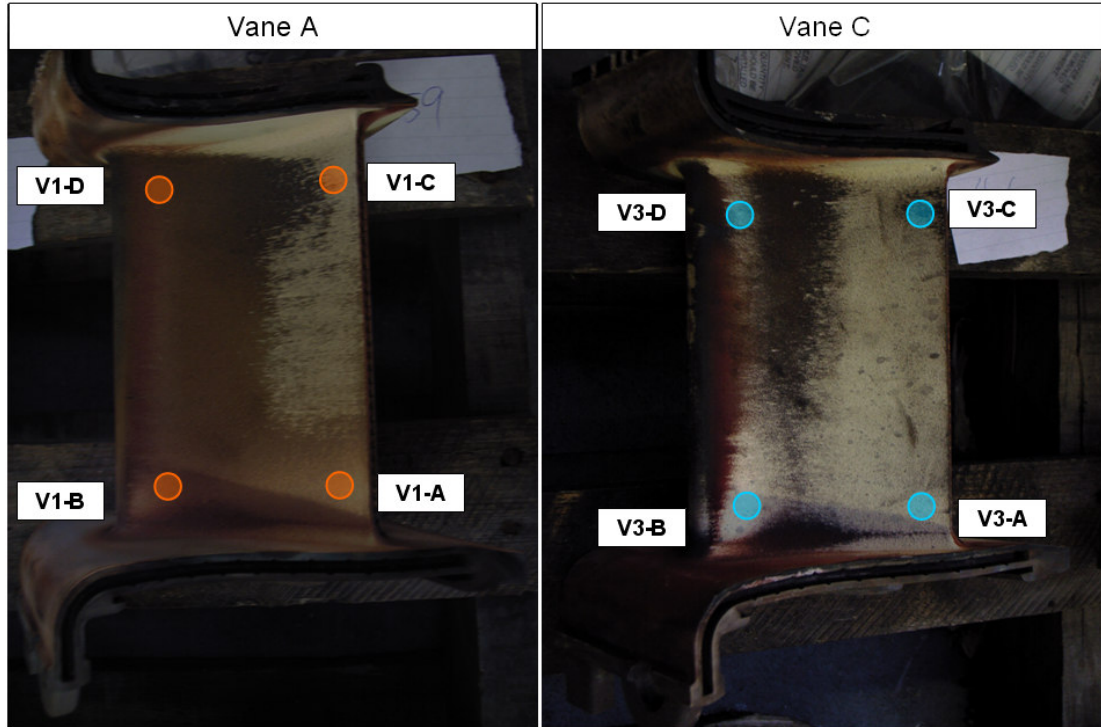


Figure 49 Gamma prime examination sites for Vane A and C

Microscopy:

Cross-sections of these eight specimens were carbon coated and examined using a field-emission-gun scanning electron microscope (FEGSEM; LEO Gemini) with an accelerating voltage of 20 kV and a working distance of 15mm. BSE mode was selected for better image contrast of the gamma prime particles. Images were taken through the cross-section of each specimen and the thicknesses of the YSZ top coat, MCrAlY bond coat, and TGO were measured and recorded by ImageJ [64]. Final values for all the measurements are the average from 10 ImageJ measurements. It is to be noted that measurements for the TGO are measured normal to the bond coat surface. As illustrated in Figure 50, for each specimen, 5 BSE images of the gamma prime were taken at the inter-diffusion zone (IDZ) and at 1 mm (1000 μm) below this zone at 20,000 x magnifications. Images obtained were also loaded to ImageJ image analysis software for gamma prime size measurement (μm^2).

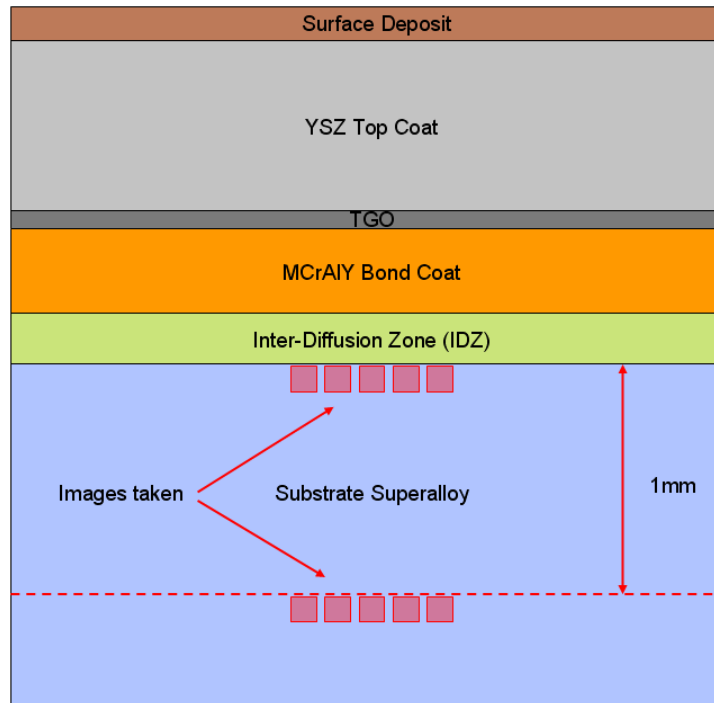


Figure 50 Schematic diagram of a vane specimen cross-sectional view, showing the gamma prime sampling locations

Results and Discussion:

Gamma Prime Size Measurements:

BSE images of gamma prime have been analyzed (Figure 51 and Figure 52) using the ImageJ software for particle size measurements. Selected BSE images (10 images for each position) were loaded to ImageJ followed by adjustment of contrast and brightness. Once maximum contrast ratio is obtained, threshold values for the images were tuned to eliminate the image processing noise resulting from the contrast and brightness adjustments. Once the images reveal clear particles of gamma prime precipitates with clear (non-overlapping) grain boundaries, “Analyze Particles” module was used to determine the average grain size (area μm^2) and diameter (μm). ImageJ computes these values through first identifying all the circular objects within a set value of circularity in the BSE image, followed by counting the number of image pixels within each circular object. The sums of pixels within any circular objects were divided by the number of objects to calculate the average object size. The circularity constraints were set constant at a range from 0.70 to 1.00. Table 5 compares the average gamma prime size in area

(μm^2) of samples A, B, C, and D of Vane A and C. From this table, several key findings have been observed. Compared to Vane A, Vane C has overall larger gamma prime precipitates near the IDZ, meaning the substrate surface temperature experienced by Vane C is higher than Vane A. Among the four corresponding points of interest, position D of each vane reveals the largest gamma prime size and is suspected to be the hottest region. The TBC surface colour above the position D on the two vanes is white. Vane A, in particular, has its position D surrounded by discoloured TBCs, leaving position D the only region with no surface deposits. Furthermore, gamma prime grain sizes were found to be larger nearer the pressure side leading edge than the trailing edge, suggesting the temperature at the leading edge is higher.

