EXPERIMENTAL CHARACTERIZATION OF THERMAL BARRIER COATINGS USING MICRO-SCALE BENDING TECHNIQUES

by

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Abstract

Layered thermal barrier coating (TBC) systems incorporate disparate materials, including a yttria-stabilized zirconia (YSZ) top coat, a thermally grown oxide (TGO), and a bond coat, all of which shield the superalloy substrate from high temperature, corrosive and oxidizing environments. There are numerous ways to spall a TBC, but in general top coat spallation is driven by the release of strain energy, which is related to the elastic modulus and the stresses that arise from the difference in thermal expansion coefficients in different layers, TGO growth and top coat sintering. The goal of this study was to measure the top coat modulus to facilitate evaluate of the strain energy in the TBC systems.

Micro-beam bending, resonance frequency and curvature techniques were developed and employed to experimentally measure the Young’s modulus of YSZ top coat manufactured via electron physical beam vapor deposition (EBPVD) and air plasma spray (APS), in both attached and freestanding conditions. The EBPVD top coats were obtained from burner rig bars and a commercial turbine vane with a more complex shape and the top coat modulus was determined as a function of substrate geometry, coating thickness, thermal exposure, and calcium-magnesium-alumina-silicate (CMAS) infiltration.

The moduli of top coats deposited on a burner rig bar were measured to be approximately 30 GPa when loaded in tension and 50 GPa in compression. The modulus of freestanding samples was shown to vary as a function of position; the modulus of the
whole top coat was measured to be 55-60 GPa, while the inner third of the coating that is closest to the bond coat was measured to be 87 GPa. The modulus of top coats infiltrated by CMAS were much higher (~190 GPa) and thermally exposed top coats had moduli that were much lower (7-10 GPa in tension and 15 to 18 GPa in compression). The TBC on the turbine vane had a modulus that varied with position and ranged from 13-20 GPa in tension and 20-60 GPa in compression.

In summary, the modulus of EBPVD 7YSZ top coats has been measured and shown to depend on its unique columnar microstructure. The tension and compression asymmetry originates from the gaps between columns that result from the EBPVD process. The variation of the top coat modulus on the commercial turbine vane is caused by the fact that convex surfaces lead to a more open microstructure, whereas the concave surfaces close the intercolumnar spacing. The local sintering that occurs during thermal exposure further enlarges these gaps and reduces the global modulus. The infiltration of CMAS filled the gaps, leading to a denser and more rigid top coat, whereas thermal cycling accentuated vertical cracking and separation.

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Chapter 1 : Introduction

1.1 Gas turbine

Gas turbine engines or gas turbines burn fossil fuel to propel aircrafts or to generate electricity. There are three main sections in gas turbines: compressor, combustor, and turbine. In a turbojet aircraft engine (illustrated in Figure 1.1), air is drawn from the ambient atmosphere and compressed to a high pressure (30 times that of ambient air pressure) as it passes through the compressor stages [1]. It is mixed with gaseous or liquid fuel in the combustion section and ignited. The hot pressurized gas then continues through the two stages of turbine at the back of the engine. Work is harvested by the expansion of hot gases and is used to drive the first stage turbine that is connected through a shaft to the compressors that draw in more air. After the combustion gases pass through the turbines and out through the nozzle, a thrust is provided to propel the jet forward.

Figure 1.1: Schematic of turbojet engine shows the three main sections: compressor, combustion and turbine [2].
Modern large commercial jetliners are equipped with turbofan engines (Figure 1.2) to generate more thrust and efficiency than turbojets. A bypass fan is incorporated before the compressors to allow more airflow. Coming through the bypass fan, the majority of the air is directed through the three sections in the same way air is directed in turbojet engines. A secondary stream of air bypasses the combustion and is directly exhausted to provide additional thrust. A third stage of turbines is included to power the bypass fan through an independent shaft. Because the thrust is contributed by two streams of air flow, the fuel efficiency is better than that of turbojets [3].

![Figure 1.2: Schematic of turbofan engine shows two streams of air flowing through to provide thrust [2].](image)

Land-based gas turbines for power generation are very similar to turbojet engines in terms of components and principle of operation. Land-based gas turbines also are composed of three parts: compressor, combustor and turbine as shown in Figure 1.3. Air
is pressurized when flowing through the compressor and is mixed with fuel and ignited in the combustor. Its release to the atmosphere drives the turbine to rotate the shaft connected to a generator. The rotation of the shaft transforms kinetic energy into electricity. The temperature of the exhausted gas is still very high (~600°C), so hot gas may be redirected to a steam turbine for additional electricity generation [4, 5]. Although the two types of gas turbine fundamentally work the same way, their differences reside in the operation and design. Components are much bigger in an industrial power turbine. Industrial turbines operate for hundreds of thousands of hours continuously between major overhauls, whereas turbo jet engines operate far less time (~10,000 hours) between overhauls. Weight is less of a concern for industrial turbines but it must be taken into account when designing aero-engines.

*Figure 1.3: Land based gas turbine for power generation shows similar components as an aero-engine [6].*
1.2 Brayton cycle

The operation principle of gas turbines can be described using the Brayton cycle. Developed by George Brayton in 1872, the Brayton cycle is used to explain how work is extracted in gas turbines from a thermodynamic standpoint [1]. A Brayton cycle is composed of four processes that can be represented in a Pressure-Volume diagram as shown in Figure 1.4. Process $a$ to $b$ represents an adiabatic change happening in the compressor stages where air is pressurized. The burning of fuel in the combustor from $b$ to $c$ adds heat to the system with an increase of air volume at a constant pressure. As air is ejected from the nozzle through the turbine from $c$ to $d$ (adiabatic process), work is harvested with a drop of air pressure. At this time, heat is passed on to the surroundings. After that, the system returns to the original configuration and another cycle starts [7].

![Figure 1.4: Brayton cycle is described using Pressure-Volume diagram [8].](image)
The Brayton cycle demonstrates the importance of temperatures in determining the efficiency of gas turbines [8]. The first law of thermodynamics states that energy can neither be created nor lost in an isolated system. Therefore, the total energy change per unit mass after the system returns to $a$ is zero as shown in Eq. 1.1.

$$\Delta u = q_1 + q_2 - w = 0$$  \hspace{1cm} \text{Eq. 1.1}

where $u$ denotes the total energy per unit mass; $q_1$ and $q_2$ symbolize the heat flux out of and into the system per unit mass, respectively; and $w$ is defined as the work done per unit mass. In the case of constant pressure, $q_1$ and $q_2$ can be calculated using the specific heat at constant pressure ($C_p$) and the temperatures at the four states ($T_a$, $T_b$, $T_c$ and $T_d$) as follows:

$$q_1 = C_p(T_a - T_d)$$  \hspace{1cm} \text{Eq. 1.2}

$$q_2 = C_p(T_c - T_b)$$  \hspace{1cm} \text{Eq. 1.3}

The work done can be calculated using Eq. 1.1 to Eq. 1.3. In turn, the efficiency of the system is calculated comparing the heat in-flux and the work done after some rearrangement in Eq. 1.4. Utilizing the relation between pressure and temperature for a reversible adiabatic process in Eq. 1.5, where $P$ is the pressure, $T$ is the temperature and $\gamma$ is the ratio between specific heats at constant pressure ($C_p$) and constant volume ($C_v$), respectively. The thermal efficiency can be calculated using Eq. 1.6.

$$\eta = \frac{w}{q_1} = 1 - \frac{T_d - T_a}{T_b - T_c}$$  \hspace{1cm} \text{Eq. 1.4}
\[
\frac{P^{1-\gamma}}{T^\gamma} = \text{constant} \quad \text{Eq. 1.5}
\]

\[
\eta = 1 - \frac{T_a}{T_b} \quad \text{Eq. 1.6}
\]

The overall efficiency can be calculated using Eq. 1.6, in which the efficiency is determined by ambient temperature \((T_a)\) and compressor exit temperature \((T_b)\). It can be proved that \(T_b\) needs to satisfy the relation in Eq. 1.7 in order for the system to perform maximum work.

\[
T_b = \sqrt{T_a T_c} \quad \text{Eq. 1.7}
\]

Substituting \(T_b\) using Eq. 1.7, the thermal efficiency of the system can be calculated in Eq. 1.8.

\[
\eta = 1 - \frac{T_a}{\sqrt{T_c}} \quad \text{Eq. 1.8}
\]

With the surrounding temperature being relatively stable, the efficiency of a turbine engine depends on the turbine inlet temperature. Accordingly, efficiency of gas turbines is raised when the turbine inlet temperature is increased [9].

1.3 Working environment

The working environment inside a gas turbine is extremely harsh, especially in the combustion section. The components are exposed to a mixture of corrosive and oxidizing gases mixed with fuel under extremely high temperatures. Kerosene, a
hydrocarbon liquid mixture, is used to power jet engines. The presence of contaminants such as sodium and potassium in Kerosene reacts with sulfur oxides from combustion gases to form corrosive alkali sulfate (Na$_2$SO$_4$, K$_2$SO$_4$), which follows the gas path and deposits on the surface of turbine blades to cause corrosion [10-12]. Corrosion is also present in gasified or liquefied coal-based electricity generation. High turbine inlet temperature is pursued to boost thermal efficiency of gas turbines. The turbine inlet temperature can reach ~1600°C on some jet engines and ~1370°C for gas turbines in power generation [1, 13, 14]. Moreover, turbine inlet temperature is not constant during different stages of a flight in the case of jet engines. Climbing usually requires higher thrust than cruising, which in turn requires operation at a higher temperature to extract more work. By comparison, the turbine inlet temperature in industrial gas turbines is relatively stable with less fluctuation for an extended period of time, usually in the order of tens of thousands of hours of operation [7]. These conditions alone are very demanding on the materials used for turbine components.

Furthermore, turbine components experience cyclic thermal-mechanical fatigue throughout their service life with engine start-up, operation and shut-down. During turbine operations, the components are under high temperature creep loading with compressive stresses induced by both thermal expansion mismatch between the top coat and substrate and TGO growth. Besides, high-speed rotation in the turbine blades (35,000 rpm) imparts a centrifugal stress on the turbine blades [15-19].
1.4 Materials

The long-term durability and efficiency of gas turbines pose high requirements on the selection of materials for gas turbine components. The structural material used for the components has to be not only oxidation and corrosion resistant but also is expected to have excellent creep and fatigue properties at high temperatures. The demand of increasing the turbine inlet temperature to boost efficiency adds another constraint in choosing materials for components at the turbine section. Nickel-base single crystal superalloys exhibit superior strength and performance under high temperature and are extensively used in the combustion and turbine sections [20-22].

In the past 30 years of superalloy development, there has been an increase in the maximum allowable temperature from one generation to the next (Figure 1.5). The third generation superalloys have a temperature capability exceeding 1000°C, which is still below the modern turbine inlet temperature. The introduction of TBCs into gas turbines in combination with convective cooling methods has successfully lowered the superalloy temperature and kept it within a safe operational limit [17]. TBCs primarily refer to 6~8% wt. yittria-stabilized zirconia top coats as the main thermal insulators. Aluminum-rich bond coats also were included [17]. TBCs are applied to many components, such as combustor liners, vanes and blades. The spallation of the top coat limits the thermal protection function of TBCs, which exposes the superalloy to high temperatures and accelerates its failure. Forced cooling adds another measure to lower the superalloy temperature by flushing air on the back surface. The primary “cost” of using cooling air to cool the internal or backside of components is the loss of cycle efficiency by
compressing air and not effectively extracting the work of that compression through the turbine expansion stages. Consequently, the forced cooling could be counter-effective in pursuit of thermal efficiency by lowering the turbine inlet temperature from the introduction of cold air to turbines [23].

![Diagram showing the development of thermal protection system over decades. Brown line represents the development of Ni-base superalloy; Green line indicates the role of thermal barrier coatings in boosting the thermal tolerance. Red line shows additional increase of the high temperature ability with the introduction of metal side cooling [9].](image)

Further improvement of Nickel-base superalloys has reached a bottleneck because the service temperature has approached the melting point of Nickel (1455°C). Replacing Nickel with other refractory metals is also not applicable because of its superior oxidation resistance capability [24]. The effect of cooling must be balanced between maintaining
high turbine inlet temperature and achieving a low substrate temperature. Thus, there is still room to improve TBCs. Considerable effort has been invested in the understanding and mitigating of TBC spallation. The understanding of its spallation mechanisms contributes to the identification and elimination of life-limiting factors. Furthermore, the benefit of TBCs thermal shielding can be maximized if the spallation can be predicted accurately. Currently, the turbine components design is conservative. The recommended service conditions will not cause component failure in the absence of TBCs before the next inspection. Reliable life prediction methods help increase the confidence of components design and achieve greater TBC performance [25].

1.5 Dissertation overview

Knowledge of the top coat in a TBC system modulus is critical to study the failure mechanisms and to develop life prediction models for TBCs. This study focuses on the experimental evaluation of the top coat modulus. Substrate geometry, thermal history and CMAS contamination also were studied to determine their influence on the top coat modulus.

This dissertation is organized in the following manner: Chapter 2 introduces the individual layers in TBC systems including their composition, function and a brief history of development. TBC failure mechanisms are discussed, and a review of current experimental characterization techniques is given. Chapter 3 describes the samples and experimental approaches in general. The operating procedure of a resonance frequency
and curvature technique to evaluate as-deposited top coats is also covered in Chapter 3. Chapters 4 and 5 presents the results of investigation of attached top coats using a novel micro-bending technique and evaluation of the modulus variation of top coat of real engine hardware with a complex geometry. Chapter 6 outlines the study of freestanding top coats as a function of thermal exposure and CMAS contamination using a three point bending method. A summary and conclusion of this study are given in Chapter 7 with possible directions for future exploration.
Chapter 2: Background

2.1 Thermal barrier coating systems

2.1.1 Introduction of a TBC system: Layers and functions

TBCs are multilayer architectures added onto turbine components after they have been manufactured to conform to the complex shapes. Current commercial TBC systems are comprised of four layers as shown in Figure 2.1: (a) a yttria-stabilized zirconia (YSZ) top coat; (b) an intermetallic bond coat; (c) a Ni-base superalloy substrate; and (d) a thermally grown oxide (TGO) between the top coat and bond coat, which grows progressively in thickness over the service life of the coated components. The application of TBCs allows a high turbine inlet temperature while keeping the substrate temperature significantly below its melting point.

![Figure 2.1: Schematic of a TBC system consists of four layers [26].](image)
Top coat. Various materials have been selected during the historical development of top coats. Frit enamel was the earliest ceramic coating for thermal protection of metals in the 1950s [27]. Alumina and zirconia-calcia were used afterwards [27, 28]. The high thermal conductivity and cracks induced by phase transformation in Alumina have hindered its further use for thermal barriers [29]. Intermetallic overlay coatings developed in the 1960s were another choice for top coats to protect superalloys from oxidation by forming an oxide layer at the outer surface [30]. In the 1970s, YSZ was adopted as the top coat material [27]. Currently zirconia is used for most commercial top coats because of its high melting point (2700°C) and low thermal conductivity. These intrinsic physical properties of zirconia ensure stability at high temperatures and reduce heat transfer. However, the transformation of zirconia from tetragonal to monoclinic when cooled down to room temperature was shown to be detrimental because the associated volume shrinkage up to 3~4%, which leads to cracking. To inhibit the phase transformation, yittria is added to zirconia as a stabilizer to hinder the transformation. Experimental studies showed zirconia top coats stabilized by 6~8% yittria to experience the longest life under cyclic thermal exposure, whereas the life of zirconia top coats with both low (4%) and high (11,17 and 24%) yittria was shorter [31, 32]. This observation is explained using toughness of YSZ top coats with different yittria contents. Although 4% yittria produces a transformation toughened top coat measured with high toughness (210 J/m²), the toughness does not maintain under turbine service temperatures. A 12% yittria tranforms zirconia to a cubic phase, at which the toughness is only 6 J/m². The toughness of 6~8% YSZ is measured to be between 45 to 170 J/m², which is still retained at high temperatures [33-36].
YSZ top coats are manufactured by two major deposition techniques: air plasma spray (APS) and electron beam physical vapor deposition (EBPVD). In APS, YSZ particles are melted in a DC arc and are accelerated towards the substrate. Layers of splats are formed when particles of molten YSZ hit the substrate sequentially and bond with each other when solidified [37]. Figure 2.2(a) shows a schematic of APS top coat morphology. Each grain is elongated parallel to the top coat and bond coat interface. Micro-cracks and open porosity lie between the grains, which can be engineered to lower the thermal conductivity and increase strain tolerance. The APS technique also can produce dense, vertically cracked top coats. A denser top coat is sprayed to lower the thermal conductivity, and the strain tolerance is provided by the generation of vertical cracks from the shrinkage in the top coat after spraying [38, 39].

In the EBPVD process, high energy is supplied from an electron beam to evaporate the YSZ and directs it towards the substrate [40]. The EBPVD technique produces columnar top coats as shown in Figure 2.2(b). The top coat columns are aligned perpendicular to the top coat bond coat interface with spaces between neighboring columns. This feature allows for a higher in-plane strain tolerance, making EBPVD top coats generally more durable than those made using APS.
Figure 2.2: Schematics of (a) APS top coat, (b) EBPVD top coat [41].

The columnar structure of the EBPVD top coats can better accommodate the deformation imparted from the underlying substrate, thus providing a longer service life span. However, the cost of manufacturing is high, so EBPVD top coats often are used only in critical applications such as jet engines where there is more temperature fluctuation during service [27]. Even though APS top coats are less durable, the low cost APS top coats are applied in gas turbines for power generation where components see a long-term isothermal exposure condition with less temperature variation. Also, EBPVD top coats are thinner (~125 µm) than APS top coats (~300 µm to 1000 µm) because size
and weight are more of a concern in aircraft engines than in gas turbines for power generation [17].

**Bond coat and TGO.** Bond coats are designed to protect the underlying superalloy substrate from high temperature oxidation. Because YSZ is oxygen transparent, a thin Al$_2$O$_3$ layer forms at the top coat/bond coat interface when oxygen reacts with the Al in the bond coat layer. The formation of an Al$_2$O$_3$ layer is facilitated by the presence of high content of Al in the bond coat. The Al$_2$O$_3$ layer is called a thermally grown oxide (TGO), thickness of which increases (from 1 to 4~5 µm) after thermal exposure [42]. The dense TGO layer has a very low rate of oxygen diffusivity, so it serves as an environmental barrier to prevent the oxygen and other detrimental gases from traveling deeper into substrate and causing damage. The TGO is subjected to very high thermally induced stresses (3~6 GPa) when the TBC system is cooled to ambient temperature because of its low CTE and high modulus [43]. The release of these stresses jeopardizes the integrity of TBC systems. In addition, the bond coat also serves as a transitional layer between the ceramic top coat and superalloy substrate to improve top coat adhesion [26, 43-48].

There are two types of bond coats commonly used in TBC systems: diffusion aluminides and overlay MCrAlY (where M stands for Co or Ni or both). Diffusion aluminides bond coats (β-NiAl) are created in a process called pack cementation [44, 49]. Superalloy parts are immersed in a mixture of aluminum, alumina and ammonium halide at a high temperature (800~1000°C). Aluminum halide is formed in the mixture and deposits aluminum on the substrate surface. The interdiffusion between nickel and
aluminum on the substrate surface forms the bond coat. The addition of platinum was found to facilitate the diffusion of aluminum into the substrate and improve the oxidation resistance of the formed bond coat [50]. MCrAIY bond coats are produced by a wide variety of techniques, which include plasma spray and its variants: vacuum plasma spray (VPS), low pressure plasma spray (LPPS). The EBpVD process was also utilized to manufacture bond coat [44]. The advantage of MCrAIY bond coats over diffusion bond coats is the flexibility of tuning the material according to specific failure mechanisms because it contains more elements. Additionally, the MCrAIY is less reliant on the reaction with substrates to produce, so a thicker bond coat layer can be made from deposition.

**Superalloy substrate.** Nickel-base single crystal superalloy is the material of choice for components in the hot sections of the gas turbine such as the combustor and the turbine blades. The chemical composition of Nickel-base single crystal superalloy contains as many as 11 elements. The primary strengthening phase in the FCC Ni (γ phase) matrix is Ni₃Al (γ’ phase) [51]. Ni₃Al has a lattice parameter closely matching the matrix, which promotes homogeneous and coherent precipitation. The strength of the Ni matrix is improved due to the increased flow stress of the γ’ phase with temperature (up to 750°C) [21]. Ti, Ta, and Nb also are added to form γ’. Mo, W, Nb, and Re are added for solid-solution strengthening of the γ phase, and Cr, Y, and La contribute to the improvement of oxidation and corrosion resistance [21, 52, 53].

Alloying development has enhanced the high temperature capability and performance of Nickel-base superalloys. For example, the high temperature capability
was improved in PWA 1484 (a second generation Nickel-base superalloy) by 50°F (27.5°C) with the increase in total weight percentage of refractory metals compared to its predecessor PWA1480 (a first generation superalloy). PWA 1480 has 16% of refractory metals (4% W and 12% Ta), whereas PWA 1484 contains a total of 19.7% of refractory metals. To be more specific, the weight percentage of W is increased to 6% and Ta was adjusted to 8.7% with the addition of two more refractory metals (2% Mo and 3% Re). In third generation Nickel-base superalloys such as René N6 and CMSM-10, increases in the amount of Re up to 6% provide another 30°C of improvement compared to the second generation superalloys [52, 54]. The creep properties of the superalloys also were strengthened by alloying. The rupture life of PWA 1484 is increased by almost four times compared to that of PWA 1480. Tested under a constant stress of 36 ksi (248MPa) at 1800°F (982.2°C), PWA 1484 ruptured at 350 hours whereas PWA 1480 failed at 90 hours. Extracted from the plot in Erickson’s work [55], the rupture life of CMSX-10 is ~1000 hours under the same test conditions. However, all of their rupture lives fall dramatically with further increase of temperature. With a 50°F (27.5°C) increase in the testing temperature to 1850 °F (1010°C) under 36 ksi (248MPa), the life of PWA 1480 dropped to 30 hours and PWA 1484 dropped to 117 hours [54]. The rupture life of CMSX-10 was also shortened to ~400 hours at 1010°C from the same plot by Erickson [55].

The upgrading of manufacturing technology also promotes the development of superalloys [7]. The early stage superalloys were wrought due to their relatively lower strength compared to those from present day. As the strength of superalloys increased,
they were manufactured using conventional investment casting of molten superalloys in molds to shape them. This technique produces polycrystalline superalloys, in which the grain boundaries facilitate crack initiation under high temperature creep loading. Later on, directional solidification produced elongated grains with the removal of grain boundaries perpendicular to the loading direction. The introduction of single crystal superalloys leads to the complete removal of grain boundaries now, and the high temperature capability and strength are improved [53].

2.1.2 Failure mechanisms

Six types of failure modes have been identified in TBC systems for both laboratory-tested samples and real engine hardware [56]. The six failure modes can be categorized further as intrinsic and extrinsic based on the type of failure observed (as shown in Figure 2.3). The intrinsic mechanisms show failure occurring near the TGO layer. Rumpling is the first mode, which exhibits an undulated TGO layer after thermal cycling. The undulation of the TGO causes local separation along the TGO/top coat interface. In a microscopic sense, the undulation of the TGO layer is inferred to be the consequence of strain energy release locally [26]. The thickness of the TGO layer increases with the thermal exposure from the reaction between the diffusing oxygen and the aluminum in the bond coat. Because a TBC system contracts when it is cooled down, the TGO layer undergoes tremendous compressive stress on the order of 2-3 GPa due to its relatively low CTE and high modulus (~360 GPa), resulting in a large strain energy
stored [57]. Because the TGO is bonded to the bond coat, it tends to become undulated in order to increase its overall length to reduce strain energy [42, 58-60].

**Edge delamination** is the second mode, which happens at the TGO/bond coat interface when the TGO layer detaches from the bond coat due to loss of adhesion. The degradation of the interface is explained by the segregation and migration of sulphur to the TGO/bond coat interface, causing it to become brittle. The toughness of the interface is lowered due to the embrittlement and debonding is driven by strain energy release [61]. The roughness of the interface serves as a stress concentrator, increasing the propensity for the debonding to happen [62]. Another interfacial degradation at the top coat/TGO interface is associated with aluminum depletion. The formation of spinel in the absence of aluminum accelerates the oxidation of the bond coat and deteriorates the interface [63].

**Voids** are formed in the bond coat layer and expose the bond coat in the third mode [64]. The formation of voids in β-NiAl bond coats has been attributed to a bond coat volume reduction. Three diffusion processes happen in bond coats and are described as: aluminum diffuses outwards from the bond coat to form the TGO layer; aluminum also diffuses into the substrate; and Ni diffuses from the substrate to bond coat. The product of the three diffusion processes is the formation of γ′-Ni₃Al in the bond coat and depletion of aluminum to form a TGO. The β-NiAl to γ′-Ni₃Al transformation in the bond coat considerably reduces its volume [56, 63, 64].

All three failure modes lead to top coat spallation with the formation, propagation and coalescence of cracks and voids driven by the strain energy built up in TBCs together
with the degradation of the top coat/TGO or TGO/bond coat interfaces. Strain energy is accumulated in TBCs from a mismatch of the thermal strains between the materials at the interface experiencing thermal cycling.

Three extrinsic mechanisms involve TBC failure from interactions with the environment. **Erosion** is caused by small particles that are drawn from the inlet and travel though the combustor and directly hit the top coat surface of turbine blades. The impingement of small particles on the top coat surface gradually removes the TBC. The erosion rates of EBPVD and APS top coats were measured experimentally after being impacted with 60-100 µm alumina or silica particles at room temperature and 910°C by Nicholls [65]. The results showed that EBPVD top coats have better erosion resistance than APS top coats under either temperature due to the poor bond between the splats of APS top coats [65]. **Foreign object damage** refers to the local impact damage from larger particles that transfer higher momentum to the top coat. The top coat damage is more severe in this case with cracks throughout the top coat thickness near the impact region. **CMAS molten deposits** occur as a result of dust- and sand-rich environments. Upon heating above 1200°C, many environmental deposits create a low melting eutective know as CMAS. When such material is deposited on the top coat surface, the molten eutectic infiltrates the porous top coats, changes chemistry, and generates a dense region with high local stiffness and high stresses upon cooling. Strain tolerance is comprised in this dense region and spallation is more likely after CMAS penetration [66-68].
Figure 2.3: Schematic classification of TBC failure mechanisms has been identified from lab tested samples and real engine hardware [56]
2.1.3 TBC life prediction methods

Life prediction is essential to bring TBC systems to their full potential. Its importance is based primarily on the avoidance of coating loss and partly on the high cost of manufacturing of TBC-coated parts [17]. Successful life assessment promotes a reliable design of TBC systems and avoids early replacement of parts in the operation stage. It also would allow for higher turbine inlet temperature. However, the development of life prediction methods is a complicated task especially since TBCs are highly interacting multilayer systems with disparate properties that evolve with thermal exposure.

A brief review of the development of life prediction methodologies highlights the importance of mechanical properties of the top coat. Historically, the TBC life prediction method is somewhat empirical. Hillery et al. [69] proposed a simple model for a furnace cycle test (Figure 2.4(a)) such that.

\[
Cycle\ life = 400(GF)(CF)(TF)(BF)-100(PF/FT)
\text{Eq. 2.1}
\]

where GF is the geometry factor (Button = 1, cylinder = 1/3); CF is the bond coat creep factor and is a function of creep strength; TF is the temperature factor (2000°F = 1, 2075°F = 1/3, 2150°F = 1/8); BF is the bond coat application factor (LPPS = 1 and APS = 1/2); and PF and FT are the TGO thickness before test and at failure.
Later, power law fatigue models were developed to predict the remaining life of TBCs [70-72]. Meier [70] proposed that TBC life is assessed from the ratio between the cyclic plastic strain and a single cycle failure strain in the top coat in Eq. 2.2.

$$N = A \left( \frac{\Delta \varepsilon_p}{\Delta \varepsilon_t} \right)^{-b}$$  \hspace{1cm} \text{Eq. 2.2}

where $N$ is the number of cycles to failure; $A$ is a constant assumed to be 1; and the value of $b$ depends on the material. $\Delta \varepsilon_p$ is the cyclic plastic strain, and $\Delta \varepsilon_t$ is the single cycle failure strain in the top coats. In this model, TBC durability is assumed to be dictated by the magnitude of cyclic plastic strain and growth of the TGO. The cyclic plastic strain is a combination of transient strains upon heating and cooling and the CTE mismatch strain, in which the elastic strain is subtracted. The single cycle failure strain of the top coat combines the failure strain in the as-deposited stage and a coupling term of TGO growth and plastic strain. The material of the top coat is assumed to be elastic-perfectly plastic. No differential between compression and tension in the material behavior was taken into account.

Recently, a more complicated model was developed using the Finite element (FE) method, in which thermally induced residual stress is assumed to drive the top coat spallation and is calculated as a function of accumulated thermal cycle time. Busso et al. [73] developed a model based on a TBC system composed of a MCrAlY bond coat, an EBPVD 7YSZ top coat, and a CMSX4 substrate. Threshold stress representing global failure was set as the TBC failure criterion, which was measured experimentally using Raman spectroscopy. The remaining life of TBCs was predicted by the additional thermal
cycles for the residual stress to reach the threshold value. The model takes into account the evolution of the top coat due to sintering, bond coat creep, and TGO morphology in calculating the residual stresses. Time- and temperature-dependent mechanical properties of the top coat and a steady state bond coat creep were assumed during the analysis. The TGO morphology was measured from the cross-section of TBCs after thermal cycling.