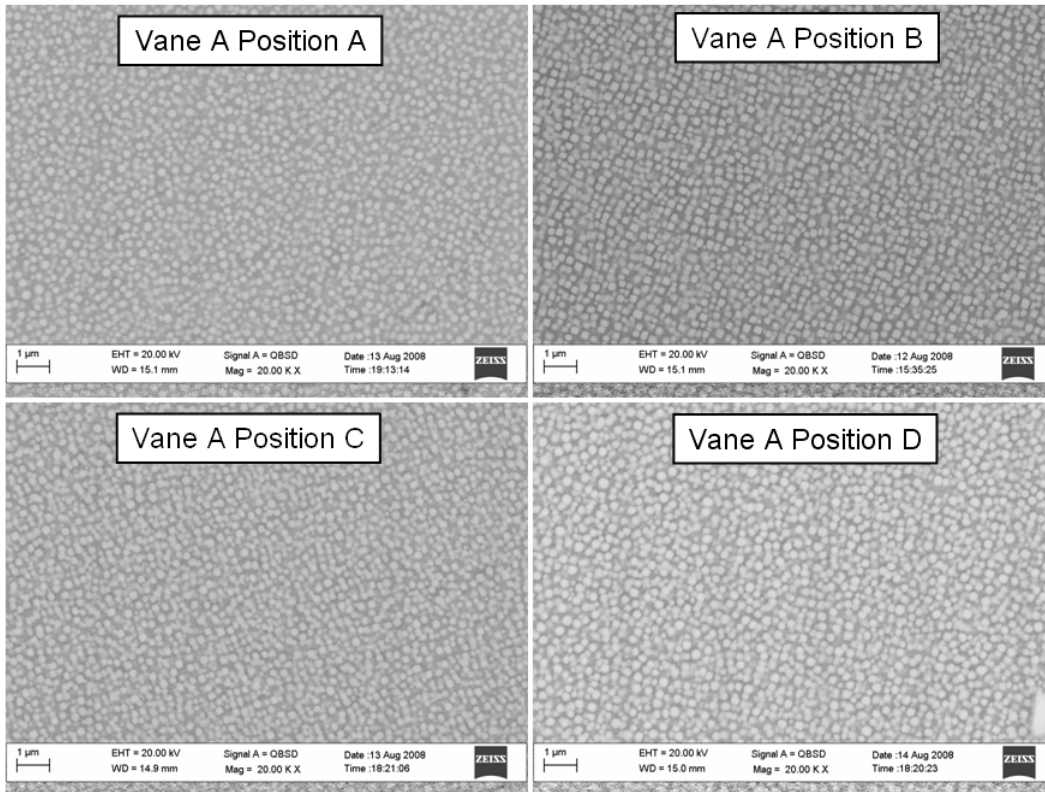


Figure 51 BSE images of gamma prime for Vane A

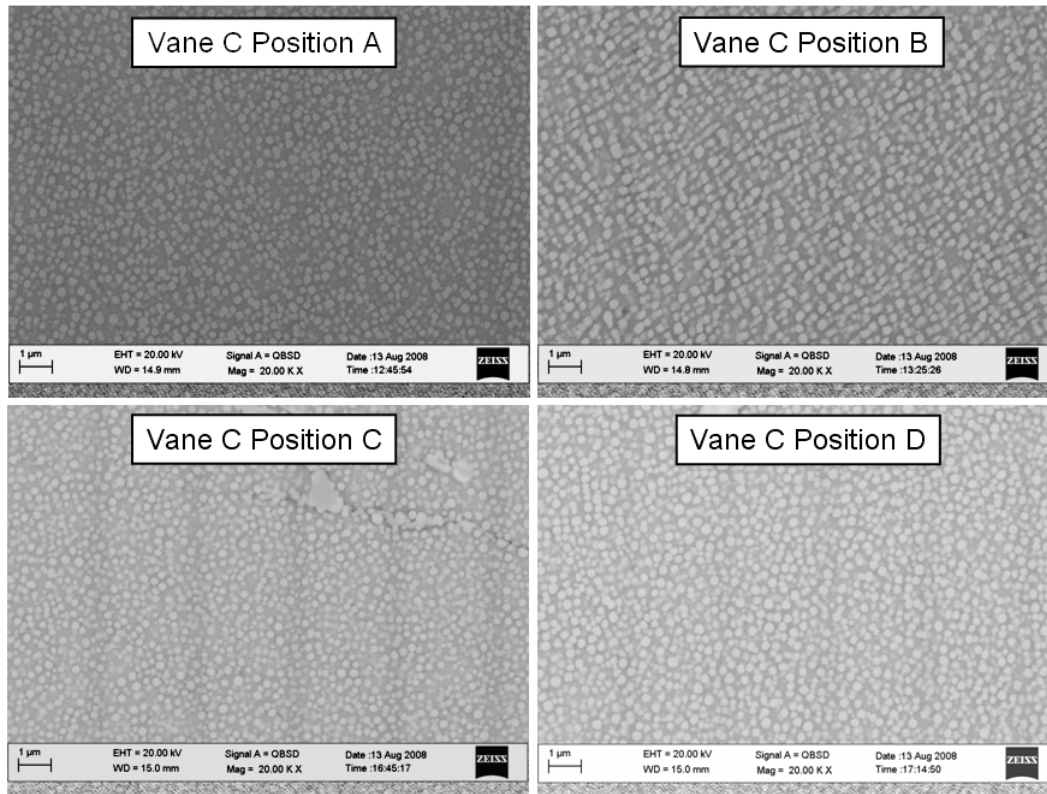


Figure 52 BSE images of gamma prime for Vane C

Table 5 Average gamma prime size measurements (μm^2) at IDZ and at 1 mm below the inter-diffusion zone

GAMMA PRIME AT THE INTER-DIFFUSION ZONE								
	V1-A	V1-B	V1-C	V1-D	V3-A	V3-B	V3-C	V3-D
AVG	0.037	0.040	0.035	0.045	0.041	0.042	0.035	0.043
STDEV	0.012	0.013	0.011	0.015	0.014	0.015	0.011	0.016

VIRGIN GAMMA PRIME AT 1 MM BELOW THE INTER-DIFFUSION ZONE								
	V1-A	V1-B	V1-C	V1-D	V3-A	V3-B	V3-C	V3-D
AVG	0.030	0.033	0.035	0.033	0.030	0.030	0.031	0.036
STDEV	0.013	0.015	0.016	0.014	0.015	0.014	0.014	0.019

Thermally Grown Oxide Thickness Measurements:

ImageJ was again used for the thickness measurements. “Set Scale” was the first step before any measurements, using the “Line” function to draw a straight line matching the scale bar of each BSE image, followed by entering the corresponding length (with unit) for the particular scale bar would automatically set the measuring scale on ImageJ. Table 6 summarizes the average thickness measurements for YSZ top coat, TGO, and bond coat. One of the main discoveries from Table 6 is the YSZ and bond coat thickness variation between Vane A and C. Vane A, which had an overall smaller gamma prime grain size

than Vane C shows a thicker top coat and bond coat. The variation in top coat thickness between the two vanes is as high as 30 %. As the purpose of the YSZ is for thermal protection, 30% less protection for Vane C could make it more vulnerable for coating spallation. In addition, variation in bond coat materials could also lead to insufficient oxidation protection. Vane A, which has approximately 30 % more YSZ and 20 % more bond coat, has its entire surface TBC intact. In contrast, Vane C, which has less effective thermal and oxidation protection, exhibits coating spallation at its pressure side leading edge. The variation in coating thickness is likely due to process control during coating deposition. In the EB-PVD coating process for YSZ, slight changes to process parameters can often result in large deposited thickness variations. In addition, YSZ coatings are found to be thicker at the trailing edge than leading edge on the same vane, which could be the reason why spallation occurred at the leading edge first, Figure 25 (Vane C site of failure).

TGO measurements of Vane A reveals no significant change in TGO thickness (or temperature) from position A to B, whereas going from C to D, a significant increase in TGO thickness is observed. TGO measurement on Vane C (V3-A, V3-B, V3-C and V3-D) was not possible due to the presence of a key coat. The key coat is an additional coating between the top coat and the bond coat for better adhesion. When measuring the TGO with the presence of a key coat, the TGO layer is rather irregular and difficult to identify. Figure 53 is an example of TGO layers with the presence of a key coat; TGO layers form at the YSZ / key coat, key coat / MCrAlY interface as well as within the key coat itself, making it difficult to measure the TGO thickness.

Table 6 Average YSZ, TGO, and MCrAlY thickness measurements in μm

YSZ THICKNESS								
	V1-A	V1-B	V1-C	V1-D	V3-A	V3-B	V3-C	V3-D
AVG	319	239	317	229	247	187	318	193
STDEV	33	17	13	24	25	16	24	19

TGO THICKNESS								
	V1-A	V1-B	V1-C	V1-D	V3-A	V3-B	V3-C	V3-D
AVG	0.72	0.71	0.44	0.61	n/a	n/a	n/a	n/a
STDEV	0.40	0.35	0.20	0.18	n/a	n/a	n/a	n/a

MCrAlY THICKNESS								
	V1-A	V1-B	V1-C	V1-D	V3-A	V3-B	V3-C	V3-D
AVG	321	302	264	346	279	271	260	255
STDEV	29	17	17	16	26	14	25	12

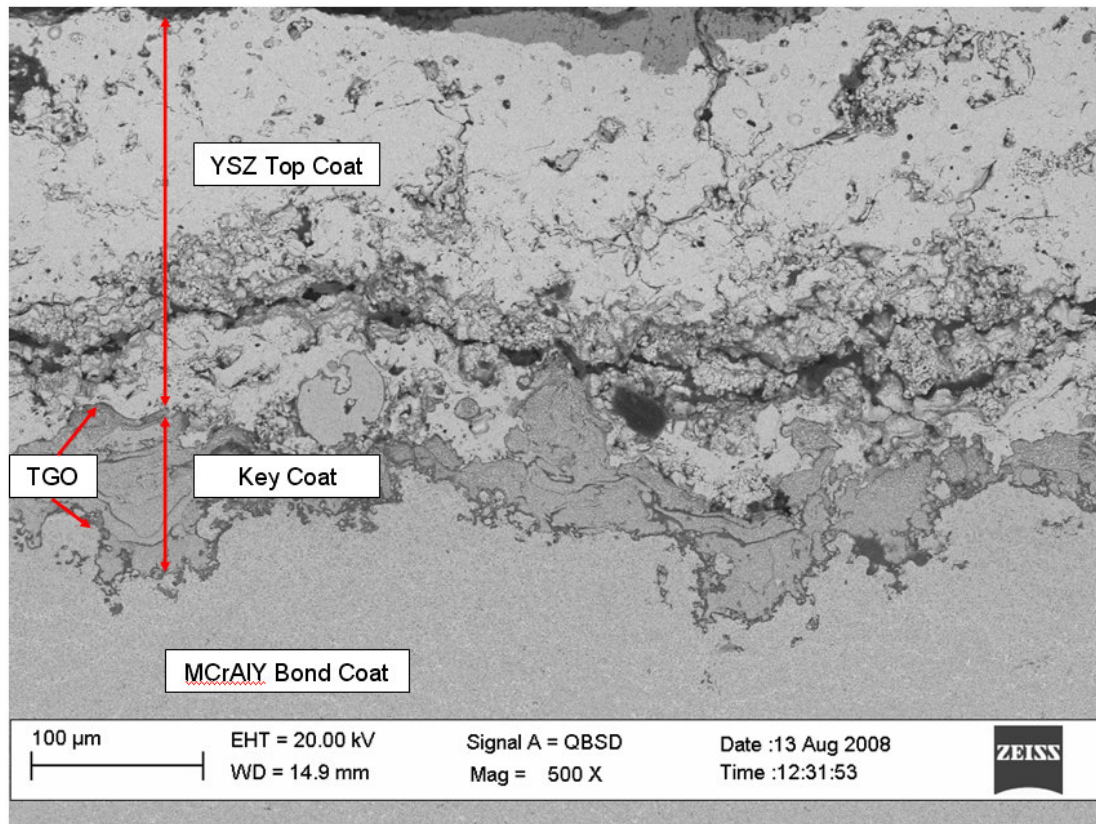


Figure 53 TGO layers with the presence of a key coat

Cross-sectional and surface SEM analyses on the deposits reveal their microscopic features. At this point, the surface discolouration can be categorized into darker colour and lighter colour deposit groups. Darker deposits include black and dark brown where as lighter deposits include red and light brown colours. These groups have explicit

microstructural features. Flagstone-like plates were only observed on the darker deposit surfaces whereas granular surfaces were mostly observed for lighter deposits. Densification possibly by sintering is observed in the darker deposit layers but not on the lighter deposits suggesting that the darker colour deposit covered regions experience higher temperatures for longer. This is in agreement with the observations of TGO thicknesses.

From the visual inspection, darker deposits (black and dark brown) were normally found near the pressure side leading edge and trailing edge of the vanes observed. However, in some cases, black deposits were also observed on the pressure side face such as Vane C, which had coating spallation at the pressure side leading edge. After visual inspection of nearly 50 nozzle guide vanes, it is concluded that the pressure side leading edge has the highest chance of YSZ spallation. Pressure side leading edges of these nozzle guide vanes were found to have the highest deposit accumulation. It is suspected that contamination particles continuously impact the leading edge at nearly a 90° angle whilst in service, the impact energy make the leading edge prone to spallation. XRD analyses at the surface of the deposits across the pressure side have discovered the co-existence of magnetite and hematite phases. The $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ pressure-temperature phase diagram adapted from Chiang et al. [58] (Figure 48) is used to correlate the range of TBC surface temperature. The predicted TBC surface temperature in these regions could be reaching ~1365°C, assuming the oxygen partial pressure in the CCGT is at ~0.21 atm.

3. Analysis of Erosion on TBC Surfaces

The author would like to acknowledge that the work in this chapter was conducted using the facilities at the National Institution for Materials Science in Tsukuba, Japan.

The variations in top and bond coat thickness discussed in the previous section suggest a relationship between reduced coating thickness and observed spallation. To determine additional factors in loss of TBC, failure analysis on a 2nd stage turbine blade service-retrieved from a PW4000 series engine was conducted to determine the potential cause of early TBC spallation using SEM analysis. Severe erosion attack was observed on the pressure side of the blade. Mapping of regional thermally grown oxide (TGO) thicknesses provide an approximate surface temperature profile experienced by the particular blade during service. The temperature profile was then compared with the regional attack suffered by the yttria stabilized zirconia (YSZ) top coat. In contrast to the observations on the nozzle guide vanes where thinner coatings resulted in spallation for the land based turbine, it was suspected in this case that the rate of erosion has a direct relationship with the TBC surface temperature. Regions with low surface temperatures tended to suffer severe erosion attack, whereas hot surfaces suffered less. Although erosion attack on the hot TBC surface was relatively low, the gradual thinning of the YSZ in the hot zones clearly reduced the thermal barrier capability in these regions.