A mechanistic approach demonstrated in Figure 2.4(b) is proposed by the Hemker group. This method is more quantitative as compared to the empirical furnace cycle time test by evaluating the degradation of the interface using interfacial toughness and the strain energy release rate. The interface deteriorates after thermal exposure, which causes the interfacial toughness to drop, while the strain energy release rate increases over time. For all continuum mechanics-based models, the elastic modulus of the YSZ top coat is needed to evaluate the energy release rate and interfacial toughness.
2.2 Experimental measurements of top coat modulus in the literature

It is important to have the capability to experimentally measure the modulus of the top coat as an input parameter for life prediction. Any assumptions of the top coat modulus might not reflect the real behavior and might lead to error in further usage. However, it is challenging to experimentally measure the top coat modulus because of its small scale. The thickness of top coats is on the order of only a few hundreds of micrometers, and it is extremely brittle. As such, a small scale test technique capable of capturing the elastic response of top coats before brittle failure is required.

Several experimental techniques have been employed to measure the elastic modulus of materials. Micro- and nano-indentation can be used to evaluate the
mechanical response of materials at small scales [75]. A permanent deformation left upon unloading makes the technique virtually nondestructive. The mechanical properties (Young’s modulus, hardness) of homogeneously elastic materials can be extracted analytically based on the load and deflection information from the tests [75-77]. **Resonance frequency technique** has been used to measure the elastic modulus of isotropic and homogeneous materials [78]. Either impulse or continuous excitation is provided to a prismatic beam sample and causes it to vibrate in the flexural mode. Resonant frequency is measured to determine the elastic modulus with the knowledge of the mass and geometrical dimensions of the beam. **Beam bending** is advantageous in testing brittle materials [79]. Larger deformation can be achieved before brittle failure compared to uniaxial tensile and compressive tests. Analytical solutions for beam deflection are developed to extract the elastic modulus of the material [80, 81]. On the other hand, the disadvantage of bending includes the creation of a complex stress state across the thickness of the sample. The large deflection may induce nonlinear elastic behavior in the material. The friction between the pins and the sample can also affect the stress distribution [82].

A literature survey of the top coat modulus measured by different techniques was carried out, and the results were summarized. Table 2.1 presents the moduli from literatures for the EBPVD top coat. The modulus results from indentation experiments usually are the highest and have a large scatter. The indentation probes a localized stiffness response. Indenting on intercolumnar gaps, cracks, and pores produces lower modulus than those on solid areas in YSZ top coats, which also can be used to explain the
scatter in the data. The sizes of the indent also play a role in the stiffness response, in which large indents covering more columns and the gaps in-between result in a lower modulus than that from small indents [83]. Besides, the elastic modulus of EBPVD top coats also has been found to depend on indentation depths, with a higher indentation depth yielding a lower modulus than that of the lower depth [83-85]. The YSZ top coat modulus is contributed from the interactions between the stress field underneath the indentor and microstructural features such as intercolumnar cracks and pores below the test location. The deeper the indents, the more of those features are sensed by the stress field, affecting the stiffness response [86]. Furthermore, the EBPVD exhibit a higher stiffness response in out-of-plane direction than from in-plane, indicating that the top coats are anisotropic. The anisotropy of EBPVD top coats can be explained by the deformation mode of the columns. Out-of-plane indentation mainly compresses the columns along their length, whereas in-plane indentation bends the columns laterally. The indentation depth dependency of the YSZ top coat modulus can be explained from a microstructure point of view. The indentation results could be affected by so many factors and could be difficult to represent the macroscopic behavior of the top coat.

The results from the resonance frequency technique were shown to be affected by the microstructure of the top coat from different deposition conditions. This technique evaluates a macroscopic top coat when still attached, which resembles the configuration of real engine hardware, but it does not differentiate the stiffness response under tensile and compressive loadings. Sensitivity of the instrument and sample temperature was later found to affect the results substantially in Chapter 3. A comparison of the three
techniques shows that beam bending has advantages in measuring the top coat modulus. The beam bending technique measures the lowest modulus because it probes a macroscopic in-plane behavior of YSZ top coats, which is more appropriate to represent the performance on real engine hardware. The deformation in bending can be tailored with respect to the top coat orientation. However, report of using the technique to study EBPVD top coat has been rare. Only two examples were found: Wang et al. [87] tested freestanding EBPVD 8YSZ top coat beams using the three-point bending technique. Pfeiffer et al. [88] tested freestanding as well as attached EBPVD YSZ top coats using a four-point bending method. More data needs to be collected to gain a comprehensive understanding of the stiffness response of EBPVD YSZ top coats.

Table 2.2 shows the literature moduli for APS top coats. The scattering and larger modulus of APS YSZ top coats from the indentation method could be explained by the interaction between the indentor and inter-splats cracks and pores using the same rationale. The cylindrical punch indentation only measures the compression modulus, but the beam bending results show that the tension modulus is different from the compression modulus. There are more literature reports for the APS top coat modulus using beam bending technique. Thompson and Clyne [89] used the cantilever test on freestanding APS 8YSZ, and measured a low value of 10 GPa. Another low value was reported by Tang et al. [90], who attribute it to the weak bonding between the splats. Schwingel et al.[91] used a four-point bending test on freestanding plasma sprayed 7-8YSZ, and found different stiffness response of YSZ top coats when tested in two directions within the coating plane. Top coats are more rigid under compression than tension, which was
explained by the cracks segregation along the thickness of the top coat. However, the quantification of modulus was absent. A comparison of bending results between the APS and EBPVD top coats has shown that the APS has higher modulus.

*Table 2.1: Literature review of EBPVD top coat modulus measured using different techniques.*

<table>
<thead>
<tr>
<th>Technique</th>
<th>Top coat</th>
<th>Young’s modulus (GPa) In-plane</th>
<th>Out-of-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YSZ [83]</td>
<td>81.16</td>
<td>151.88</td>
</tr>
<tr>
<td></td>
<td>4YSZ [84]</td>
<td>53.3</td>
<td>142.8</td>
</tr>
<tr>
<td>Indentation</td>
<td>4YSZ [92]</td>
<td>80~200</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>4YSZ [93]</td>
<td>126</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8YSZ [86]</td>
<td>129.8</td>
<td>-</td>
</tr>
<tr>
<td>Resonance</td>
<td>YSZ[94]</td>
<td>76.7~116</td>
<td>10.3~19.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15.3~50.9</td>
</tr>
<tr>
<td>Beam bending</td>
<td>8YSZ (FS)[87]</td>
<td>5~10</td>
<td>-</td>
</tr>
<tr>
<td>(3pt and 4pt)</td>
<td>YSZ (FS)[88]</td>
<td>17</td>
<td>-</td>
</tr>
</tbody>
</table>

*Table 2.2: Literature review of APS top coat modulus measured using different techniques.*

<table>
<thead>
<tr>
<th>Technique</th>
<th>Top coat</th>
<th>Young’s modulus (GPa) In-plane</th>
<th>Out-of-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indentation</td>
<td>7-8YSZ[95]</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7YSZ[96]</td>
<td>94~146</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7-9 YSZ[97]</td>
<td>64</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8YSZ[98]</td>
<td>122</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8YSZ[89]</td>
<td>140~150</td>
<td>-</td>
</tr>
<tr>
<td>Cylindrical Punch Indentation</td>
<td>8YSZ[99]</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>Beam bending</td>
<td>8YSZ[90]</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>(4pt and cantilever)</td>
<td>8YSZ[89]</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7-8YSZ[100]</td>
<td>15~40</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>6-8YSZ[101]</td>
<td>40~61</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7-8YSZ[91]</td>
<td>2.5~20</td>
<td>-</td>
</tr>
</tbody>
</table>
In this study, the elastic modulus of EBPVD 7YSZ top coats was probed using custom micro-scale beam bending techniques. This technique employed novel sample designs, which subjected the top coat to both macroscopic tensile and compressive deformation. Digital image correlation (DIC) was used to extract the deflection of top coat beams. The experimental results were interrogated with Finite element (FE) analysis and analytical solutions when applicable.
Chapter 3 : Experimental methodologies

3.1 Production of commercial TBC samples at Pratt & Whitney

A commercial TBC system that was manufactured at Pratt & Whitney was provided by Dr. Mike Maloney and Brian Hazel for this study. All coatings were deposited on a PWA1484 Ni-base single crystal substrate with a low pressure plasma sprayed NiCoCrAlY bond coat. The nominal composition of the bond coat is 40.4 at.% Ni, 18.8% Co, 16.4% Cr, 23.3% Al, 0.3% Y, 0.1% Hf and 0.7% Si [102-104]. A thin TGO (< 1µm) was observed between the top coat and bond coat of the as-deposited samples. The TGO is reported to consist of two layers: the inner layer closer to the bond coat is α-Al₂O₃, which mainly contains Al and O with small amounts of Y; the outer layer closer to the YSZ top coat could be γ-Al₂O₃, containing Al, O, Y, Hf, Cr, Co, Ni and S [105]. The 7YSZ top coat was manufactured by EBPVD process.

The samples were received in three forms: 12 mm diameter burner rig bars, wedge-shaped burner rig bars with two flat grooves machined into them, and a PW2000 2nd stage turbine vane. All samples were received in the as-deposited condition without subsequent thermal exposure. Burner rig bars are an industrial standard procedure for empirically assessing TBC durability when subjected to thermal cycling [106]. A wedge-shaped burner rig bar used for this study has two inclined straight edges and two curved edges. The burner rig bar is about 20 mm long and the cross-section (Figure 3.1) is 12.75 mm tall and 6 mm wide. The diameter of the curved edges is 12 mm. The layers on this
burner rig bar are shown in Figure 3.2, in which the top coat is 150µm and the bond coat is 110µm on the top of the substrate. The TGO layer between the top coat and bond coat is observed to be less than 1 µm thick and its morphology is tortuous and discontinuous.

Figure 3.1: Cross-section of a wedge-shaped burner rig bar. The light colored area is the superalloy and the grey area around the edge is the EBPVD 7YSZ top coat.
Figure 3.2: Four Layers are presented on the cross-section of burner rig bar.

Figure 3.3: TGO layer is located between the EBPVD 7YSZ top coat and NiCoCrAIY bond coat.
The PW2000 2\textsuperscript{nd} turbine vane has the same TBC system. The substrate geometry of the turbine vane is very complex. The curvatures are different around the turbine vane with a large variation of radius curvature from 313 mm to 4.7 mm. The curvature also varies around the vane from concave to convex. The top coat thickness is also different around the vane due to variable deposition condition. Figure 3.4 shows an example of the layers from the trialing edge. The top coat thickness is 275 \(\mu\)m and the bond coat thickness of 140 \(\mu\)m. the TGO is measured to be less than 1 \(\mu\)m.

![Figure 3.4: TBC system on the trailing edge of Turbine vane.](image)
3.2 Micro-beam bending experiments of attached EBPVD 7YSZ top coats

3.2.1 Overview

Due to the fragile nature of the EBPVD 7YSZ top coats and the difficulties associated with loading in pure tension or compression, the following techniques were developed to characterize them in bending. Three-point and four point bending offer flexibility in testing fragile sample by providing support for the samples without application of any external forces to reduce damage. Bending also tailors deformation through a series of boundary and loading conditions. Both attached and freestanding top
coats were characterized to determine the elastic modulus. Here we talk about the evaluation of attached top coat.

Eberl et al. [107-109] first demonstrated the utility of testing a micro-bridge beam with top coat supported by a thin layer of bond coat. Electron Discharging Machining (EDM) was used to create doubly clamped micro-beams by precisely removing a certain depth of bond coat and substrate leaving behind a uniform layer of top coat supported by a thin layer of bond coat. Using the micro-beam bending method, the modulus of the top coat was measured and calculated analytically by locating the neutral axis of the micro-beam. Fracture toughness of the interface was measured by creating a vertical crack and observing the crack propagation along the interface due to loading.

Wang and Jones [110] developed a methodology for preparing and testing cantilever beams. One coupled end of the bridge beams was cut off to create cantilever. The cantilever beams were tested by pushing down from the top coat free surface side to impose tension and the pulling from the bond coat side to induce compression in the top coats. The boundary condition was relaxed at the free end and allowed the cantilever beams to deflect more than doubly clamped beams under the same load. Preliminary observations of Wang [111] suggested a difference in the elastic response of top coat subjected to tension and compression, which were supported by subsequent measurements by Pandey [112].

The current study employed both bridge and cantilevers fabricated on the same top coat system using the micro-beam bending technique to determine the elastic
modulus of the EBPVD 7YSZ top coats. Finite element (FE) analysis was then used to account for the exact geometry of the specimens and to extract the in-plane elastic properties of the top coat. The elastic modulus systematically verified is used to fit all the tests at the same time for the best match. The technique was first utilized to obtain the top coat specimens cut from the wedge-shaped burner rig bar. With the methodology validated, it was then applied to measure location specific top coat modulus on the commercial turbine vane.

3.2.1 Preparation of samples from EBPVD 7YSZ top coats on burner rig bar

Samples taken from a wedge-shaped burner rig bar were used for the top coat modulus evaluation. The burner rig bar was cross-sectioned at approximately half length to avoid edge effects. The cross-sections were polished to a 1 μm surface finish using diamond abrasive films on a MULTIPREP™ auto-polisher from Allied. The thicknesses of the two specific slices were ~490 μm and ~400 μm, respectively. Micro-beams were designed on the slices and a 3-D illustration of the window on the straight edges is shown in Figure 3.6(a). The green layer is the top coat and the yellow layer is the bond coat on the top of the substrate (silver). The size of the window was 1mm by 1mm with a corner radius of 45 μm. One edge was to be created by uniformly removing 70 μm of bond coat parallel to the top coat and bond coat interface, leaving 40 μm of bond coat. For the curved edge, the edge of the window was designed to follow the curved top coat and bond coat interface with an offset of 40 μm towards the substrate. Through-thickness
windows were designed on both straight and curved edges of the burner rig bar samples as indicated in Figure 3.6(b). Two windows were located on each straight edge and one window is on each curved edges. The two windows are 1.5 mm apart on the straight edges. A 2 mm diameter center hole was included for mounting the specimen on the fixture during experiments.
Wire EDM was used to fabricate the micro-beams. EDM is an electro-thermal process where a plasma channel created from electrical discharge locally increases the temperature of the material above its melting point and the spark erodes the material away. The melting and resolidification process creates a recast (Figure 3.7) layer but does not damage the surrounding materials. The sample is immersed in dielectric fluid during machining and fluid is constantly pumped into a working chamber to create a steady flow and flush the molten material away from the parts. The entire process takes place at a certain frequency to advance the machining. The cutting path is preprogrammed by user and controlled by computer. Due to the interaction with electricity, the material has to be
electrically conductive for the technique to work. The bond coat and substrate are made from metal-based material and are therefore machinable using this process [113].

![Figure 3.7: Recast layer is formed on the bond coat after removal.](image)

The machining of one sample was performed by Viteris, a Utah based company, who has a special micro-wire EDM process that can be used to machine small parts. A second sample was machined by another micro-wire EDM company, Leer technologies. Figure 3.8 presents the micro-wire EDM machine from Viteris used for this study. Since wire EDM is not a self-drilling technique, starter holes were drilled on a CNC mill using a 0.5 mm diameter carbide drill. The location of the starter hole was determined in a CAD file based on the location of the windows. Once the holes were drilled, the burner rig sample was transferred to the EDM and the on-machine optical system shown in Figure 3.9 was used to center the starter hole and located its position relative to the top coat/bond coat interface. A machining code that creates the $1\text{mm} \times 1\text{mm}$ windows with
an allowance of 5 microns was programmed and loaded into the machine controller. As illustrated in Figure 3.10, the alignment can be observed from the camera and by using a crosshair as a reference. After alignment, the wire was manually threaded through the starter hole and the optical system was used to ensure the alignment after some preliminary cutting. Upon verifying the critical dimensions (spacing between the upper edge of the window and the top coat/bond coat interface), the cutting process was restarted to yield a window with the proper depth for the remaining bond coat. The synthetic oil used as the dielectric fluid during machining leaves behind a carbon-rich layer on the machined surfaces. This layer was removed in a 20-minute long ultrasonic bath of acetone.

Figure 3.8: micro-WEDM machine is the MW250 from Viteris Technologies (www.viteris.com).
Figure 3.9: The on-machine optical system is mounted parallel to the EDM wire to increase the precision and the offset between the optics and the wire was pre-determined [113].

Figure 3.10: The on-machine optical system allows the user to perform distance measurements without having to take the work piece out of the machine. This avoids losing reference and yields extremely high accuracy machining results [113].
3.2.2 The Micro-beam bending experiments

Bi-layer bridge beams were created along the edges of the burner rig bar samples. An example of one bridge beam that was prepared and tested by Wang [111] is shown in Figure 3.11(a), note that a uniform top coat on top of a thin bond coat layer. The as-manufactured bridge beams have both ends clamped. Cantilever beams (Figure 3.11(b)) were created by removing one clamped end using a miniature cutting system developed by Jones [114]. Figure 3.12 presents the micro-bridge and cantilever beams on curved edges. A total of 12 windows on two cross-sections of the burner rig bar were fabricated. An example of the window geometry from the sample process by Viteris is show in Figure 3.13. A uniform bond coat layer remained after micro-wire EDM. The remaining bond coat thickness and the corner radius were decreased for the current beam design. The same technique was used to create cantilever beams for this study. However, the bond coat was sheared off during cutting and the top coat was delaminated from the bond coat as shown in Figure 3.14. Several micro-beams were damaged in this way. The cutting of other beams was successful and micro-bending tests were carried out on these beams.
Figure 3.11: (a) Example of post micro-wire EDM Bridge beams is from the previous study (b) Cantilever beam was created by cutting off one end on the bridge beam.
Figure 3.12: Curve beams were used at previous study (a) curved bridge, (b) curved cantilever.
Figure 3.13: Post-EDM windows are shown for the current study: (a) straight bridge beam, (b) curved bridge beam.
Bending forces imposes macroscopic deformation to the top coat of the bi-layer beams. Eberl et al.\cite{108} experimentally demonstrated that the neutral axis in their bi-layer bridge beams was located at the TGO layer. The current bridge beams had similar dimensions and the TGO were assumed to be located at the same place. However, the cantilever beams have a much thicker bond coat layer. Because the bond coat is much rigid than the top coat, it is safe to assume that the neutral axis moves away from the TGO into the bond coat layer. The bridge beams were pulled on the bond coat side only since pushing on the top coat free surface might damage the fragile top coat. The bridge test puts the top coat in the middle of the beam under tension, and the top coat at the two ends is in compression. The cantilever beams were both pulled on the bond coat side and pushed on the top coat free surface. By pulling on the bond coat side during a cantilever
test, the entire top coat was placed in compression. Pushing on the top coat free surface subjected the entire top coat to tension. In both cases, bending results in in-plane tensile and compressive deformation of the top coat, which allows for a direct measurement of in-plane modulus.

A small scale loading frame was developed to test the small and fragile microbeams. The details of the test setup were described by Eberl et al[109]. The experimental test configuration for the current study is presented in Figure 3.15, showing a post-EDM burner rig sample bolted down onto a motorized stage. The motorized stage is installed on the top of a 5-axis stage, which is used to align the beams relative to a small hook. The wedged shaped hook has a 20-µm-wide tip on both sides, providing control of loading on both top coat and bond coat side. The hook is connected to the load cell through an air bearing to eliminate friction. During the experiments, the beams were loaded quasi-statically at a constant rate (150nm/sec) and images of beams were recorded at a rate of 1/sec. The load was recorded at every 0.5 second interval. The maximum load for all the tests did not exceed 1 newton to avoid fracture at top coat.
Figure 3.15: Experimental setup shows the sample rests on a fixture connected to a motorized stage. Hook is connected to a load cell through an air bearing.

Digital image correlation (DIC) and tracking suite (File ID: 12413, Matlab file exchange) created by Eberl [115] was used to analyze the recorded images and extract the deflection of the beam due to external loading. The importance of DIC is that it directly measures the displacements on the samples to avoid correction for the machine compliance. As shown in Figure 3.16, displacements were measured at two places on the beam and used to determine deflection: One was right next to the loading tip of the hook, which accounts for the deflection of the beam at the tip together with the rigid body motion of the entire sample; the other location was on the shoulder away from the beam to correct for the rigid body motion of the sample. The position of the loading hook is schematically pointed out since it is out-of-focus from the images. An area of tracking
consisting of 10 points × 8 points was imposed at both locations with a point to point spacing of 40 pixels (1 μm = 3.81 pixel), covering a rectangular area of ~105μm along the beam depth and ~84 μm along the length. The displacements of the tracking grid were decomposed into X and Y components. The X component accounts for the deflection of the beam. The net deflection of the beam was taken as the subtraction of the averaged displacements from the X component between the two locations. The values of the Y component indicate the rotation of the sample. However, no obvious rotation was observed for the micro-beams, since the Y component was very small as compared to X. Force versus deflection curves for each test was obtained by matching the loading and deflection histories using time as a common variable.

Figure 3.16: DIC tracking locations for the digital image correlation analysis to obtain the net deflection of the micro-beams at the hook. Image was recorded using a 20X objective lens. A schematic of hook to indicate its location relative to the beam during experiments.
3.2.3. Application and limits of beam bending theories

Two widely used theories to model bending of beams are Euler-Bernoulli and Timoshenko. The two theories predict the deflection of beams based on the geometry, loading, boundary conditions and elastic modulus of the beam [80]. The appropriateness of using either of these approaches needs to be investigated before applying the theories to the micro-beams and extracting the elastic modulus of top coat layer. To do that, a few basic concepts need to be understood.

The development of Euler-Bernoulli theory uses the assumption of small deformation. A brief derivation is given as follows. The relation between the radius of curvature $\rho$ at the neutral axis of a bent beam and displacement $w$ and the position along length $x$ is

$$\frac{1}{\rho} = \frac{d^2w}{dx^2} \quad \text{Eq. 3.1}$$

The strain along the thickness can be formulated by assuming a small elongation relative to the neutral axis. When coupled with Hooke’s law, the stress $\sigma$ in the beam is given by

$$\sigma = E \frac{e}{\rho} \quad \text{Eq. 3.2}$$

where $E$ is the Young’s modulus of the material; $e$ is the distance of the offset from the neutral axis. Integrating the stress $\sigma$ times $e$ over the entire cross-section, the bending moment can be obtained from
\[ M = \int \sigma e \, dA = \int E \frac{e^2}{\rho} \, dA = \frac{E}{\rho} \int e^2 \, dA = \frac{EI}{\rho} \]  

Eq. 3.3

in which, \( M \) is the bending moment. The integration \( \int e^2 \, dA \) is the second moment of inertia, often represented by the letter \( I \). When substituting \( \rho \) with Eq. 3.1 and rearranging, the bending moment is related to the displacement as

\[ \frac{d^2 w}{dx^2} = \frac{M}{EI} \]  

Eq. 3.4

The derivation of the equations above essentially assumes a plane problem in which the beam is uniformly loaded along the width. The calculated stress and strain are in-plane as well. The transverse displacement along the beam can be calculated by integrating Eq. 3.4 and the constants are addressed by applying the boundary conditions. There are three assumptions associated with its application: (i) geometrically, the beam has a uniform cross-section along the length; (ii) the beam has a high aspect ratio. (iii) the deflection is small such that each cross-section remains planar after deformation and is still perpendicular to the local neutral axis.

Compared to the Euler-Bernoulli theory, the Timoshenko theory is more rigorous. It relaxes the requirement to have a high aspect ratio by taking into consideration the contribution of the shear force. Accordingly, it is unnecessary for the cross-sectional planes to remain planar. In Timoshenko’s theory, the deflection of a beam has two contributors, one from both bending and one from shear deformation. The contribution of bending is the same as Euler-Bernoulli theory. The shear deformation contribution can be shown to be given by
where \( w_s \) is the deflection due to shear, \( \tau_{max} \) is the maximum shear stress at the cross-section, \( G \) is the shear modulus, \( V \) is the shear force, \( K \) is the correction factor depending on the cross-section (\( K = 6/5 \) for rectangular cross-section), \( A \) is cross-sectional area, and \( v \) is the shear force per unit length. The Timoshenko solution to calculate beam deflection is obtained by superimposing Eq. 3.4 and Eq. 3.5.

The Euler-Bernoulli and Timoshenko solutions were evaluated to understand whether they are proper for modeling the micro-beams. The two solutions for homogeneous beams were derived as a function of aspect ratio. Obtained from the work of Wang [116], Eq. 3.6 to Eq. 3.8 compare the deflections of the two solutions at the loading point for three conditions: (i) a cantilever beam loaded at the free end (Eq. 3.6); (ii) a cantilever beam loaded at mid-span (Eq. 3.7); and (iii) a doubly clamped beam loaded at mid-span (Eq. 3.8).

\[
\frac{d^2 w_s}{dx^2} = K \frac{dV}{AG \, dx} = K \frac{v}{AG} \tag{Eq. 3.5}
\]

\[
W_T = \frac{FL^3}{3EI} \left( 1 + 3 \left( \frac{1}{L/h} \right)^2 \right) = W_E \left( 1 + 3 \left( \frac{1}{L/h} \right)^2 \right) \tag{Eq. 3.6}
\]

\[
W_T = \frac{FL^3}{24EI} \left( 1 + 9 \left( \frac{1}{L/h} \right)^2 \right) = W_E \left( 1 + 3 \left( \frac{1}{L/h} \right)^2 \right) \tag{Eq. 3.7}
\]

\[
W_T = \frac{FL^3}{192EI} \left( 1 + 18 \left( \frac{1}{L/h} \right)^2 \right) = W_E \left( 1 + 12 \left( \frac{1}{L/h} \right)^2 \right) \tag{Eq. 3.8}
\]
where $W_T$ is denoted as the Timoshenko solution for deflection and $W_E$ is the Euler-Bernoulli solution for deflection; $F$ is the applied load; $L$ is the length of the beam; $h$ is the thickness; $E$ is the elastic modulus; $I$ is the second moment of inertia. The three conditions correspond to the experimental configurations of the micro-beams. The results are shown in Figure 3.17. Timoshenko solutions predict much higher deflection when the aspect ratio of the beam is low for all the three cases. As the aspect ratio increases, the two solutions approach each other. The aspect ratio for the micro-beams is highlighted in Figure 3.17, which shows that Timoshenko solution is more appropriate to model the stiffness response of the micro-beams. However, attempts to model the stiffness responses for the micro-beams using Timoshenko solutions have also met several challenges in the current study:

- The theoretical solutions with the clamped ends assume an infinitely rigid boundary. The effect of the boundary is small when the beams have a high aspect ratio, but becomes important when the aspect ratio is low such as for the current micro-beams. The clamped ends on the micro-beams incorporate a curved shoulder on the bottom and a flat top. This geometry is not considered in Timoshenko solution.

- Three layers of materials (top coat, bond coat and superalloy substrate) are involved in the deformation for the micro-beams, each with a different elastic modulus. The Timoshenko solutions were developed under the
assumption of isotropic material. The top coats are not homogeneous or isotropic but can be modeled as a transversely orthotropic material.

- The bending of beams with finite initial curvature also adds to the complexity of the solutions.

Figure 3.17: Comparison of Timoshenko and Euler-Bernoulli beam bending solutions over a range of aspect ratios and for different loading and boundary conditions for homogeneous isotropic material. The Poisson’s ratio assumed to be 0.25 is used to relate the elastic modulus and shear modulus.
Consequently, the utilization of beam bending theories to interpret the experimental results provides an initial estimate of modulus but is neither precise nor robust enough to be used as the only means to determine modulus. By contrast, FE methods offer more flexibility in building models with complicated geometry and allowing more robust interpretation of the experimental results. In FE analysis, mesh models of the beam can be constructed based on the measured geometries of each micro-beam. The employment of FE analysis provided a more quantitative representation of the effects of geometry and boundaries.

3.2.4. Finite element analysis

A parametric study was carried out to demonstrate how the stiffness response of the beams is affected by the boundary conditions and geometry. Another goal was to find the optimum size of models such that the FE calculation was both accurate and computationally efficient. The boundaries for the beam were divided into four sub-components (a. shoulder width; b. substrate depth; c. window height; d. corner radius) for independent analysis.

The model was constructed with the sequential addition of each component after the influence of the previous component was understood. The dimensions were taken directly from the micro-beams. Starting from a doubly clamped bilayer beam, shoulders were added at the two ends in Figure 3.18. The bilayer beam was composed of a 150 µm top coat layer and 40 µm bond coat layer in the beam section with a length of 1mm. The
shoulder was designated as the section at the ends of the bilayer beam. The thickness of the top coat on the shoulder was kept the same and the thickness of the bond coat was 110 μm. A step in the bond coat shows the transition from shoulder to beam.

Both the top coat and bond coat were assumed to be isotropic material only for this study of effect of boundaries and geometry. The top coat modulus was assumed to be 50 GPa and the bond coat modulus is assumed to be 155 GPa, which are used for all the models for this parametric study. A 10 μm mesh size was used for the model. The two edges of the shoulder were fixed and the top surface is free to deform. A 2.5 N load was applied at the mid-span on the bond coat side, and the mid-span deflections of the beam were calculated as the width of the shoulder was increased. The mid-span deflection of the bilayer beam for a number of shoulder widths is plotted in Figure 3.19.
As the shoulder width increases, the beam appears to be more compliant and it deflects more. The deflection increases sharply in the early stage and the rate of increase declines with further widening of the shoulders. The deflection approaches an asymptote when the shoulder width is increased to 0.75mm as shown by a star. The further increase in the width does not change the deflection of the beam but adds to the computation expense, so 0.75 mm shoulder width was used for the subsequent study.

The second step was to add a third material (substrate) below the bond coat layer. The deflection was calculated for various substrate thicknesses. Figure 3.20 shows the FE mesh of the three layers. The fixed boundary condition was extended to the substrate. The
The elastic modulus of the substrate is assumed to be 200 GPa and other conditions were inherited from the last shoulder width in the previous case. The results are shown in Figure 3.21, in which the deflection also followed a similar trend of increasing initially and then reaching a plateau. The last substrate thickness value (1.6 mm) was used for the next study of window height, which has minimum influence of the stiffness response of the beam.