3.1. Background

Erosion on thermal barrier coatings (TBCs) has been described as constant wearing of the YSZ top coat. The gradual removal of YSZ has been reported as the cause of early coating failure in both land-based [42] and aerospace [43, 44, 65] turbines. The sources of erosion are environmental external particles, such as CMAS particles (intake from the exhaust) and metallic debris from the wear of internal engine components. The first stage in aerospace gas turbine typically operates in the range between 1400 °C to 1600 °C, which is higher than that of CMAS melting temperatures reported in the literature [26]. CMAS particles impacting the turbine components in the first stage are mostly in the molten form, which adhere onto the pressure side TBC surface as chemical deposits.

However, second stage turbines operate at a much lower temperature, typically in the range between 1000 °C to 1200 °C, and the type of environmental attack shifts from CMAS deposition to erosion and foreign object damage (FODs). Eroders with various sizes gradually remove the top coat of the second stage turbine blades, reducing its thermal barrier capabilities. Due to the direction of the hot gas path and uneven distribution of internal cooling, a temperature gradient on the TBC surface always exists.

This chapter investigates the coating spallation induced failure of 2nd stage gas turbine blades. Mapping of the TGO growth and YSZ thickness loss provide information about the surface temperature profiles and regional erosion attack. The relationships between TBC surface temperature and erosion were compared and discussed.

3.2. Experimental Procedures

Four service-retrieved second stage blades received from a commercial airliner are shown in Figure 54. For these blades, spallation failures are observed, such as, the coating on blade #1 has already failed on the pressure side towards the trailing edge. Each service-retrieved blade was sectioned into 28 pieces (Figure 55) using Heiwa Fine Cutter and cross-sections of all the pieces were polished to 1 µm. Scanning electron microscopy (SEM) analyses on these samples were conducted using Philips XL30 SEM at 20kV. Images taken by the SEM were loaded into Image-Pro Plus (Media Cybernetics) for measurement of the average thicknesses of TGO and YSZ of all 28 pieces in a similar way as described in section 4.3 *Thickness measurements*.

Sixteen sectioned blade pieces with deposits were heat treated with different temperature and time periods to determine the melting temperature of the erodents (CMAS particles) on the TBC surface. Sectioned samples were heat treated at 1100 °C, 1150 °C, 1200 °C, and 1250 °C for periods of 1, 5, 8, and 20 hours. Samples were removed from the furnace and air cooled at the end of each heat treatment test.

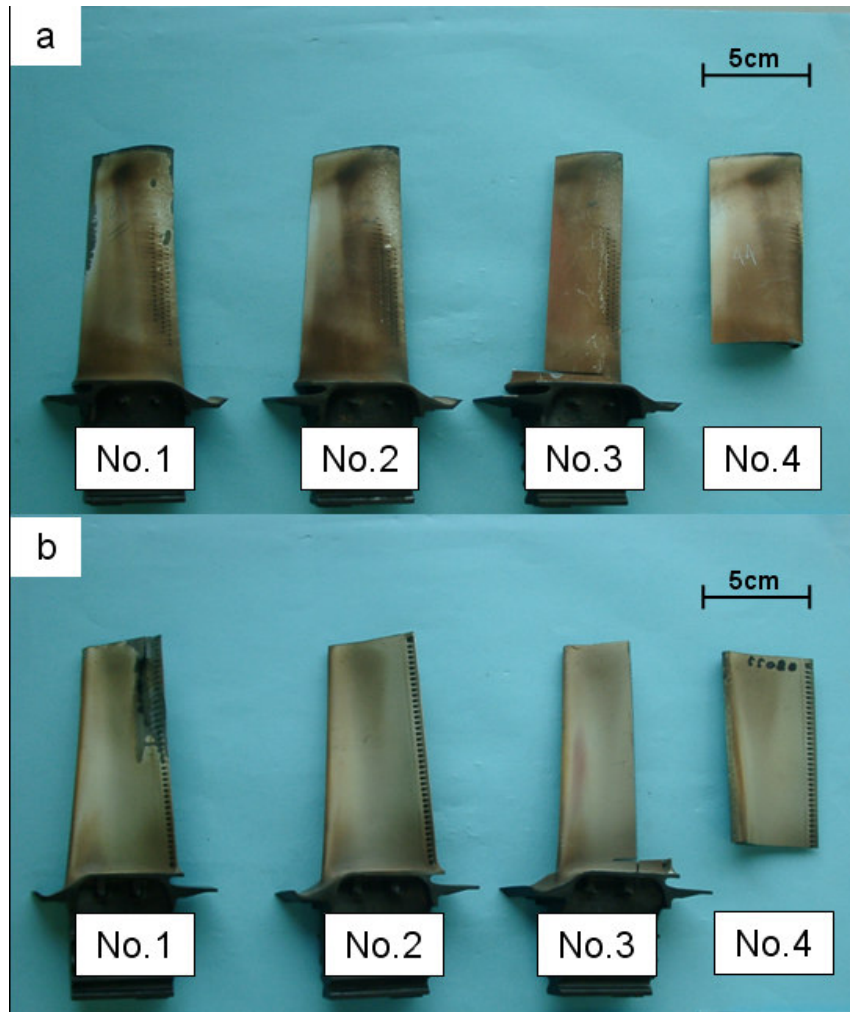


Figure 54 Second stage turbine blades received a) pressure side, b) suction side



Figure 55 Blade #2 is divided into 8 horizontal sections and 28 pieces

3.3. Results and Discussion

3.3.1. Temperature Profiles

By looking at the blades visually, gradients of surface colours were observed (Figure 54). It was proposed that the colour gradients were linked to the temperature experienced. To gain insight into the operating conditions of the service-retrieved blades, TGO thickness across both the pressure and suction sides was first plotted to understand the temperature profile experienced by the 2nd stage turbine blades. Figure 56 presents maps of TGO thickness with complementary photographs of the pressure side and suction side. Boxes in red represent regions of thicker TGO, implying hot zones. Maps of TGO growth reveal that the temperature near the trailing edge is relatively higher. When the TGO plot of blade # 2 is compared with the visual appearance of blade #1 (Figure 57), it is clear that the high temperature regions match with the failure sites.

Similar to the TGO mapping, the surface color of the TBC was also translated into information about the TBC surface temperature. Regions without any discolorations (white surface) are usually hot; in these areas the surface temperature exceeds the melting temperature of the chemical deposits. In contrast, a dense surface deposit is observed from all four blades near the cooling holes on the suction side, suggesting cooler surface result in heavy discoloration. According to the heat treatment test results, Table 7 and Table 8, TBC surface color changed to white after 20 hours at 1150 °C. Therefore, the melting temperature of the deposits on this blade is between 1100 °C to 1150 °C. It was observed that TBCs next to the failure site have completely turned white (Figure 58); the surface temperatures in these white areas are expected to be (experiencing) 1150 °C or higher during service. It was unclear whether these 2nd stage blades were designed to withstand such a high temperature; however, it is certain that TBC surface color can be useful in terms of estimating relative surface temperature.

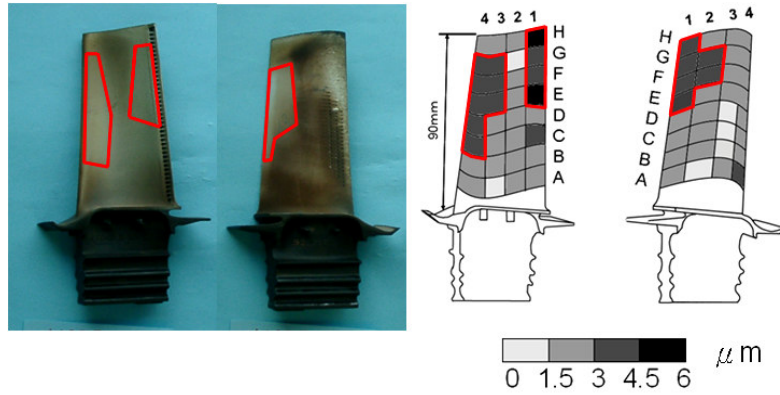


Figure 56 Comparison of TBC surface discoloration and temperature profile of blade #1

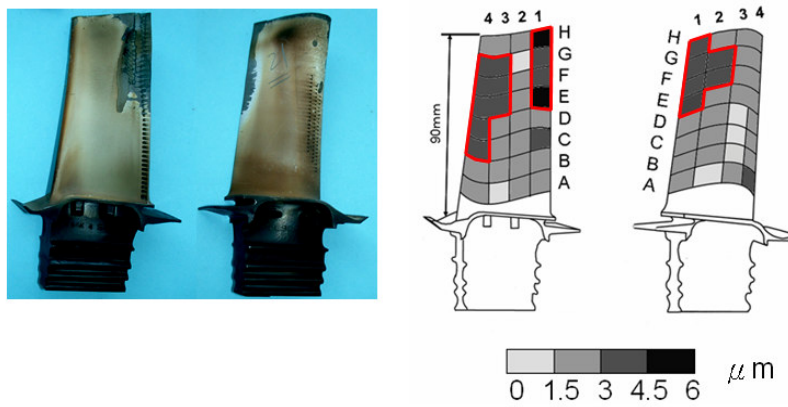


Figure 57 Comparison of failed blade #1 with the TGO plot of blade #2

Table 7 Heat treatment result showing the pressure side of the TBC

Before Heat Treatment					After Heat Treatment				
	1h	5h	8h	20h		1h	5h	8h	20h
1100°C					1100°C				
1150°C					1150°C				
1200°C					1200°C				
1250°C					1250°C				

Table 8 Heat treatment result showing the suction side of the TBC

Before Heat Treatment					After Heat Treatment				
	1h	5h	8h	20h		1h	5h	8h	20h
1100°C					1100°C				
1150°C					1150°C				
1200°C					1200°C				
1250°C					1250°C				



Figure 58 Blade #1 white surface observed right next to TBC failure site

3.3.2. Erosion Mechanisms

SEM analysis revealed two types of erosion attack, namely type I and type II. Type I erosion attack was observed on the pressure side of the blade. The tips of the EB-PVD coated YSZ were completely eroded on the pressure side (Figure 59a) giving a smooth surface, whereas the feather-like tips were preserved on the suction side of the blade (Figure 59b). Closer examination of the tips of the YSZ reveals lateral micro-cracks caused by particulate impact (Figure 60).