Figure 3.20: FE mesh shows the three layers to study the effect of substrate thickness.
The third parameter to delve into was the height of the window. The substrate is connected on the bottom of the window for the micro-beams. The window height was determined in the design of the beam and it’s also important to understand its influence for establishing an accurate micro-beam model. The other two parameters (shoulder width and substrate thickness) were from the previous two studies. The same loading and boundary conditions were applied on the model as shown in Figure 3.22. As shown in Figure 3.23, beam deflection increased with the height of the window, but the effect is insignificant as compared to the previous two parameters. The solid star shows the actual window height in the micro-beams, which is used for micro-beam models later on. The
fourth parameter is the radius of the window corner as illustrated in Figure 3.24 (a). A close-up look of the corner is shown in Figure 3.24(b). The results in Figure 3.25 shows that a larger radius increases the stiffness response of the beam by lowering the mid-span deflection. Both the corner radii for the current and previous studies are pointed out in Figure 3.25, which shows that the radius for the current window corner has a smaller influence in the stiffness response of the beam.

Figure 3.22: FE mesh to study the effect of the window height in which the bottom of the window is closed by substrate.
Figure 3.23: Effect of window height is very small. The star shows the window height of the micro-beams.

Figure 3.24: (a) Meshed model to study the effect of corner radius; (b) Details of mesh at the corner.
The parametric study demonstrated that understanding boundary conditions and geometry of the micro-beams is critical in modeling the stiffness response of the micro-beams. Any inadequate consideration of those four parameters would cause the extracted top coat modulus to include the contribution from boundaries and geometry. An optimum size of the FE mesh was determined and used to account for the influence of the boundaries and geometry for each specimen. The FE mesh includes a shoulder width of 0.75mm and a substrate thickness of 1.6 mm. The window height and corner radius are measured for each micro-beam.
The material properties are defined for each layer assuming elastic deformation. Both substrate and bond coat were assumed to be homogeneous and isotropic. The material properties were defined for the substrate (E= 200GPa, v=0.25) [117] and bond coat (E=155GPa, v=0.3) [118], respectively. The EBPVD 7YSZ top coats are defined as a transversely orthotropic material in FE analysis. The out-of-plane stiffness response has been shown to be different than the in-plane response using the indentation method [83]. The out-of-plane modulus was measured to be higher than that of the in-plane[119]. A literature survey of the EBPVD top coat modulus found that it has been reported the top coat is more rigid in compression than it is in tension [87, 120]. A UMAT subroutine was used to assign different top coat moduli in tension and compression and was coupled with the FE model during calculation. The out-of-plane modulus is assumed to be 150 GPa [121]. The Poisson’s ratio for the top coat was assumed to be 0.2 for both the in-plane and out-of-plane direction.

UMAT can be used to define either 3D or 2D (plane stress/strain) material. The details of the UMAT could be found in the appendix. The application of this subroutine is to compose a complex, nonlinear mechanical behavior for shell elements. Besides material definition, the subroutine can also be used to input an initial condition of the model. SIGINI is used to define an initial stress state in the model. Subroutines are not necessarily used alone; multiple subroutines can be tied up together in the input. A case in point is that UMAT can be used together with SIGINI during the analysis by assembling them together as one file. As far as the systems are concerned, the installation
of Intel Fortran compiler and Microsoft visual studio are required to run the analysis in ABAQUS with subroutines [122].

3.3 Micro-beam bending experiments of attached EBPVD 7YSZ top coats on a PW2000 2nd stage turbine vane

The variability or homogeneity of the top coat modulus across commercial components is of considerable interest and currently unknown. The micro-bending experiments provide an opportunity to measure the top coat modulus as a function of position and in doing so to study the effect of variations in substrate curvature, deposition conditions and coating thickness.

A PW2000 2nd stage turbine vane was used in this study. Figure 3.26(a), (b) and (c) present the turbine vane from different side views and (d) is a top view. The EBPVD 7YSZ top coat that was deposited onto the substrate is shown as white; the green material is the superalloy. A few slices of the turbine vane were prepared at Pratt & Whitney by sectioning at mid-height. Prior to making further analysis, one piece of cross-section was ground down to a thickness of 450 µm and later polished to 1 µm surface finish using diamond lapping film. The cross-section of the prepared turbine vane slice was reconstructed digitally (Figure 3.27) and was used to determine representative locations of interest on the vane.
A close inspection of the polished cross-section under the optical microscope and the subsequent measurements reveal two things: (i) the radius of curvature along the top coat surface around turbine vane differs significantly in sign and magnitude from one place to another and (ii) the top coat thickness and microstructure also varies from one place to another. To represent the exact positions on the vane, the entire cross-section was reconstructed using AutoCAD based on the dimensions taken under an optical microscope.

Figure 3.26: PWA2000 2nd stage turbine vane seen at different sides. The four letters indicates the locations of interest for the top coat modulus.
microscope, see Figure 3.27. The radii of curvature presented in this figure were obtained along the top coat free surface. Each color indicates the span of length corresponding to a specific radius. As is shown, the radius varies from a high of 313 mm at the trailing edge to a low of 4.7 mm at the leading edge. The radius of the inflection point between location C and D in Figure 3.27 is infinity when the curvature changes sign. The turbine vane also has numerous cooling channels. The concave curvature is defined as positive, whereas the convex curvature is defined as negative. Figure 3.27 shows that there is significant variation of the substrate geometry around the vane, raising the questions to understand whether there is a relationship between substrate geometry and the top coat modulus.

*Figure 3.27: Radii of curvatures are measured at the top coat surface around the turbine vane.*
Four locations of interest were selected for the top coat modulus measurement after examining the cross-section, which are: (a) the highest convex radius of curvature near the trailing edge designated as Location A, (b) the second lowest convex radius of curvature designated as Location B, (c) the lowest convex radius of curvature on the leading edge as Location C and (d) the lowest concave radius of curvature as Location D. These locations were chosen since they are the extremes of the substrate geometry on the turbine vane. The knowledge of top coat modulus at these locations could be extrapolated to understand top coat modulus variation on the entire turbine vane cross-section. Table 3.1 summarizes the information about the top coat at the four locations of interest for modulus measurement, which shows a variation of the top coat thickness at these locations.

<table>
<thead>
<tr>
<th>Location</th>
<th>Convex: negative</th>
<th>Concave: positive</th>
<th>Radius of curvature (mm)</th>
<th>Top coat thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>negative</td>
<td></td>
<td>313</td>
<td>275</td>
</tr>
<tr>
<td>B</td>
<td>negative</td>
<td></td>
<td>17.3</td>
<td>320</td>
</tr>
<tr>
<td>C</td>
<td>negative</td>
<td></td>
<td>4.7</td>
<td>275</td>
</tr>
<tr>
<td>D</td>
<td>positive</td>
<td></td>
<td>20.2</td>
<td>200</td>
</tr>
</tbody>
</table>

The micro-beam geometries were re-designed on which the length were increased to be 2mm long and 1.5 mm in height as compared to those from the burner rig bar. The change of the window size was made out of two considerations: (i) the top coats are much thicker on the turbine vane than it on the burner rig bar and a longer beam would keep the
aspect ratio close to those on the burner rig bar; (ii) the size of the window, primarily the length is also dictated by the length of the locations of interest.

Two windows need to be accommodated at each location with a spacing of 2 mm between the edges such that the influence of the stiffness response will not be affected by the existence of the neighboring window. Other dimensions on the micro-beams includes an approximately 45μm thick bond coat remaining to support the top coat. The corner at the ends of the beams was specified to have a radius of 40 μm in order to minimize its influence on the test results. The slice of the post micro-EDM turbine vane is shown in Figure 3.28. The turbine vane was cut into two halves for micro-EDM machining to facilitate handling. Figure 3.28 also illustrates the locations of the micro-EDM cuts. A total of seven beams were fabricated with two beams at each location except for Location C, where only one beam was created due to area constraint.
Figure 3.28: Cross-section of a PWA 2nd Stage turbine vane with micro-beams created using micro-EDM.

The stiffness response of the micro-beams was obtained using the same micro-bending techniques developed for the burner rig bars. Each half was glued onto a fixture before testing. Tests were performed on bridge and cantilever beams at each location except Location C where only one beam could be accommodated. Two tests were carried out on the cantilever beams by pulling on the bond coat side and pushing on the top coat free surface. The bridge beams were only loaded from the bond coat side. The test results were analyzed using DIC and a load deflection response was obtained for each test. FE analysis was carried out to account for exact specimen geometry and quantify the modulus values at those locations. A full scale FE model for the turbine vane was
established to account for its complicated boundary conditions. The top coat was assumed to be transversely orthotropic and the UMAT subroutine was used to define its modulus. The bond coat and substrate were assumed to be isotropic and homogeneous. Results will be discussed in Chapter 5 and used to show the modulus variation of the top coat and relate it to the corresponding microstructures observed in a scanning electron microscope (SEM).

3.4 Three-point bending of freestanding top coats

3.4.1 Preparation of freestanding EBPVD 7YSZ top coat samples

Freestanding top coat samples from the burner rig bar were obtained using acid etching. Several slices of the cross-sections from the burner rig bar were polished to even the thickness. The freestanding top coat samples were taken from the two inclined straight edges on the cross-sections, so the two curved edges were cut off using a diamond saw (Figure 3.29). The remaining center piece was immersed in the diluted Hydrochloride acid (HCL) with 5 molar concentration preheated to 80°C. The HCL dissolved the bond coat and separated the top coat from the substrate. To demonstrate the etching process, one piece of curved edge was also dipped in the HCL. The sample was taken out of HCL three times with one hour in between for observation. Figure 3.30(a) to (d) illustrates the process in which the HCL slowly eroded the bond coat away without etching the substrate. It generally took 3 to 5 hours to fully dissolve the bond coat and
create a freestanding top coat sample. Upon detachment, the residual HCL on the beam was neutralized using baking soda followed by rinsing the beams with acetone and water.

![Image of preparation of freestanding top coat](image)

*Figure 3.29: Preparation of freestanding top coat. Sample is immersed in diluted HCL solution at a temperature of 80°C.*

![Image of bond coat etching process](image)

*Figure 3.30: Bond coat etching process at different stages: (a) As-deposited, (b) 1 hr, (c) 2 hrs, (d) 3 hrs.*
A. Depth-dependency

Freestanding top coat beams of three different thicknesses (67, 100 and 150 μm) were prepared to study the depth-dependence of top coat modulus. The smaller thicknesses of top coats were obtained by carefully polishing the same top coat from the free surface towards the bond coat interface. Thinner top coats (67, 100 μm) were prepared by polishing back the original 150 μm thick top coat (Figure 3.31). After polishing, the top coats were stripped of substrate using the same acid etching process. Upon detachment, the top coat originally deposited on the straight edges of the substrate was observed to develop a curvature in Figure 3.32. The top surface of the beam is the top coat free surface and the bottom surface was the bond coat interface. The curvature signals the release of residual stress, which was developed during top coat deposition.

Figure 3.31: EBPVD 7YSZ top coat was mechanically thinned down to 100 and 67 μm.
A total of four 150 μm, three 100 μm and three 67 μm top coat beams were prepared and the radii of curvature of the beams were measured by fitting an arc along the concave top coat free surface using ImagePro software. These measurements are summarized in Table 3.2. It is likely that there is a gradient of residual stress and the top coat modulus, such that when the metal constraint is removed, the beams bend to different degrees. Those freestanding top coat beams were tested on a three point bending setup to determine their modulus.

Figure 3.32: Example of freestanding EBPVD top coat beams with different depths developed curvature: (a) 150 um, (b) 100 um and (c) 67 um.
Table 3.2: Radius of curvature of the freestanding TBC beams

<table>
<thead>
<tr>
<th>Beam depth (µm)</th>
<th>Number of beams</th>
<th>Averaged radius of curvature at top coat free surface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>152</td>
<td>4</td>
<td>33.5</td>
</tr>
<tr>
<td>100</td>
<td>3</td>
<td>23.7</td>
</tr>
<tr>
<td>67</td>
<td>3</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Backscattered SEM images of the top coat cross-section were used to inspect the morphology of the EBPVD 7YSZ top coat at the cross-section. The sample was polished up to 1 µm surface finishing when attached to the substrate and Figure 3.33 shows the entire top coat with TGO and bond coat layer. A columnar structure was presented with dark contrast being the space (crack and pores) between columns. The area inside the white box was inspected under higher magnification. Figure 3.34(a) to (c) shows the details of the top coat at different thicknesses. The porosity was calculated at each thickness using ImageJ. The porosity was estimated in a way that the dark contrast was assumed to be the open pores and the area is calculated off the light colored region. A gradient of porosity was found along the depth of the top coat with the area close to the free surface having the highest porosity.
Figure 3.33: EBPVD Top coat morphology is shown on a straight edge of the burner rig bar sample.
Figure 3.34: SEM micrograph of EBPVD top coat at different depths and the calculated porosity: (a) top, (b) middle, (c) bottom of the top coat.
B. Thermal exposure

EBPVD 7YSZ top coat samples were thermally exposed to study the effect of top coat sintering on its modulus. A cross-section of burner rig bar was thermally exposed when the top coat was still attached to the bond coat. A tube furnace constructed by Stephen Ryan from Hemker group was used to conduct the thermal exposure in Figure 3.35. The setup has two separable parts: A Lindberg tube furnace that slides on two parallel rails; and a quartz tube that houses the sample. A long thermocouple is inserted into the quartz tube for measuring temperature above the sample. In the current case, the samples were heat treated at 1100°C with a dwelling time of 8 hours in an ambient air atmosphere. After heat treatment, attempts were made to cut off the curved edges on the sample and immerse the remaining piece in the HCL bath for bond coat etching. However, the cutting process triggered the top coat to delaminate from the bond coat. Figure 3.35(b) shows the remaining half top coat barely attached on the cross-section of burner rig bar. Curvature was also observed in the thermally exposed top coat beams. Two post-heat treatment beams were obtained and tested on a three point bending setup.
Figure 3.35: (a) Tube furnace setup for heat treatment of TBC coupon[123], (b) Post-heat treated TBC coupon showing top coat partially attached. The spallation was induced by cutting from one edge.