Type II erosion attack was found only on the suction side leading edge (Figure 61). Several TBC spallation sites were observed at the leading edge and the damage is likely to be due to erosion or FOD. Figure 62 demonstrates the nature of type II erosion damage observed. Unlike type I erosion previously discussed, type II erosion exhibits a more rough and irregular YSZ surface. Due to the curvature of the blade, erodents carried by the hot gas impact this region almost perpendicularly. According to the erosion test done by Wellman et al. [38], the erosion rate is greatest when particulates strike at 90°. Impact angle plays a key role in the nature of the erosion.

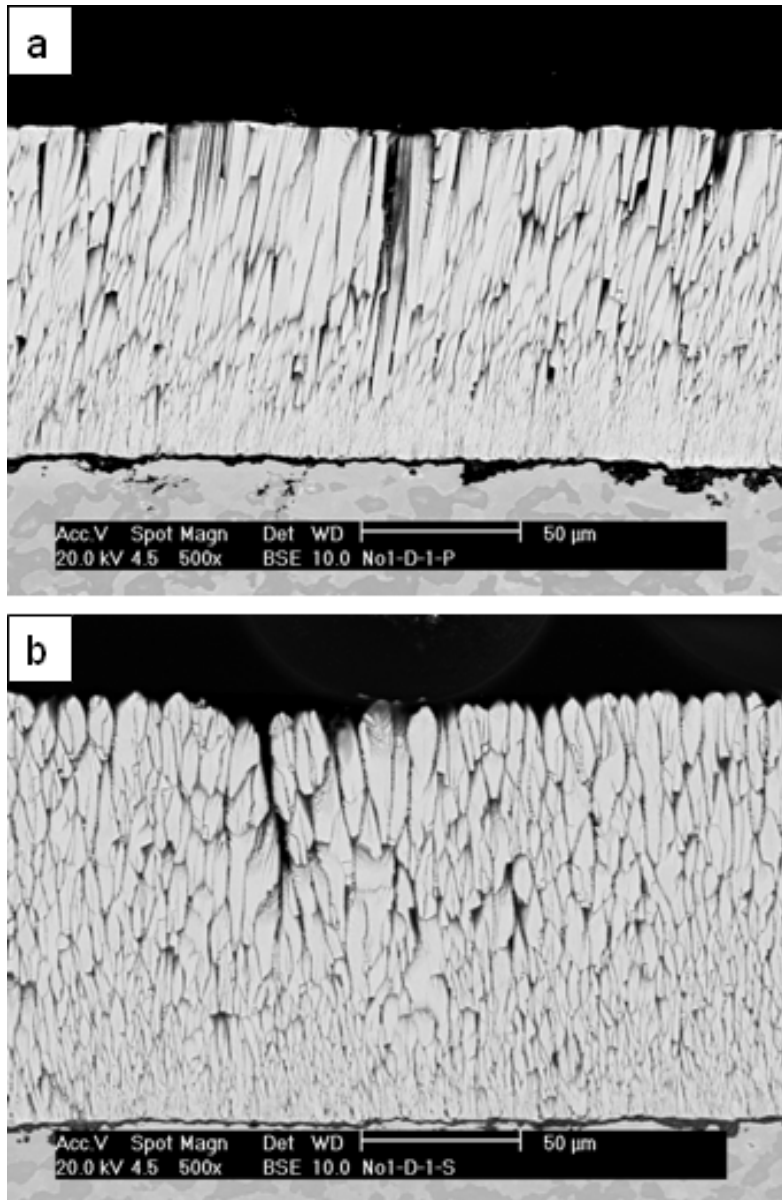


Figure 59 SEM image showing the a) Type I erosion eroded pressure side (flat smooth surface), and b) a non-eroded suction side of a sectioned blade piece of blade #2

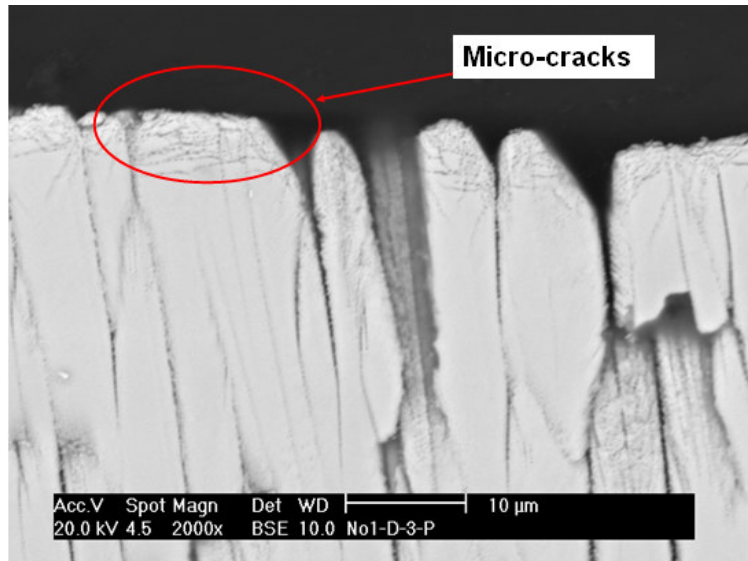


Figure 60 Micro-cracks near the tip of the YSZ on the pressure side of blade #2



Figure 61 Spallation of TBCs on the suction side leading edge of blade #1

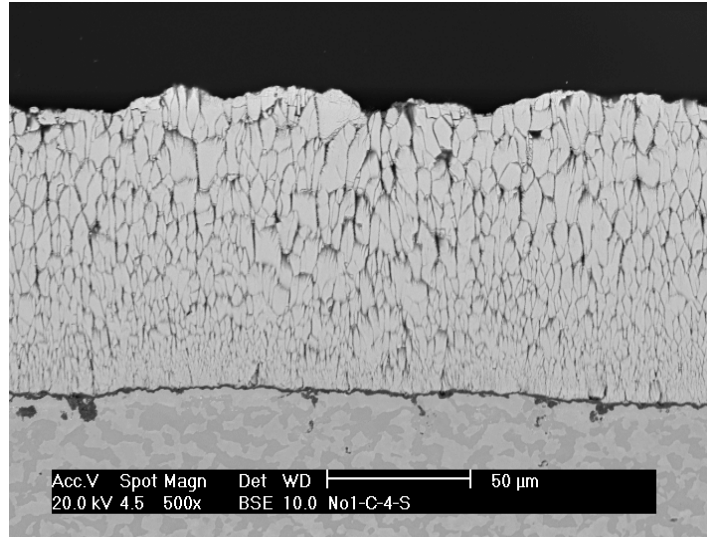


Figure 62 SEM image of Type II erosion near the suction side leading edge of blade #2

3.3.3. YSZ Thickness Variation

YSZ thickness measurements were recorded to understand the degree of erosion attack at potential failure sites, such as pressure side leading edge, trailing edge, and suction side leading edge. Figure 63 and Figure 64 present the YSZ thickness of pressure side leading edge and trailing edge respectively. Letters A to H on the x-axis represent each blade section (Figure 55), with section A being closest to the platform and H being the furthest. At the pressure side leading edge, the thickness gradient across the total vertical displacement is $47.6\mu\text{m}$ with section A being the thinnest at $92.1\mu\text{m}$ and section G being the thickest at $139.7\mu\text{m}$. Whereas, in pressure side trailing edge, the thickness gradient across the total vertical displacement is $47.9\mu\text{m}$ with section A being the thinnest at $83.9\mu\text{m}$ and section H being the thickest at $131.8\mu\text{m}$. The same trend was also observed at the suction side leading edge (Figure 65). According to the measurements done by Image-Pro Plus, YSZ coatings near the platform side of the blade were significantly thinner. It is known that the EB-PVD coating process generates a certain degree of thickness variation due to the geometry, but such variance should be minor. It is suspected thickness gradients result from different rates of erosion and the rates of erosion are related to TBC surface temperature. Unlike first stage gas turbines, second stage gas turbine blades experience a much lower temperature; such temperatures are very close to that of the CMAS melting temperature. Once the surface temperature

exceeds that of the CMAS melting temperature, the TBC colour change would occur as demonstrated by the heat treatment test (Table 7 and Table 8). CMAS melting temperatures reported in the literature are in the range 1136°C [31] to 1275°C [66]. In regions where the TBC is hot, the erodents could become softened or partially molten which significantly reduce the wearing effect on the YSZ. In cooler regions (bottom half of the blade), the TBC surface temperature was much lower and the erodent demonstrated a stronger wearing effect.

Bruce [49] studied the effect of particulate size on erosion and discovered small and intermediate size particulates cause more damage to TBCs than large particulates with slower velocity. Nicholls et al [46, 47, 53], Tabakoff et al. [48], and Toriz et al. [54] have all concluded from their studies that erosion rates increase with particulate velocities. Wellman et al [38], Taylor et al [55], Toriz et al [22], and Rao [56] each studied the effect of particulate impact angle on TBCs and all showed 90° as the critical impact angle for maximum erosion rate. There are also studies on EB-PVD and plasma sprayed YSZ coatings with respect to erosion rate [45-47]; however, coating thickness reduction or mass loss due to erosion with respect to TBC surface temperature has not been reported.

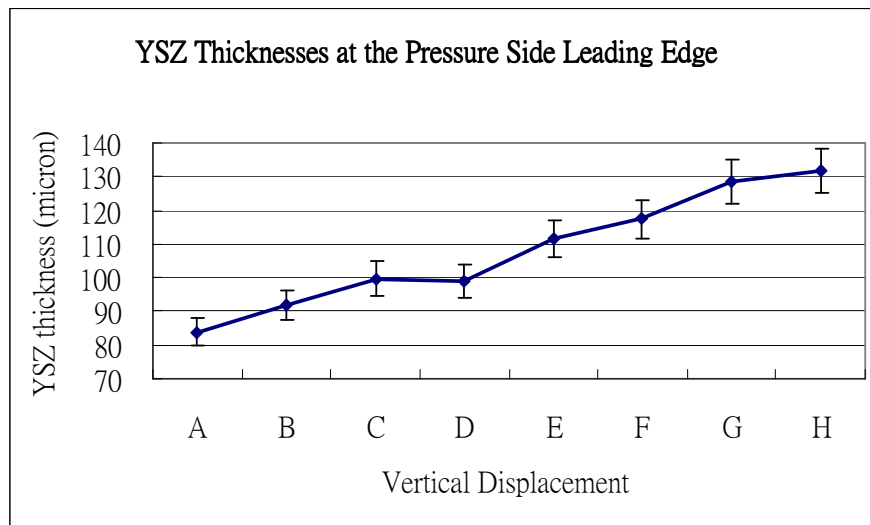


Figure 63 YSZ thickness recordings at the pressure side leading edge

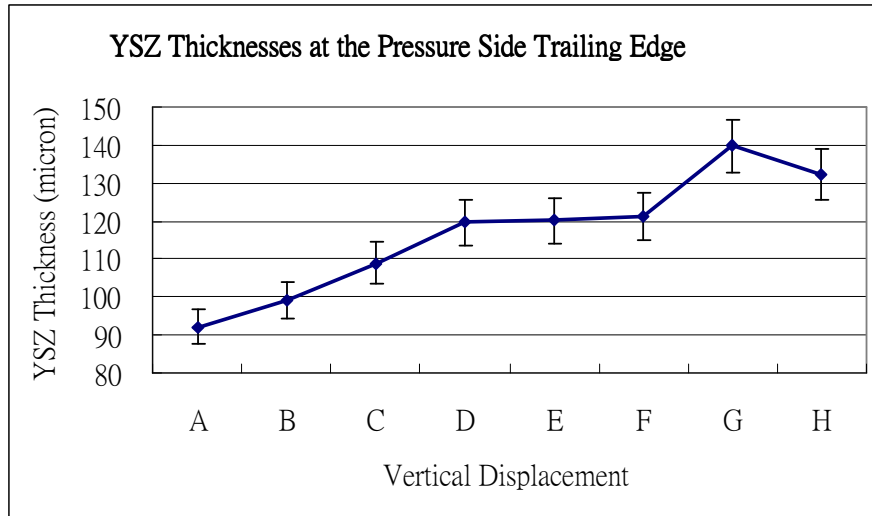


Figure 64 YSZ thickness recordings at the pressure side trailing edge

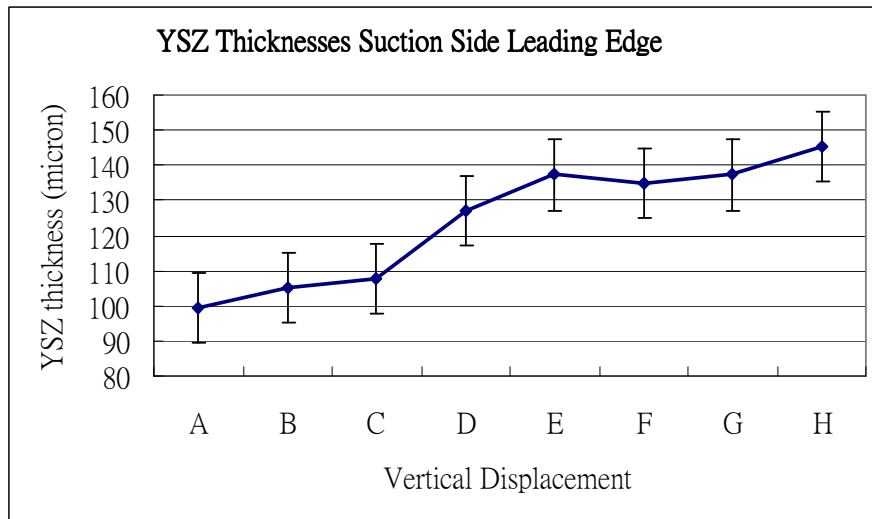


Figure 65 YSZ thickness recordings at the suction side leading edge

4. Conclusions and Future Works

Fe-rich chemical deposits from land-based CCGTs have been characterised. In contrast to CMAS, (the main chemical contamination experienced in aerospace applications) these iron oxides neither penetrate through the TBC nor dissolve yttrium content from the YSZ. There is no direct evidence that iron oxide deposits would lead to early coating failure of the TBCs; however, the surface discolouration has a direct relationship with important TBC surface conditions such as temperature and oxygen partial pressure. Regions covered by dark colour deposits are generally hotter than regions covered by light colour deposits. Cross-sectional SEM analysis has revealed a sintering effect and rapid TGO growth under the dark colour deposits. Surface images reveal flagstone-like plate and granular surface configurations with the former correspond to hot surface and later correspond to cool surface. XRD analyses have identified hematite and magnetite to be the primary contaminants.

The gamma prime coarsening effect has also been analyzed to further understand the relative temperature profile across the pressure side of the received nozzle guide vanes. Regions with black surface deposits (position B & D) reveal larger gamma prime grains than regions with light brown deposits (position A & C) in both vane samples examined; this conclusion is confirmed with the previous TGO thickness evaluation in chapter 3. What is also discovered is that TBC surface temperatures tend to be higher near the platform side of the vanes as well as the leading edges. Regions away from the platform side and near the trailing edge are the coolest area among the pressure side. This predicted temperature distributing pattern explains the fact that most of the failures occur at the pressure side leading edge but not on the trailing edge.

Relative temperature profiles experienced by the 2nd stage turbine blade service-retrieved from PW4000 series engine were again derived from TGO thickness measurements and assessment of surface colour. However, in this case, trailing edges of the blades were found to be the hottest whilst in service and most susceptible to temperature induced TBC spallation; whereas, suction side leading edges were vulnerable to erosion and FOD

induced coating failure. Surface thin film cooling, internal cooling paths and the aerodynamics of hot gas flow were all suspected for causing the variation in temperature profile across the blade surface. TBC surface discoloration provided some general understanding about the approximate surface temperature profile and the distribution of surface deposits could provide useful information for on-site gas turbine engineers in maintenance decision-making.

The TBC coated components from land-based CCGT and aerospace gas turbine engines suffer from different types of environmental attacks. Land-based CCGTs operating at different countries or different continents would suffer from different chemical attack, and aerospace gas turbine engines operating between different airline routes would also experience various level of erosion or FOD. In order to fully understand the mechanism and cause of these environmental attacks, more service-retrieved samples of gas turbine component pieces should be examined as future works.

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Appendix A

ANALYSIS OF SURFACE CHEMICAL CONTAMINATION ON EX-SERVICE INDUSTRIAL GAS TURBINE COMPONENTS

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Abstract

The origin of surface discoloration on Thermal Barrier Coatings (TBCs) of land-based industrial gas turbine hot gas path vanes has been investigated. Three ex-service row one (R1) vanes have been examined. Dense black colour deposits were observed on the pressure side leading edge and trailing edge, whereas red and brown deposits were present on the pressure side surface. Energy dispersive spectroscopy (EDS) analyses reveal a significant amount of iron oxide present with smaller amount of calcium, magnesium, aluminium, and silicon. X-ray diffraction revealed that the surface film was mixture of hematite (Fe_2O_3) and magnetite (Fe_3O_4) phases. This research aims to characterise these surface oxides with the aim of understanding the TBC surface condition whilst in service.

Introduction

Inlet gas temperatures for modern gas turbine engines are reaching 1650°C or higher for their turbine sections and the first and second stage vanes and blades are now fully protected by state-of-the-art thermal barrier coatings (TBCs) [1]. The TBCs protect the underlying substrate from the hot gas while the intermediate bond coat provides additional oxidation resistance. Since land-based industrial gas turbines (IGTs) operate isothermally and continuously for thousands of hours before making any stop for maintenance, TBC lifetime estimation for coated components is critical. Failure of a turbine blade whilst in service would lead to considerable economical loss. It is critical to understand all the surface and interfacial parameters, such as the behaviour of any deposits as well as their relationship with the surface temperature and oxygen partial pressure. Understanding the formation and distribution of surface deposits would provide

valuable information about the regional TBC surface condition *during* service. Such knowledge could help provide data for TBC life estimation.

A modern combined cycle gas turbine (CCGT) power plant has reported heavy surface contamination on the TBC coated nozzle guide vanes and blades. Since the particular CCGT has an advance air filter system, the contaminants were mostly debris from internal sources such as compressor blades. Chemical deposits found were most significant on the R1 vanes which revealed various bands of color on the surface of the TBCs. Three serviced-retrieved R1 nozzle guide vanes were examined. Among these vanes, various levels of TBC surface discoloration have been confirmed. The distribution and variation of these deposits show marked differences along cooling channels within some of the single vanes indicating that the deposit (or the deposition process) is strongly affected by temperature. Additionally there are notable differences from one vane to another suggesting that each vane had experienced a slightly different exposure to the deposit or a temperature or pO_2 profile whilst in service.

Experimental Procedures

Three R1 vanes were removed from a Siemens V94.3 gas turbine after ~ 14,000 equivalent operating hours. This machine consists of silo combustors feeding into the R1 vanes with a turbine inlet temperature of ~ 1160 °C. There is a swirl in the gas as it enters the row 1 vanes meaning that the gas is hotter for some vanes than others. The amount of discolouration on the vanes varies and three vanes were selected showing marked differences in their surface discolouration. Vane A, B, and C were chosen to represent the variation of possible temperature profiles based on their geometric arrangement in-plane.

In order to have a better understanding of the deposit chemistry and morphology, a range of techniques were used. Surface and cross-sectional scanning electron microscopy (SEM) were conducted on five selected positions across the pressure side of the discoloured nozzle guide vane. Figure 1 illustrates position 1 to 5 on a sectioned vane piece. This particular vane piece has 4 different colours of deposits: black, light brown, dark brown,

and red. SEM examinations were performed on sectioned vane pieces with various TBC discolorations. Field-emission-gun scanning electron microscopy (FEGSEM; LEO Gemini) was used to examine the surface and cross-section of sectioned pieces. The in lens secondary electron mode was employed and images were taken at 5 kV with a working distance of 7 mm. For cross-sectional images of the surface deposits, backscattered electron mode (BSE) was selected to show the phase contrast within the deposit layer. Oxford Instruments ISIS EDS was used to perform surface and cross-sectional mappings to determine the elemental composition and distribution of the deposits. X-ray diffraction was conducted on discoloured TBC surfaces using Philips PW 1710 diffractometer with Ni filtered Cu K α radiation. A step size of 0.04° and scan step time of 30 s per step size was set for all XRD spectra.