C. CMAS

Freestanding EBPVD 7YSZ top coat samples were also infiltrated with CMAS to study its effect on modulus. A small plate of freestanding top coat was obtained in Figure 3.36. A freestanding top coat plate was sent to Wesley Jackson in Prof. Carlos Levi’s group at University of California at Santa Barbara to be infiltrated with CMAS. Prior to
the infiltration, the porosity of the coating was evaluated by Jackson in order to calculate the quantity of the CMAS needed. The porosity was assessed by mass density of the coating and compared against the theoretical value of fully densed 7YSZ (6.08 g/cm³) [124]. A suspension of CMAS and ethanol was applied onto the top coat surface and the whole system was given two thermal cycles at 1250 °C with a dwell time of 10 minutes each. The composition of the CMAS and the corresponding weight percentage includes CaO (33.2wt %), MgO (6.5wt %), Al₂O₃ (11.9wt %), SiO₂ (48.4wt %). The mass and bulk density were also measured at pre- and post-infiltration to see the effectiveness. The pre- and post-infiltration masses of the top coat were measured to be 0.0463 grams and 0.0553 grams and the bulk densities were measured to be 5.11 g/cm³ and 6.11g/cm³, respectively [125]. The original porosity of the top coat is calculated to be 16.4% based on the density measurement, which is higher than measured using ImageJ. The deviation is likely because of the microstructure variation from one polished surface to another. In addition, residual CMAS was found on the top coat beam after infiltration, which increased the weight. The CMAS infiltration has caused the mass density of the sample to be equivalent to the fully dense ZrO₂, indicating that the columnar gaps are filled with CMAS. A post-infiltration top coat cross-section is shown and compared with as-deposited top coat in Figure 3.37. CMAS has successfully infiltrated the columns, leaving a dense top coat. To prepare samples for three point bending tests, the CMAS infiltrated top coat was sliced into beams using a diamond wire saw. A hardened epoxy resin secured the top coat and prevented it from crack during slicing. The epoxy resin was dissolved away using epoxy remover and freestanding CMAS infiltrated top coat beams were acquired.
Figure 3.36: A sheet of as-deposited EBPVD top coat prepared for CMAS infiltration at UCSB.

Figure 3.37: Micrographs compare CMAS infiltrated EBPVD top coat and as-deposited top coat.
3.4.2 Analytical models of three point bending

The high aspect ratios of the top coat beams enable the possibility to employ the three point bending theory to extract the modulus of the top coats. The three-point bending solution is developed base on Euler-Bernoulli theory for a rectangular cross-section as previously given in Eq. 3.4. Integrating the equation four times and applying the appropriate boundary conditions gives the deflection of the beam along the length as:

\[ w(x) = \frac{F}{48EI} \left[ 4x^3 - 3L^2x - 8(x - \frac{L}{2})^2 \right] \quad \text{Eq. 3.9} \]

where, \( F \) is the applied load and \( L \) denotes the length of the beam; \( E \) is the elastic modulus; \( x \) is the location along the length. The mid-span deflection can then be obtained by replacing \( x \) with \( L/2 \), which gives

\[ W^E = \frac{FL^3}{48EI} \quad \text{Eq. 3.10} \]

where \( W^E \) is the Euler-Bernoulli solution. To ensure it is appropriate to use the three point bending solution, the two solutions needs to be checked. The Timoshenko solution for a three point bending case is [126].

\[ w^T = \frac{FL^3}{48EI} \left[ 1 + \left( \frac{E}{KG} \right) \left( \frac{h}{L} \right)^2 \right] \quad \text{Eq. 3.11} \]

where, \( w^T \) is the Timoshenko solution; \( F \) is the applied load and \( L \) denotes the length of the beam; \( E \) is the elastic modulus; \( x \) is the location along the length; \( K \) is the shear correction factor (\( K = 5/6 \) for rectangular cross-section; \( G \) is the shear modulus; \( h \) is the
thickness of the beam. If the Poisson’s ratio is assumed to be 0.25, comparison of the two solutions gives:

\[
\frac{w_T}{w_E} = 1 + 3 \left( \frac{h}{L} \right)^2 \quad \text{Eq. 3.12}
\]

The difference between the two solutions can be quantified by substituting the aspect ratio for three point bending of freestanding top coats. The aspect ratio of the top coat beam can be calculated by dividing the thickness of the top coat beam (0.15 mm) by the length (4.3 mm), which gives 28.7. The ratio of the two solutions gives 0.36% of different, so the Euler-Bernoulli solution would be adequate.

The feasibility of a three point bending solution on a curved beam is checked for the current beam geometry. The location of the neutral axis for a curved beam with a rectangular cross-section was determined as follows. The radius of the neutral axis with the knowledge of the cross-sectional area and the radius of curvature for the beam is

\[
R = \frac{A}{\int \frac{dA}{r}} \quad \text{Eq. 3.13}
\]

where \( R \) is the radius of the neutral axis; \( A \) is the cross-sectional area and \( r \) is the radius of an arbitrary fiber along the thickness of the beam. Eq. 3.13 can be simplified for a rectangular cross-section, which gives:

\[
R = \frac{A}{\int \frac{dA}{r}} = \frac{b(b_2 - b_1)}{b \ln \frac{b_2}{b_1}} = \frac{r_2 - r_1}{\ln \frac{r_2}{r_1}} = \frac{d}{\ln \frac{r_1 + d}{r_1}} = \frac{d}{\ln(1 + \frac{d}{r_1})} \quad \text{Eq. 3.14}
\]
where $b$ and $d$ are the width and thickness of the beam; and $r_1$ and $r_2$ are the radius from the lower edge and the upper edge, respectively. By substituting the thickness $d$ (0.15 mm) of the beam and varying the radius of the lower edge, the neutral axis of the beam was calculated and is plotted in Figure 3.38(a). The location of the neutral axis increases sharply for highly curved beams, but moves towards the mid-depth of the beam as the radius of the beam increases. A magnified view of the initial portion of the change is shown in Figure 3.38(b). The initially radius of the freestanding beams used in this study is highlighted in Figure 3.38, so the neutral axis clearly falls in the middle of the beam. The utilization of beam bending solution is justified.
Figure 3.38: (a) location of the neutral axis of beam with rectangular cross-section is a function of the radius of curvature; (b) initial portion in (a) is magnified to show the trend.
3.4.3 Three point bending experiments of freestanding top coats

A three point bending technique was utilized to test the freestanding EBPVD top coat beams. The test configuration is presented in Figure 3.39. The freestanding top coat beams rest on two pins that are 4.3 mm apart serve as the boundaries. A groove in the middle of the fixture facilitates alignment of the hook in the mid-span of the beam. The tests were conducted with the fixture moving towards the hook at a rate of 150 nm/s.

Figure 3.39: Three point bending test of freestanding top coat beams on both sides: (a) Central pin on the top coat/bond coat interface, (b) Central pin on the top coat free surface.

Each freestanding beam was loaded by pushing on the bond coat side of the top coat and then pushing on the top coat free surface. The high aspect ratio of the beam greatly relaxes boundary effects as compared to those of the attached top coat beams. The freestanding top coat beam was inspected in SEM (Figure 3.40(a)), which shows a columnar structure and the bottom of the top coat was also examined in Figure 3.40(b).
No trace of TGO layer was found at the bottom of the etched top coat using SEM. Thus, this three point bending experiment only evaluates the modulus of the top coat. The bending results reflect the stiffness behavior of the top coat, eliminating the influence from other materials.

Figure 3.40: (a) an overview of freestanding EBPVD 7YSZ top coat; (b) Bottom edge of freestanding top coat shows no trace of TGO.
The location of the neutral axis was also experimentally measured for these three point bending specimens. A 20× microscope lens was used to image the area next to the hook loading pin. A DIC tracking grid was placed near this area and used to calculate the in-plane strain during loading as shown in Figure 3.41. The distance between the two tracking points was 10 pixels in the Y direction and 20 pixels in the X direction. 1 pixel is equivalent to 3.81 µm. The displacement maps were averaged and used to determine the in-plane strain ($\epsilon_{yy}$) as a function of depth. Strains were calculated for four different loads (0.05, 0.1, 0.12 and 0.15 N/mm) in Figure 3.42. The strains at the four loads cross and are zero at the same point which shows that the location of the neutral axis (zero strain) located about 90 µm below the top coat free surface and 60µm above the bond coat interface.

*Figure 3.41: Tracking area were defined for in-plane strain measurement*
3.5 Resonance frequency and curvature methods for measuring top coat modulus and residual stress

3.5.1 Overview of the resonance frequency and curvature technique.

A resonance frequency method together with a curvature technique were introduced to measure the Young’s modulus and the residual stress of the top coat on the top of a substrate [94]. The technique was developed and implemented by Johnson and
coworkers at GE global research to investigate the EBPVD and APS top coats in TBC systems [94]. During a 12-week internship at GE Global Research, I had the opportunity to learn and use this technique to test TBC coated samples. This section is dedicated to the introduction of this technique.

The basic principle of the method is to compare the change quantified from resonance and curvature measurements before and after a portion of the top coat was removed and use it to back out the in-plane elastic modulus and the residual stress of the top coat. As illustrated in Figure 3.43, the removal of the top coat has two consequences: it changes the overall stiffness of the original TBC system, which causes a shift in the resonance frequency and it disturbs the internal force equilibrium leading to a change in the beam curvature profile. The elastic modulus and the residual stress of the removed top coat could be calculated analytically using the captured change in terms of resonance frequency and the curvature of the sample.

Figure 3.43: Resonance frequency and curvature method to measure the Young's modulus and residual stress in a thin coating.
3.5.2 Theory

A. Resonance frequency method

German scientist Von Gones first developed the theory to relate the natural frequency of a prismatic beam to its geometric parameters, mass and the Young’s modulus of the material in 1931. Subsequently, researchers modified the solution to include the correction factors to take into account the aspect ratio of the beam [127-129]. Chandra and Clyne [130] paved the way to use it on bi-material system by deriving the relations between the average modulus of a composite beam and its individual components. Johnson has used the technique to evaluate the elastic modulus of the thin EBPVD TBCs as a function of depth [94].

Eq. 3.15 describes the relationship between the Young’s modulus of a homogeneous isotropic beam with a rectangular cross-section and its natural frequency \( f \), span length \( L \), width \( b \) and depth \( t \). \( T_1 \) is a correction factor that depends on the aspect ratio \( L/h \) of the beam. Eq. 3.16 is used to calculate \( T_1 \), if the aspect ratio is less than 20. On the other hand, Eq. 3.17 is used when aspect ratio is equal or greater than 20. \( \mu \) is Poisson’s ratio.

\[
E = 0.9465 T_1 \frac{mf^2 L^3}{b \ t^3}
\]

Eq. 3.15
\[ T_1 = 1 + 6.585 \left( 1 + 0.0752\mu + 0.8109\mu^2 \right) \left( \frac{t}{L} \right)^2 - 0.868 \left( \frac{t}{L} \right)^4 \]

\[ - \left[ \frac{8.34 \left( 1 + 0.2023\mu^2 \right) \left( \frac{t}{L} \right)^4}{1 + 6.338 \left( 1 + 1.1408\mu + 1.536\mu^2 \right) \left( \frac{t}{L} \right)^2} \right] \]

Eq. 3.16

To obtain a depth dependent Young’s modulus of a coating on the surface of a beam, the top coat is polished to remove certain thickness. The resonance measurement is implemented with beam sitting on its “edge”, in which the amplitude of flexural vibration is contained in the plane of the coating interface. In this configuration, the neutral axis of the beam stays in the mid-thickness, whereas the position of the neutral axis shifts with each thinning of the coating. Both before and after the coating removal in addition to the geometry and mass, which are used to calculate the elastic modulus. Eq. 3.18 shows the relation between bending rigidity \((EI)\) of a composite beams with that of each component. An assumption was made to consider all of the remaining portion of the beam as “substrate”, which includes a portion of top coat, bond coat and substrate, denoted as subscript \(S\). Subscript \(C+S\) symbolizes the removed coating and the substrate. \(I\) is the moment of inertia of the systems considered. The Young’s modulus of the removed coating can be obtained by manipulating Eq. 3.18 and Eq. 3.15, leading to Eq. 3.19.

\[ E_{C+S}I_{C+S} = E_CI_C + E_SI_S \]

Eq. 3.18
\[ E_C = E_S \left[ \frac{m_{C+S}}{m_S} \left( \frac{f_{C+S}}{f_S} \right)^2 - 1 \right] \frac{t_S}{t_{C+S} - t_S} \]  \hspace{1cm} \text{Eq. 3.19}

Eq. 3.19 describes that the Young’s modulus of the removed coating is related to the Young’s modulus of the “substrate”, the mass before and after removal \((m_{C+S}, m_S)\), the resonance frequency before and after removal \((f_{C+S}, f_S)\) and the thickness of the beam before and after removal \((t_{C+S}, t_S)\). In this case, a precise measurement of the resonance frequency in addition to weight and dimension change is needed as input for the calculation. The Young’s modulus of the “substrate” can be obtained using Eq. 3.15 by treating the composite beam as a homogeneous system.

\textit{B. Curvature method}

The residual stress was measured by comparing the shape change of the beam before and after the coating removal process. A TBC coated beam is in equilibrium without external force acting on it; but the individual components of this composite beam are under internal stress mainly due to the mismatch of the thermal expansion coefficients and then cool down to room temperature after deposition. When a certain depth of coating is removed, the equilibrium condition was broken with a change in the curvature. If the change in curvature can be captured, the residual stress in the removed top coat can be calculated using Stoney’s equation shown in Eq. 3.20. In this case, \(h_s\) is the thickness of the remaining portion after top coat removal; \(\Delta \kappa\) is the change of curvature; \(h_f\) is the thickness of the removed top coat and \(\nu_s\) is the Poisson’s ratio for the substrate.
\[ \sigma_f = \frac{E_s h_f^3 \Delta \kappa}{6h_f (1 - \nu_s)} \]  
Eq. 3.20

An alternative way to derive the residual stress in the top coat analytically based on the change in curvature was proposed by Ramsey et al.\cite{131}. They obtained the analytical solution for the residual stress based on Timoshenko’s analysis. They presented the linear distribution of the stress throughout the thickness. \( N_s \) and \( N_c \) are the normal forces acting on the substrate and the coating and they should be equal in magnitude and opposite in sign. \( \nu_c \) is the Possion’s ratio for the coating. \( \rho \) is the curvature for the entire beam. \( \sigma_{cs} \) and \( \sigma_{ci} \) are the stress at the free surface and the interface, between which a linear interpolation was assumed. The residual stress can be calculated once the elastic modulus of the substrate and the removed top coat are known in addition to the thickness and curvature of the sample.

3.5.3 Standard operating procedure

A. Sample sectioning

The sample preparation procedure includes three major steps: sample sectioning combined with cleaning, pre-thinning, and initial measurement (dimension and weight). The first resonance frequency and curvature measurements are taken after the initial preparation. To measure the top coat modulus as a function of depth, the resonance frequency and curvature measurements are repeated after each thinning process.
TBC is usually deposited onto plates or buttons. As a result, the samples first need to be cut into beams in order to carry out the measurements. At GE, the TBC coated samples are sectioned using a programmable dicing saw (Thermocarbon, Tcar®864-1). The sample is mounted onto a stage on the saw using crystal bond, which can rotate 360 degrees with a very fine solution and travel out-of-plane in the Z direction. The dicing blade with a thickness of 250 μm travels in-plane during the sectioning process. The direction of rotation of the blade needs to induce shearing from the free surface towards the interface to avoid spallation. The microstructure of the top coat along the edge of a button or plate is always different, which will lead to different properties. To avoid this edge effect, the beams were cut at least ¼ inch away from the outer edges. Three 2 inch long and ¼ inch wide beams were prepared from the same plate with high precision. Three sister samples provide a chance to cross-check the results but do not impose a heavy work load on the operator. The selected length and width were only for convenience during handling and do not carry any other significance. After sectioning, a visual inspection is needed to find if there are burs on the edge of the substrate. The burs will not necessarily cause measurement errors but they might cause errors during mounting processing for top coat removal, resulting an uneven removal between the sister beams. A deburring process is accomplished by gently polishing the edge on 400 grit silicon carbide paper. The samples were moved back and forth on the paper by hand along the length direction instead of width direction. The backside (metal side) of the sample was also polished to reduce the roughness. The curvature was measured on the backside of the metal. After polishing, the surface condition of the metal side is held constant to compare the curvature change after subsequent removal of top coat.
B. Pre-thinning

After deburring, a pre-thinning of the top coat is carried out to even the original rough surface. The purpose of the pre-thinning is to create a smooth surface on the top coat to facilitate the thickness measurement. As shown in Figure 3.44(a), the three beams were glued onto a special sample mount using crystal bond to prepare for pre-thinning. The mount is a circular plate with three groves in a triangular array. The plate is placed onto a hot plate and crystal bond is applied on the bottom of the grooves. Then, the beams are placed on the substrate in the grooves. The beams are located in the mid-length of each groove to ensure an evenly distributed weight during polishing. The grooves and the beams are paired such that the sample is placed in the same groove each time for polishing. When the plate is removed from the hot plate, a weight is placed on the top coat surface in order to squeeze out the residual crystal bond before it cools and hardens, see Figure 3.44(b). This helps assure that the top coat surface of each sample is at the same height and facilitates even polishing. A coupling was installed onto the mount to connect to the polisher in Figure 3.44(d) and a 2 pound force can be programmed and applied onto the mount during polishing. A diamond impregnated plate (40 grit, 3M) was used as the polishing medium. Since it is not intended for removing a large amount of the top coat, the pre-thinning is a very short process such that the top coat is only on the polishing wheel for a short time (~60 seconds) or until the surface is smooth, and all regions of the TBC surface are being polished.

The samples are taken off of the plate, soaked in acetone, and cleaned in a sonicator bath to remove the residual crystal bond before any further steps. This cleaning
process is repeated twice and the samples are oven dried at a temperature at least 100°C to remove any moisture. At this point, the samples are handled with the operator wearing gloves to avoid any contamination from finger oil.

Figure 3.44: Thinning of top coat (a) sample mount, (b) weight to be placed on the mount, (c) coupling to the polisher, (d) Auto-polisher[132].

C. Initial measurement

Baseline measurements of height, width, length, weight, resonance frequency and curvature are taken after pre-thinning of the top coats. The resonance frequency and the curvature will be discussed in detail later. This section emphasizes the physical measurements such as dimensions and weight. The beam sits on its edge such that the thickness of the beam is perpendicular to the normal of the top coat surface and the width
is parallel to the same normal. The width and the length are measured at three different locations across the beam along the edge. The thickness is measured using a micrometer with a sphere head to contact the sample surface. The width is taken at five locations on the sample: Four are towards the two corners of the beam and one is taken at the mid-span of the beam. Figure 3.45 shows the relative locations of the width measurement.

![Figure 3.45: Location of width measurement on the TBC coated beams indicated by the circle.](image)

**D. Resonance frequency and curvature measurement**

The test is designed to find the Mode I resonance frequency of a prepared beam in its flexural vibration. The schematic of the experimental setup is illustrated in Figure 3.46(a). The sample is resting on two strings to provide support and create a free-free boundary condition in which the sample movement is unrestricted. The strings are placed about 0.22L away from each end stipulated by the ASTM standard (C1259 – 15), with L being the length of the sample. These locations correspond to the nodes for the fundamental mode of flexural vibration. A tube is placed above the beam as a guide for the excitation source (zirconia ball with a diameter of ~2mm). The ball is dropped from the opening on the top of the tube and falls along the tube, hitting and exciting the beam. A studio grade microphone was placed under the beam to pick up the vibration. The
received signal is strengthened with a pre-amplifier hooked up to a digital oscilloscope with Fast Fourier Transform (FFT) capability.

A schematic of the transmitted signals are displayed on the oscilloscope in the frequency domain as shown in Figure 3.46(b). The spikes in Figure 3.46(b) with decreasing amplitude correspond to the resonance frequency at different modes of the transverse vibration for sample. The frequency with the highest amplitude typically corresponds to Model I, with the higher modes being shown with decreasing amplitude. More often than not, the ball hits the top surface of the sample off its center, which will induce not only transverse vibration but also torsional and horizontal vibration as well. The side bands sitting next to Mode I, Mode III and IV frequency spikes in Figure 3.46(b) are the frequencies from the excitation of the torsional and/or horizontal vibration modes. Only Mode I frequency from the transverse vibration is needed to determine the modulus of the substrate and the top coat using Eq. 3.15 and Eq. 3.20.

The Mode I frequency was expanded for measurement as shown in Figure 3.47. The horizontal axis is the frequency and the vertical axis is the amplitude. Instead of measuring the location of the peak, the frequency is taken at the full width half maximum of the spike since the peaks are different from each excitation due to the fact that the ball may not hit at the same location.
The higher mode frequencies can be derived analytically for the beam once the Mode I frequency is measured and Young’s modulus is calculated with the assumption of a homogeneous beam. The derived higher mode frequencies are compared with those from the experiments. Since the stiffness of the composite beam is dominated by that of the substrate due to the top coat being very thin and more compliant as compared to the substrate, the values of the derived higher mode frequencies should be close to those from the measurement. When they are, the measured mode I frequency is verified. One thing to note is the placement of the sample during the experiment. To avoid multiple excitation from the ball bouncing up and down, the sample is slightly tilted as shown in Figure 3.48 such that the ball will bounce off once hitting the surface, providing only one excitation.
Figure 3.47: Zoomed-in view of the Model I frequency shows the frequency is measured at full width half maximum.

Figure 3.48: Side view of exaggerated tilt of the sample to avoid multiple excitations from the ball.
The curvature measurements were carried out on the metal side of the sample since that surface condition is held constant after the initial preparation. At GE, a chromatic white light profilometer (FRT, Germany) was used to measure the surface profile of the entire metal side. The metal surface of each sample was measured with a step size of 100 μm. The collected three dimensional data was reduced down to two dimensional by averaging the thickness (Z) height along the width (Y) direction for each length (X). A Matlab script was created to carry out the averaging. The data near the specimen edges are discarded due to ambiguity in the measurement caused by burs chamfers, radii and other edge imperfections. The two dimensional curve was fitted to a circle to extract the radius of curvature.

E. Thinning and re-measurement

To measure the Young’s modulus of the coating as a function of depth, a certain thickness of the top coat was removed after the initial measurement. The test results for the resonance frequency and curvature both before and after the removal are used to calculate the Young’s modulus and the residual stress of the removed top coat. The thinning process is very similar to that of the pre-thinning in terms of the polishing fixture, sample mounting, polishing and cleaning. The difference lies in the depth of removal. After the pre-thinning, the remaining depth of the sample is measured using a micrometer at the five locations on the beam. Two things need to be taken into account when removing the top coat. First of all, to come up with the number of steps for top coat
removal, one needs to remember that increasing the number of steps yields more depth dependent information about the Young’s modulus, but also tends to accumulate more error because each thinning step will remove less material, resulting in smaller differentials in dimension, mass curvature and frequency. Since two thinning steps seem not enough to learn the Young’s modulus as a function of depth, a three-step removal was planned with resonance frequency and curvature measurements before and after each removal. Secondly, some top coat is left on the sample when the removal approaches the interface, the reason being that the Young’s modulus and the stress state are different in the bond coat layer. The results will be confusing when testing the sample if some bond coat is removed. As a result a thin layer of the top coat remains untouched to avoid changing the bond coat.

3.5.4. Sensitivity study

Despite the simplicity of the instrumentation and execution for the resonance technique, a sensitivity study reveals that the repeatability and the reliability of the technique can easily be compromised during sample preparation and testing. Two factors were identified to influence the measurements to various degrees, namely oscilloscope and sample temperature. The resolution of the oscilloscope in measuring frequency determines the accuracy to calculate the top coat modulus; the sample temperature changes the modulus of the substrate which is transferred to the top coat if not accounted for. Table 3.3 shows two sets of data collected after pre-thinning and after the first
thinning on a beam composed of as-deposited porous APS 8SZ top coat and bond coat sprayed onto an Inconel 718 superalloy respectively. The data was collected using a Tektronix TDS 420A oscilloscope with a resolution of 10 Hz in the frequency domain.

<table>
<thead>
<tr>
<th>Measurements</th>
<th>Pre-thin</th>
<th>1st thin</th>
</tr>
</thead>
<tbody>
<tr>
<td>L (mm)</td>
<td>50.82</td>
<td>50.82</td>
</tr>
<tr>
<td>Width (mm)</td>
<td>4.329</td>
<td>4.138</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>6.307</td>
<td>6.307</td>
</tr>
<tr>
<td>Weight (gram)</td>
<td>10.18204</td>
<td>9.90929</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.167</td>
<td>0.167</td>
</tr>
<tr>
<td>Mode I Frequency (Hz)</td>
<td>11200</td>
<td>11280</td>
</tr>
</tbody>
</table>

A. Oscilloscope

The resolution of the oscilloscope was proven to be important to accurately identify the Mode I resonance frequency. The removed top coat is typically very thin (a couple hundred micron meters) as compared to the substrate (a few millimeters). Moreover, the substrate is much stiffer than that of the top coat. Accordingly, the change in the measured frequency is very small. Using the data in Table 3.3 as an example, a quick calculation (Eq. 3.15 and Eq. 3.19) would yield that the Young’s modulus of the removed coating is 46.85 GPa. Due to the restraint of the resolution (10 Hz), the oscilloscope does not read the last digit. In the actual case, it is possible that the measured resonance frequency is 11285 Hz for an example, which gives a modulus of 43.65 GPa.
A ~7% deviation was registered simply from the lack of +/- 1 Hz frequency measurement. Using an oscilloscope with higher resolution (~0.1 Hz) and multiple measurements seems justified.

B. Sample temperature

A second factor to influence the result is the difference in sample temperature from one test to another. The change in temperature of the sample brings about changes in the dimensions as well as in the Young’s modulus of the material. The change in dimension is studied first with the assumption of a constant Young’s modulus. Consider the case of a carbon steel substrate (E = 201.5409 GPa at 20 °C) with a dimension of L=50 mm, b = 3.3 mm, t = 6 mm and weight of 7.77 gram. Since the stiffness of the entire sample is dominated by that of the metal substrate, the change in dimensions is imposed by the substrate to the top coat. The thermal expansion coefficient of the substrate is assumed to be 14×10^{-6} /°C. A slight temperature rise (e.g. 7° increase from 20 °C) induces a very small change in the dimensions (ΔL = 4.9 µm, Δb = 0.32 µm, Δt = 0.588 µm). The resonance frequency of the sample increases from 12506.22 Hz at 20 °C to 12506.78 Hz at 27 °C. The shift in the resonance frequency is minimal as compared to the expected resolution of the oscilloscope. Accordingly, the error due to the dimension change caused by the temperature change is not significant.

The temperature change can also affect the Young’s modulus of the beam. From Figure 3.49, it is found that the Young’s modulus of the metals and their alloys is
inversely proportional to the temperature. The Young’s modulus of carbon steel is extracted from the figure as an example and is comparable to many superalloys. The Young’s modulus increases by 0.22% from 201.101 GPa to 201.541 GPa with a temperature drop from 27°C to 20°C. Furthermore, if we use the example in Table 3.3 in the pre-thinned state, an increase of 10Hz in the measured frequency will lead to an increase of the average modulus of the entire beam by ~0.18% from 161.117 GPa to 161.405 GPa, as calculated using Eq. 3.19. The percentage increase of the substrate modulus caused by the temperature drop of 7 °C is comparable with the variability associated with a frequency resolution of 10 Hz. Thus, temperature correction of approximately +/- 1°C is desired.

*Figure 3.49: Elastic modulus of metals as a function of temperature [133].*
3.5.5 Example results of top coat modulus on substrates

A total of 6 beams from two types of as-deposited top coats were investigated to understand the Young’s modulus and residual stresses. The first type of top coat is porous APS 8YSZ and the second type is denoted as Coating B to leave out the GE proprietary information. The porous 8YSZ beams includes a ~750µm top coat and a 3.44 mm substrate plus bond coat and Coating B has a ~1000 µm top coat, 4.33mm substrate plus bond coat before pre-thinning. Each beam is prepared to be 2 inches long and ¼ inch tall as shown in Figure 3.50. The width is defined to include the depth of the three components (top coat, bond coat and the substrate).

![Figure 3.50: Beam dimensions used for resonance technique and residual stress measurement. The picture is taken from the top coat surface[132].](image)

A. Results for porous 8YSZ samples

Three sister beam specimens of porous 8YSZ were tested in parallel. In addition to the pre-thinning step, the specimens were thinned in three progressive thinning steps with measurements of mass, dimensions, curvature and resonance frequency made before
and after each thinning. The top coat depth was measured after pre-thinning to be ~703 µm (~47 µm removed during pre-thinning). Three thinning steps were carried out with a total top coat removal of ~520 µm in Table 3.4. ~183 µm top coat still remained on the bond coat after the third thinning. Between two thinning steps, the resonance frequency and the backside curvature of the sample were measured after measuring dimensions and weight.

Table 3.4: Thinning steps for 8YSZ APS top coat samples

<table>
<thead>
<tr>
<th>Thinning step</th>
<th>Removed thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-thin</td>
<td>~47</td>
</tr>
<tr>
<td>1</td>
<td>~200</td>
</tr>
<tr>
<td>2</td>
<td>~180</td>
</tr>
<tr>
<td>3</td>
<td>~140</td>
</tr>
</tbody>
</table>

The test results are shown in Figure 3.51 for Young’s modulus and residual stress as a function of removed depth. In Figure 3.51(a), the Young’s modulus of the top coat was scattered among different samples. Sample 1 shows a higher overall Young’s modulus than the other two. Within Sample 1, the Young’s modulus in the mid-portion of the top coat is lower than outer part closer to the free surface and the inner part closer to the bond coat interface. The other two samples show a gradient in the Young’s modulus with a steep increase close to the interface. The residual stress in Figure 3.51(b) measured for this type of top coat also has a large deviation among the three samples over different depths. Also, the outer portion of the top coat seems to be under tension for all the three samples. It turned to compression for Sample 1 and 2 when going down to the interface.
One thing to note is that the experiments were done before the sensitivity study, so the results contain the noise in the resulting stress and modulus due to coarse resolution of the resonant frequency and inadequate correction of specimen’s temperature.