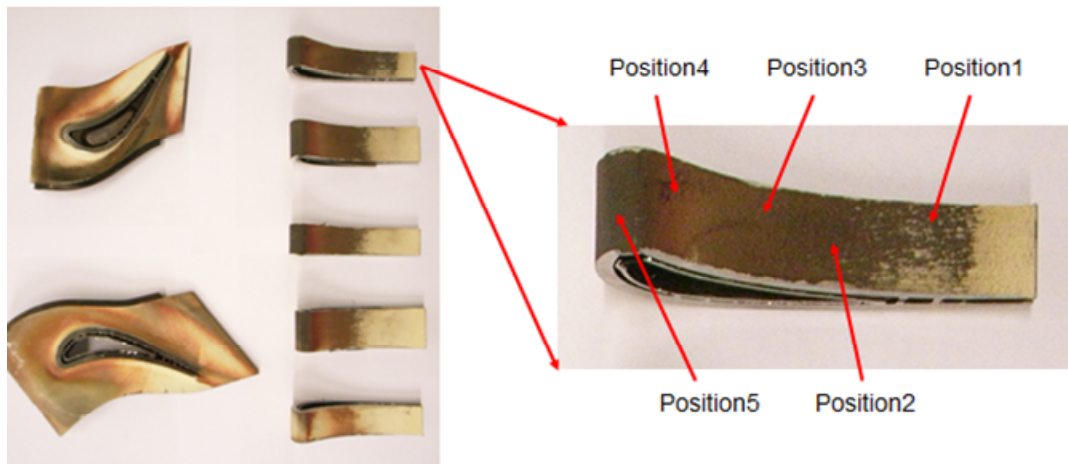


Figure 1 Sectioned blade pieces and areas selected for SEM examinations

Results and Discussion

Visual Inspection

Pressure side images of Vanes A, B, and C are shown in Figure 2. The TBC coatings on these vanes were prepared by air plasma spraying method. The TBC surface discoloration as monitored by visual inspection varies dramatically between the vanes: Vane A had most of its surface covered (approx 75 % surface area) by the deposit, Vane B 50% and Vane C had the least (approx 35 %). The discolored areas reveal dark / light brown, red and black deposits on all three vanes. Dark / light brown deposits tend to cover most of

the area on the pressure side. Red deposits can only be seen near the pressure side leading edge. Lastly, black deposits are observed on both pressure side leading edge and trailing edge. Vane C, which reveals the highest ratio of black deposit has TBC coating spallation observed at its pressure side leading edge, as shown in Figure 3.

The vane platforms were also examined and have a notable discoloration pattern. One of the interesting observations is that the distribution of red deposits tends to align with the path of cooling air from the trailing edge as shown in Figure 4. Unlike the hot gas exits from the combustor, this internal cooling air contains much higher oxygen content (close to atmospheric pO_2).

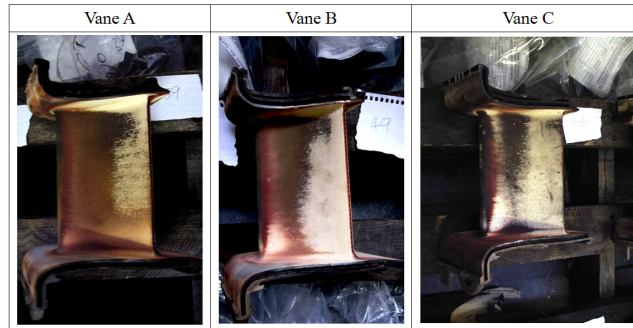


Figure 2 Pressure side surface images of Vane A, B, and C



Figure 3 Spallation of Vane C on the pressure side leading edge

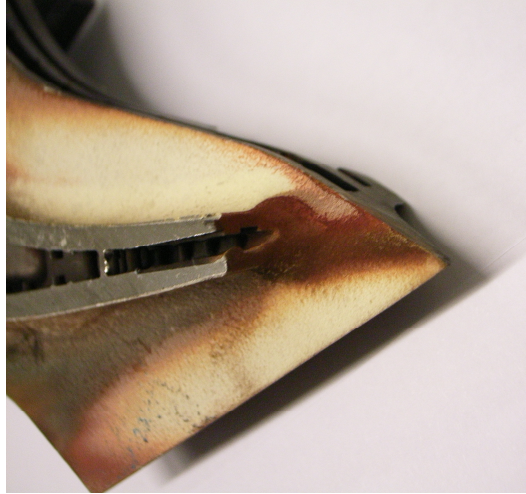


Figure 4 Red deposit near the cooling duct

Microstructural Examination

Surface Analysis:

Surface SEM imaging on the deposit has revealed several surface morphologies across the pressure side vane surface. The most commonly observed surface structures were granular and flagstone-like plates (Figure 5 and Figure 6). The size of the granular particles was relatively uniform ranging from 2 to 4 μm . The flagstone-like plates on the other hand had much more variation in size with typical plate sizes ranging from 3 to 10 μm . For the larger plates, a horizontal ridged surface was also observed. Consolidated region (Figure 7) and needle-like structures (Figure 8) were also observed; however, these microstructural features occupied only a minor fraction of the total surface area analyzed.

In general, regions with brighter surface deposits (light brown, bright red) tend to have uniform granular macrostructures. Regions with darker surface deposits (dark brown, black) reveal flagstone-like plates. The black deposits in particular, have almost the complete surface dominated by large plates whereas dark brown deposits have mixtures of granular and plate surfaces.

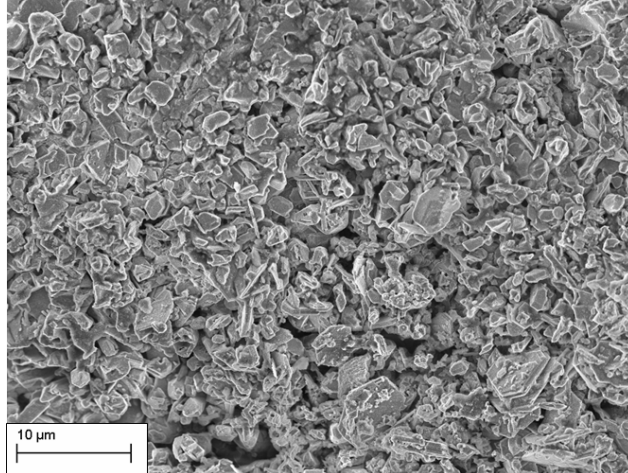


Figure 5 Granular structures on the commonly observed on the lighter colour deposit surface

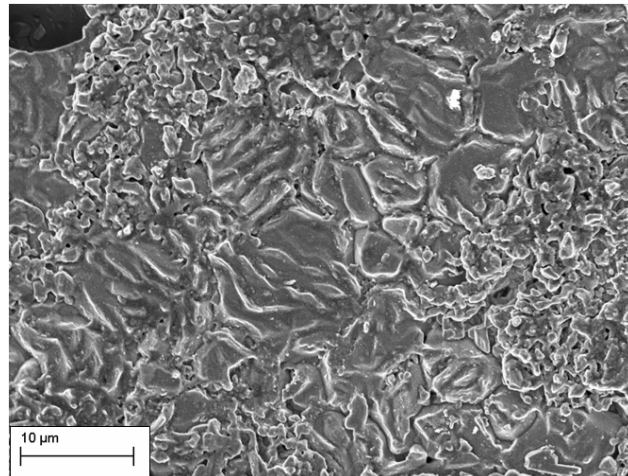


Figure 6 Flagstone-like plates commonly observed on darker deposit surface

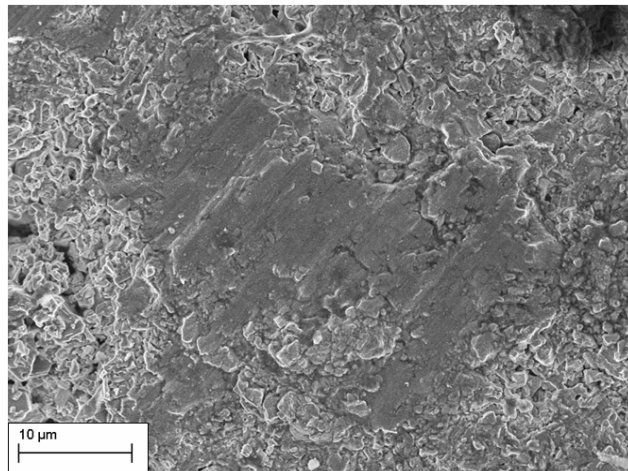


Figure 7 Large area of consolidated region on top of granular layer

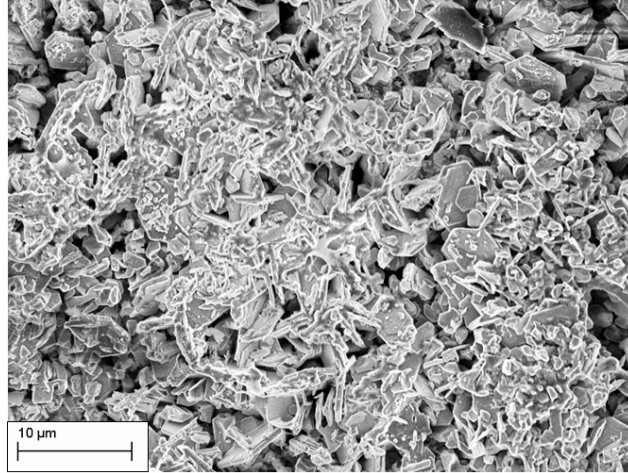


Figure 8 Needle-like structure surface observed in lighter colour deposits

Energy Dispersive Spectroscopy

In terms of chemical composition, surface EDS mappings have detected iron with traces of calcium (~5 at%), magnesium (~1 at%), aluminium (~5 at%), and silicon (~1 at%). The calcium, magnesium, aluminium, and silicon, are primarily sand and dust particles which pass through the filter system from outside. It was first suspected that these elements are forming the form of CMAS (calcium-magnesium-alumino-silicate) which is commonly reported in aerospace and most land-based gas turbine applications [2, 3]; however, the EDS results from Figure 9 and 10 does not provide enough evidence to this assumption. This particular CCGT avoids environmental attacks such as CMAS through equipping with efficient air filters which block most external impurities. Iron oxide, which is the major contaminant in this case, is suspected to come from the wear debris of the steel components within the gas turbine, particularly from the compressor stages.

Figure 9 shows the EDS mapping of a granular surface from a light brown coloured surface. Results indicate signals of calcium, magnesium, aluminium, and silicon in combination with much larger iron signals. The flagstone surface structure shows high intensity of iron and oxygen. Figure 10 is the EDS mapping of the flagstone plate from a region covered by black deposit. Signals of calcium, magnesium, aluminium, and silicon come from the gaps and openings of the flagstone-like plates. It is therefore believed the

flagstone plates are iron oxide and granular particles are either a mixed Fe-oxides or multiphase grains.

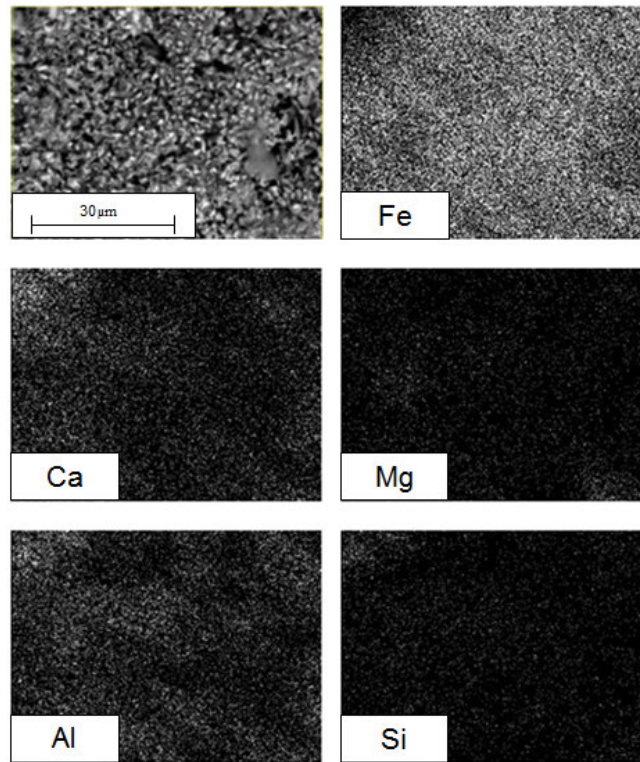


Figure 9 EDS Mapping on granular surface reveals the chemical composition and distribution of Fe, Ca, Mg, Al, and Si

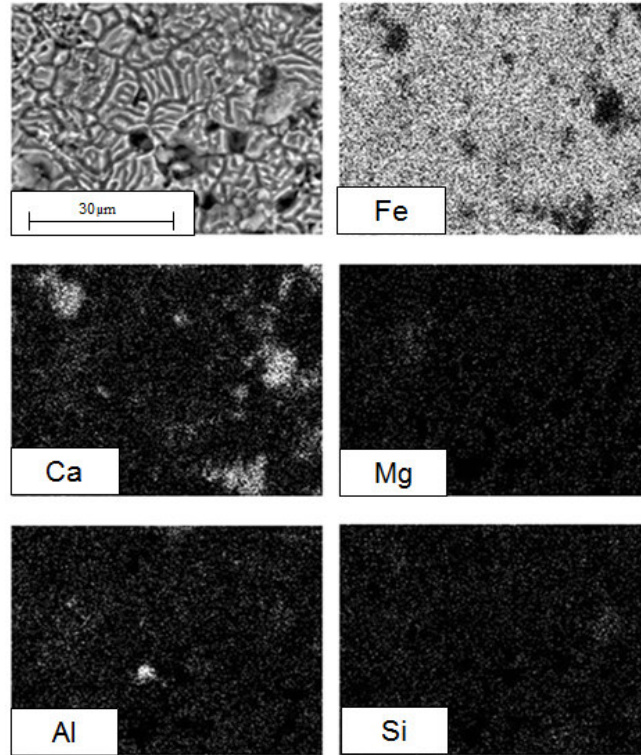


Figure 10 EDS Mapping on Flagstone plate surface reveals mostly iron on the surface

Cross-sectional Analyses

Cross-sectional analyses have been conducted on the various deposits. Figure 11 and Figure 12 show the light brown and red deposits respectively. A large amount of voids were observed within these deposits. The back scattered electron mode (BSE) images also revealed multiple phases within the deposit layer such that a dense, high atomic number layer exists at the outer most layer of the deposit. This outer layer is not uniform in thickness and has a granular structure. It is confirmed from the surface SEM that granular structure dominates the surfaces of lighter colour deposits (light brown and red). These cross-section images revealed that the granular layer is only a thin layer on the surface while a compact layer lies underneath. The granular layer shows high BSE - contrast, indicating the presence of high atomic number elements.

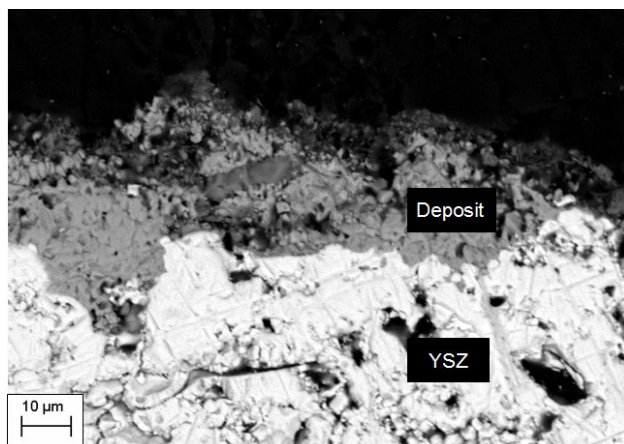


Figure 11 Cross-sectional SEM of light brown deposit

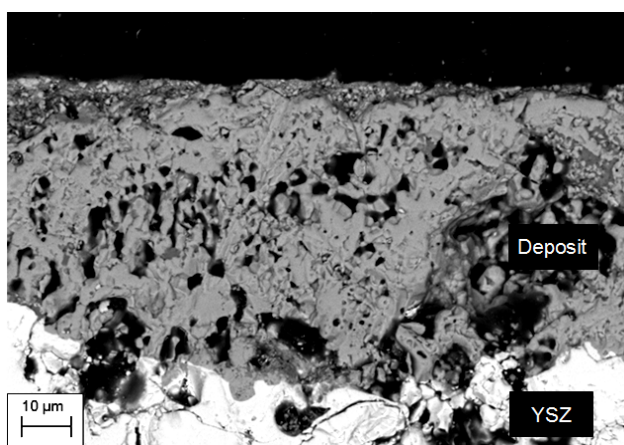


Figure 12 Cross-sectional SEM of red deposit

Figure 13 and Figure 14 show the cross-section SEM images of dark colour deposits (black and dark brown). From these microstructures, the dark colour deposits are clearly more consolidated than those light colour deposits. The denser deposit layer reveals less porosity which suggests a sintering effect may have taken place at these sites. Multiple phases are also identified from these SEM images. Recall from the surface EDS mapping of flagstone-like plates, calcium and aluminium signals were also identified. Signals of these elements came from the calcium and aluminium containing layer right under the flagstone-like plate surface; however, this denser phase is only a thin layer ($\sim 5 \mu\text{m}$) and is not representative of the bulk of the deposit.

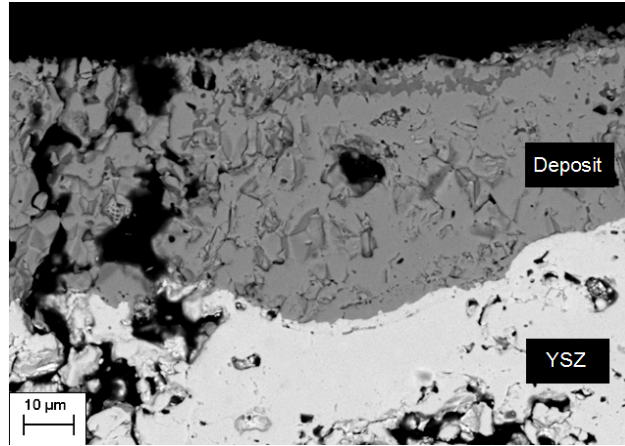


Figure 13 Cross-sectional SEM of black deposit revealing a dense layer near the surface

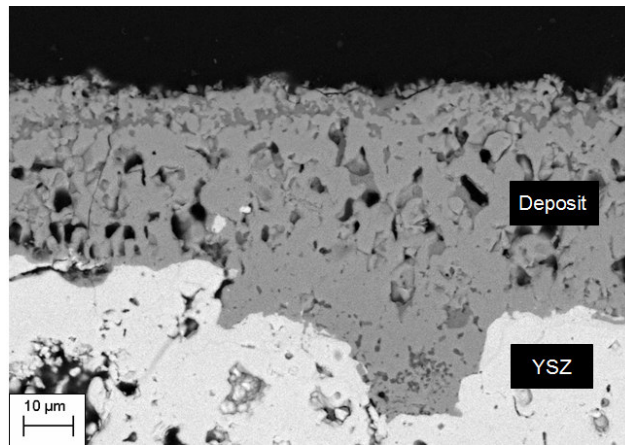


Figure 14 Cross-sectional SEM of dark brown deposit revealing a dense layer near the surface

Growth of the thermally grown oxide (TGO) can also be measured from the cross-sectional SEM images. The thickness of the TGO layer under the black deposit surface (Figure 15) is considerably thicker than that of light brown deposit site (Figure 16). The growth rate of the TGO between a TBC and a MCrAlY bond coat is dependent upon temperature [4, 5]. Formation of TGO therefore provides evidence about the relative temperature experienced at these two sites. *i.e.* these data imply that the black deposit covered area had experienced a relatively higher temperature than the region with light brown deposit. Further analytical work will be performed to quantify this.

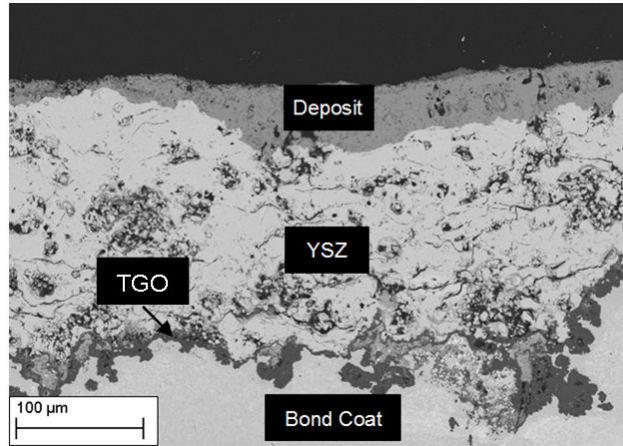


Figure 15 Cross-section SEM image of black deposit

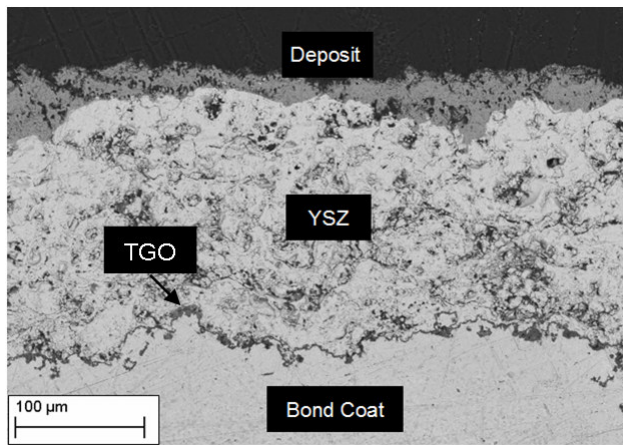


Figure 16 Cross-section SEM image of light brown deposit covered TBC

Energy Dispersive Spectroscopy

Cross-sectional EDS analysis examined the chemical composition and distribution of the contamination deposit. EDS mapping again reveals heavy iron content (~30 at%) with minor trace of calcium (~2 at%) and aluminium (~5 at%). Figure 17 shows the EDS mapping of a light brown deposit site. Calcium and aluminium were observed near the surface and the deposit / YSZ interface, whereas the bulk of the deposit is primarily iron oxides. The calcium and aluminium appear to be inhomogeneous, suggesting the existence of two different compounds. As comparison, EDS mapping of dark brown deposit is shown in Figure 42. Minor calcium and aluminium signals were again detected from these dense regions. In the study of other environmental degradation, yttria extraction was reported. Stott et al have shown that in the case of CMAS attack, yttria content could be extracted from the YSZ top coat [6, 7, 8]. However, as for this particular

iron oxide deposits, EDS mappings reveals no sign of yttria extraction (at least within the sensitivity of this measurement).

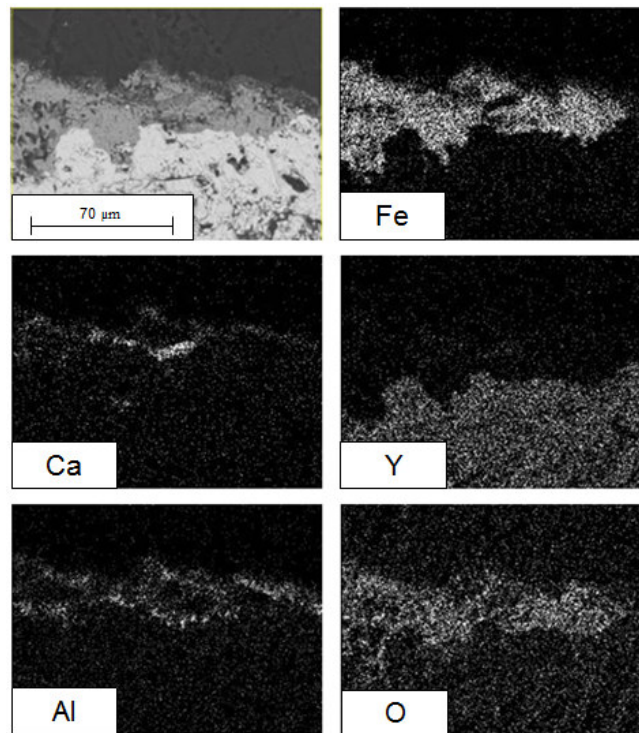


Figure 17 EDS mapping on the cross-section of light brown colour deposit site

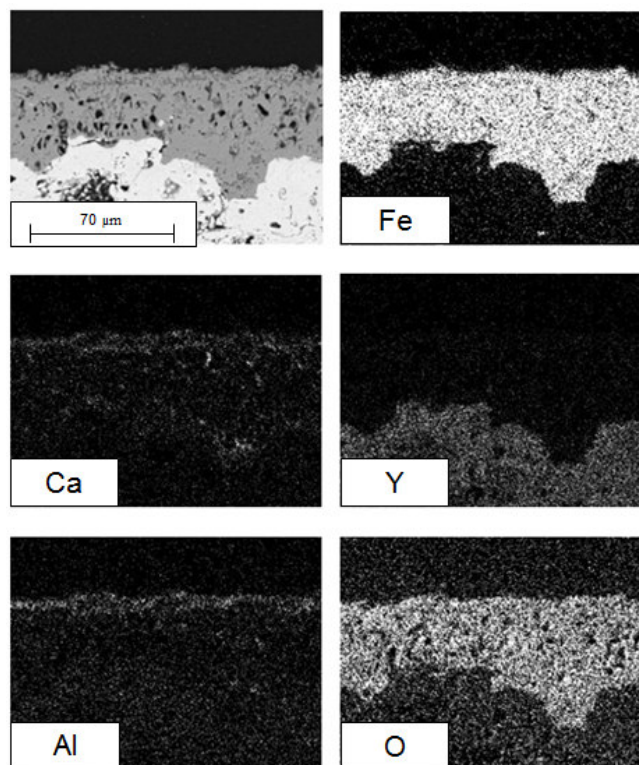


Figure 18 EDS mapping on the cross-section of dark brown colour deposit site

X-Ray Diffraction

From the EDS analyses, various elements have been confirmed. It is our interest to know the correct phases of the primary contaminant present in this system, iron. XRD has been conducted at four different positions on the pressure side vane surface, covering both light and dark coloured deposits. Figure 19 shows the XRD spectra of black, red, light brown, and dark brown colour deposit surfaces. Since the deposits layers are generally thick (greater than 30 μm in most surfaces) the XRD could only reveal the elemental phases near the surface. A mixture of hematite (Fe_2O_3) and magnetite (Fe_3O_4) phases have been identified.

In order to understand the formation of these phases it is necessary to consider the thermodynamic stability of the various iron oxide phases under typical GT operating conditions, specifically with respect to temperature and oxygen partial pressure. The air stream inside the combustion chamber experiences temperatures at over 2000°C and most Fe containing impurities are in the form of liquid phase. Once the hot gas stream exits the combustion chamber, it is then cooled to approximately 1160°C just before entering the first turbine stage (TIT). The combustion gas is then mixed with internal cooling air guided from compressor stages, resulting in an oxygen partial pressure of 0.96 atm. The $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ pressure-temperature phase diagram adapted from Chiang et al. (Figure 20) [9] was used to predict the phase changes. Through following the cooling curve at a constant oxygen partial pressure (1 atm), magnetite is the first phase to fully solidify at 1590°C . Then at 1365°C , the hematite phase solidifies and co-exists with magnetite.

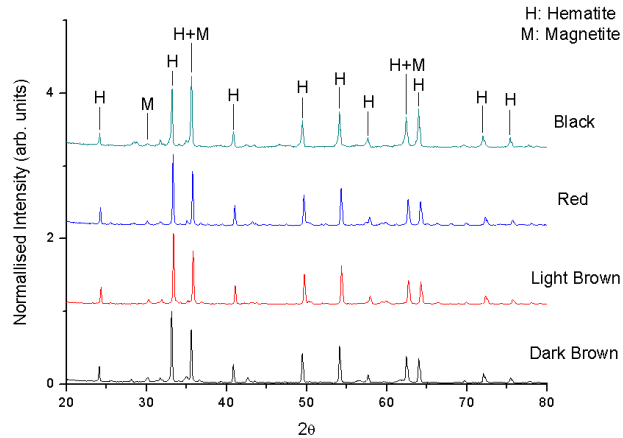


Figure 19 XRD traces of black, red, light brown, dark brown colour deposit surfaces

Temperature Profile

Cross-sectional and surface SEM analyses on the deposits reveal their microscopic features. At this point, the surface discolouration can be categorized into darker colour and lighter colour deposit groups based on the explicit microscopic features. Darker deposits include black and dark brown whereas lighter deposits include red and light brown colours. Flagstone-like plates were only observed on the darker deposit surfaces whereas granular surfaces were mostly observed from lighter deposits. Evidence of sintering is observed in the darker deposit layers but not on the lighter deposits suggesting that the darker colour deposit covered regions experience higher temperatures for longer. This is in agreement with the observations of TGO thicknesses.

From the visual inspection, darker deposits (black and dark brown) were normally found near the pressure side leading edge and trailing edge of the vanes observed. However, in some cases, black deposits were also observed on the pressure side face such as Vane C which had coating spallation at the pressure side leading edge. The pressure side leading edge and trailing edge of the nozzle guide vanes are the potential sites for coating spallation. XRD analyses at the surface of the deposits across the pressure side have discovered co-existence of magnetite and hematite phases. The $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ pressure-temperature phase diagram adapted from Chiang et al. [9] (Figure 20) is used to correlate the range of TBC surface temperature. The predicted TBC surface temperature in these regions could be reaching as hot as 1365°C.

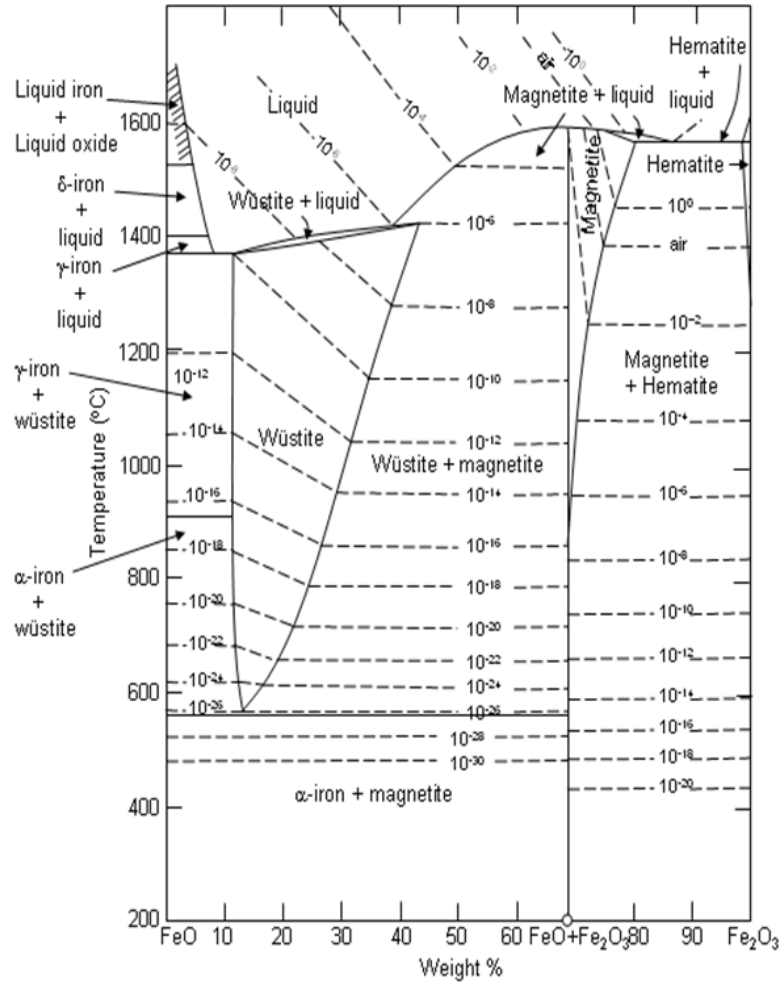


Figure 20 Fe₂O₃/Fe₃O₄ pressure-temperature phase diagram [9]

Conclusion and Future Work

Fe-rich chemical deposits from land-based CCGTs have been characterised. In contrast to CMAS, (the main chemical contamination experienced in aerospace applications) these iron oxides neither penetrate through the TBC nor dissolve yttrium content from the YSZ. There is no direct evidence that iron oxide deposits would lead to early coating failure of the TBCs; however, the surface discolouration has a direct relationship with important TBC surface conditions such as temperature and oxygen partial pressure. Regions covered by dark colour deposits are generally hotter than regions covered by light colour deposits. Cross-sectional SEM analysis has revealed a sintering effect and rapid TGO growth under the dark colour deposits. Surface images reveal flagstone-like plate and granular surface configurations with the former correspond to hot surface and later

correspond to cool surface. XRD analyses have identified hematite and magnetite to be the primary contaminants. Further work is ongoing to fully quantify the surface phases and their relative stability with respect to temperature and pO_2 .

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