![Graphs showing Young's modulus and residual stress measurements for porous 8YSZ.](image)

*Figure 3.51: Modulus and residual stresses were obtained for porous 8YSZ.*
B. Results for Coating B samples

The remaining top coat after pre-thinning for these samples is ~1mm and the three thinning steps are shown in Table 3.5. ~120 µm were left on the top coat after the third thinning. Resonance frequency and curvature measurement were performed on these three samples. The samples were tested post sensitivity study. The oscilloscope was swapped to Agilent Technologies (AT) DSO7054A with a resolution of 0.1 Hz and the samples were left in the test room such that the sample temperature was equilibrated with that of the room. The temperature was also recorded during the resonance frequency test to be 20±1°C. The test results are shown in Figure 3.52. The Young’s modulus results show greater consistency among the three samples than the previous example. The overall modulus is also higher in this type of coating. There is an apparent depth dependent behavior with the portion closest to the interface having the highest modulus, but the intermediate section of the top coat somehow has a lower Young’s modulus the other two parts. The residual stress is evaluated to be tensile, the profile of which follows the same trend for all the three samples showing an increase along the depth to the interface.

<table>
<thead>
<tr>
<th>Thinning step</th>
<th>Removed thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-thin</td>
<td>~80</td>
</tr>
<tr>
<td>1</td>
<td>~180</td>
</tr>
<tr>
<td>2</td>
<td>~350</td>
</tr>
<tr>
<td>3</td>
<td>~270</td>
</tr>
</tbody>
</table>
Figure 3.52: Modulus and residual stresses were obtained for Coating B.
The resonance frequency and curvature technique is documented in details such that the technique can be implemented in GE Global Research or at Johns Hopkins. This technique has been proved to be viable in extracting the modulus of homogeneous beams or thin top coats on substrates. The setup of the technique is simple and the tests are easy to carry out. However, the effect of temperature needs to be controlled to generate repeatable results.
Chapter 4: The Elastic responses of EBPVD 7YSZ top coats deposited on burner rig bars

4.1 Sample geometry and test information

Six micro-beams were fabricated and tested from two cross-sections of a burner rig bar using the micro-beam bending technique. One bridge beam and three cantilever beams were made from the straight edges of the cross-section; one bridge and one cantilever beams were made from on the curved edges. The geometries of each beam were examined including beam length, window height, top coat and bond coat thicknesses, curvature and corner radii of the window. Top coat and bond coat thicknesses were measured at five locations along the beam to obtain an average value. For the curved beams, window height was measured from the mid-span of the beam. Two bridge beams and four cantilever beams were manufactured at Viteris and Leer Technologies, respectively. Figure 4.1 and Figure 4.2 show the straight and curved bridge beams. The two bridge beams have a thin layer of bond coat supporting the top coat and small corner radius. Figure 4.1 also illustrates the measurement locations. The measurements of the geometry are provided in Table 4.1 and Table 4.2 for straight beam and curved beam, respectively. The bond coat has a uniform thickness averaged at 41 µm on the straight bridge and 44 µm on the curved beam. The corner radii of the two beams were fairly close, 42 µm on the straight beam and 43 µm on the curved beam. The width of the window was measured from the distance between the two vertical edges and is equal to the length of the beam for the straight beam.
Figure 4.1: Straight bridge beam shows a top coat and thin bond coat.

Table 4.1: Geometry measurements of straight bridge beam

<table>
<thead>
<tr>
<th>Window width (µm)</th>
<th>Window height (µm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1008</td>
<td>1025</td>
<td>152</td>
<td>41</td>
<td>42</td>
</tr>
</tbody>
</table>
Figure 4.2: Curved bridge beam shows top coat and a thin bond coat.

Table 4.2: Geometry measurements of curved bridge beam

<table>
<thead>
<tr>
<th>Window width (µm)</th>
<th>Window height (µm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1002</td>
<td>1053</td>
<td>150</td>
<td>44</td>
<td>43</td>
</tr>
</tbody>
</table>
The four cantilever beams were created by cutting off one end of the bridge beams. Some of the cantilever beams have a taper along the edge at the free end due to the misalignment of the cutting blade. The bond coat layers on these beams are much thicker than those of the bridge beams, and the corner radii are also much bigger. Figure 4.3 and Table 4.3 present the profile and the geometry measurements for cantilever beam 1. The length of the beam was measured from the edge of the window on the coupled end to the edge of the free end. If the free end has a taper, the length was measured to the edge, producing a smaller value. Figure 4.4 and Table 4.4 show the profile and the geometry measurement for cantilever beam 2, which had a similar bond coat thickness but a radius at the corner than those from cantilever beam 1. Figure 4.5 and Table 4.5 present the profile and the geometry measurement for Cantilever beam 3. This beam has a thicker bond coat and an equal corner radius to cantilever beam 2. The profile and measurement for the curved cantilever beam are shown in Figure 4.6 and Table 4.6. During machining the EDM wire did not cut into the bond coat, therefore retaining the entire bond coat thickness, and left a small amount of substrate on the beam. The corner radius is similar to those of the straight cantilever beams.

Both the straight and curved bridge beams were only pulled from the bond coat side at 0.5 mm away from the window edge, while the cantilever beams were loaded on the bond coat and the top coat free surface sides. The loading location on the cantilever beams was near the free end. The loading point for each beam is indicated in the corresponding beam profile figure, measuring from the edge of the window. The loading point for cantilever beam 1 was 771 µm away from the window edge in Figure 4.3 when
loaded on the bond coat side and 790 µm when load on the top coat free surface side. 

*Cantilever beam* 2 was loaded on the bond coat side at 795 µm and was loaded on the top coat free surface at 781 µm. The test span length of *cantilever beam* 3 was smaller than the previous two beams, which was 753 µm when loaded on the bond coat side and 703 µm when loaded on the top coat free surface side. The loading point for the curved beam was 770 µm on the bond coat side and 760 µm on the top coat free surface side.

![Profile of straight cantilever beam 1 with one end cut off.](image)

**Figure 4.3: Profile of straight cantilever beam 1 with one end cut off.**

<table>
<thead>
<tr>
<th>Beam length (µm)</th>
<th>Window height (µm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>826</td>
<td>935</td>
<td>150</td>
<td>104</td>
<td>185</td>
</tr>
</tbody>
</table>

**Table 4.3: Geometry measurements of straight cantilever beam 1**
Figure 4.4: Profile of straight cantilever 2 with one end cut off.

Table 4.4: Geometry measurements of straight cantilever beam 2

<table>
<thead>
<tr>
<th>Beam length (µm)</th>
<th>Window height (µm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>970</td>
<td>150</td>
<td>76</td>
<td>146</td>
</tr>
</tbody>
</table>
Figure 4.5: Profile of straight cantilever beam 3 shows one end cut off.

Table 4.5: Geometry measurements of straight cantilever beam 3

<table>
<thead>
<tr>
<th>Beam length (µm)</th>
<th>Window height (µm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>970</td>
<td>150</td>
<td>98</td>
<td>147</td>
</tr>
</tbody>
</table>
Figure 4.6: Profile curved cantilever beam shows a residual substrate underneath the bond coat.

<table>
<thead>
<tr>
<th>Beam length (µm)</th>
<th>Window height (µm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>860</td>
<td>930</td>
<td>150</td>
<td>110</td>
<td>140</td>
</tr>
</tbody>
</table>

4.2 Experimental results of attached EBPVD 7YSZ top coats

Stiffness responses were obtained for the various bridge and cantilever beams of EBPVD 7YSZ. Figure 4.7 presents the micro-bending results of the straight beams. Test A is denoted for the bridge beam case. The cantilever beams were pulled on the bond
coat side in Test B, and were pushed on the top coat free surface side in Test C. Since the hook is much wider than the beams, the loading is effectively a line load. Due to small differences in the width of each sample, the applied load was normalized by the width of the beam. The normalization allows for direct comparison of the results between samples regardless of width. As shown in both Figure 4.7, the bridge beams exhibit a much steeper slope than the cantilevers indicating that the bridge beams are stiffer primarily due to the constraints at both ends.

![Diagram](image)

**Figure 4.7:** Micro-bending results of one bridge beam and three cantilever beams on the straight edges of the burner rig bar samples. The FEA analysis is described in Section 4.3.
A closer inspection at the cantilever test results for the same beams reveals that pulling from the bond coat side (Test B) tends to generate a higher slope as compared to pushed on the top coat free surface (Test C). This observation is consistent in the results of all three cantilever beams. Loading the cantilever on the bond coat side (Test B) places the top coat free surface in compression and the bond coat side of the beam in tension. Conversely, pushing on the top coat free surface (Test C) puts the bond coat side in compression and the top coat in tension. The bridge beams in Test A were subjected to tensile stress in the top coat at the mid-span region while the two ends were under compressive loading. The location of the neutral axis for the bridge beam with the same top coat and bond coat thickness was experimentally demonstrated to be situated at the bond coat interface[108]; As discussed in Chapter 3, the neutral axis for the cantilever beams is in the bond coat. The entire top coat is under either tension or compression depending on the loading direction. As a result, the top coat can be inferred to be stiffer under compression and more compliant under tension. Since the underlying NiCoCrAIY bond coat and substrate are relatively isotropic, the tension/compression asymmetry can be entirely attributed to the mechanical behavior of the top coat.

Another observation is that the stiffness variation of the three cantilever beams in Figure 4.7, which can be explained by the different beam geometries. Since the applied load is normalized by the width, other geometric factors (e.g. length, thickness and corner radius) must be considered. From the geometry measurements, we can note that cantilever beam 1 has a thicker bond coat in the beam section than the other two cantilever beams, and the corner radius at the coupled end is also bigger. Consequently,
cantilever beam 1 shows the highest apparent stiffness than the other two beams in Test B. However cantilever beam 1 is more compliant than that of cantilever beam 3 in Test C. One possible reason could be the fact that the hook was placed closer to the free end in Test C, resulting in a longer effective span length. The results for cantilever beam 2 and 3 are self-consistent between Test B and C, showing cantilever beam 3 is stiffer than beam 2. The bond coat in cantilever beam 2 was thinner than that of cantilever beam 3, which contributes to higher stiffness of cantilever beam 3.

Figure 4.8 presents the bending results for the curved beams, which were tested in the same manner as the straight beams. The bridge beam also showed a higher stiffness response than the two cantilever beams. The results from the two cantilever tests also show that the beam is stiffer when pulling from the bond coat side and more compliant when pushing on the top coat free surface. The observation suggests the existence of the tension/compression asymmetry in the top coat on a curved substrate.
FE models designed to capture all the salient beam geometry can be used to quantitatively determine the top coat modulus. The geometry of the beams is complicated and varies from one beam to another. To interpret the stiffness response, each beam has to be modeled individually to account for those geometrical variations. The construction of FE beam models is discussed in the next section.

Figure 4.8: Micro-bending results of one bridge beam and one cantilever beam on the curved edges of the burner rig bar samples. The FEA analysis is described in Section 4.3.
4.3 Finite element analysis results

Due to the low aspect ratio of the beams, the analytical solutions are not appropriate in modeling the stiffness response of the beams and extracting the modulus of the top coats. Therefore, a detailed mesh was constructed to capture the geometry of each individual sample. FE simulations were used to predict the elastic response of each micro-beam and to obtain the modulus of the top coats. The parametric study of the boundaries effects gave the dimensions of the outer edges. Figure 4.9 depicts FE model size using a doubly clamped micro-beam as an example. The blue layer is the top coat, red layer the bond coat and white layer the substrate. The boundaries include a 0.75 mm wide shoulder on each side of the beam and a 1.6 mm thick substrate, which were used for each micro-beam. Other geometries such as the thickness, length and corner radius must be measured from the micro-beam. The size of the outer perimeter shown was used for the FE model of each beam. Figure 4.9 also shows the boundary conditions for all the micro-beam models, in which the three edges were fixed.
Figure 4.9: Size of the FE model to account for the effect of shoulder width and substrate thickness.

Table 4.7: Magnitude of displacement loading on the micro-beams

<table>
<thead>
<tr>
<th>Micro-beam model</th>
<th>Displacement loading (µm)</th>
<th>Bond coat</th>
<th>Top coat free surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight bridge</td>
<td></td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>Straight cantilever 1</td>
<td></td>
<td>2.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Straight cantilever 2</td>
<td></td>
<td>2.8</td>
<td>3</td>
</tr>
<tr>
<td>Straight cantilever 3</td>
<td></td>
<td>2.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Curved bridge</td>
<td></td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>Curved cantilever</td>
<td></td>
<td>3.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>
The FE model was modified for each beam based in the exact geometry measurements. Quadratic elements were prescribed for the majority of the model with a rectangular shape. Triangular elements were used at the corners to ensure good connectivity and avoid large element distortion. The mesh size for all the models was 20 \( \mu \)m to assure convergence and to be computationally efficient. The models were carefully constructed to include all of the small features present in the micro-beams. Figure 4.10 shows the meshed model of the straight bridge beam concentrating on the beam section. Figure 4.11 to Figure 4.13 show the FE models for Cantilever beam 1, 2 and 3. The bond coat thicknesses and corner radii are different among the three beams. Tapered free ends are presented in FE models of Cantilever 2 and 3. Figure 4.14 and Figure 4.15 present the FE model for the curved bridge and cantilever beams. Note that the curved cantilever beam model reflected the residual substrate attached to the bond coat. On the cantilever beam models, the meshed parts next to the beam do not participant in the deformation. Fixed displacements were applied to the micro-beam models as loading. The locations of the loading were taken from the micro-bending experimental measurements.

Table 4.7 shows the magnitude of the displacement loading taken from the experiment for each micro-beam model.

The properties of each layer were defined as follows: the top coat was modeled as a orthotropic material with an out-of-plane modules of 150 GPa [121]. The in-plane elastic responses were assumed to be bi-linear and a parametric study was carried out to determine the value to fit the experiments. The bond coat and substrate were defined to be isotropic materials. The bond coat modulus is 155 GPa [118] and the modulus for the
substrate is 200 GPa[117]. The Poisson’s ratio is assumed to be 0.2 for the top coat, 0.25 for bond coat and substrate.

Figure 4.10: FE model of straight bridge beam established based on the geometry measurements.

Figure 4.11: FE model of cantilever beam 1 established based on geometry measurements.
Figure 4.12: FE model of cantilever beam 2 established based on geometry measurements, showing the tapered end.

Figure 4.13: FE model of cantilever beam 3 established based on geometry measurements shows the tapered end.
Figure 4.14: FE model of curved bridge beam established based on geometry measurements.

Figure 4.15: FE model of curved cantilever beam established based on geometry measurements shows the remaining substrate.
4.4 Determination of the top coat modulus

All the micro-bending tests were modeled using FE analysis to extract the top coat moduli. The goal is to use the same material inputs for all the analyses and be able to produce comparable results to the experiments. A parametric study was carried out to find the top coat modulus that produces the best fit between experiments and FE analysis. The root mean square error (RMSE) method was used to quantify the difference between the FE analyses results with those from all micro-beam bending experiments. The input modulus that produces the smallest error was taken as one for the top coat modulus.

RMSE measures statistically the magnitude of a varying quantity by taking the square root of the mean value of a fitting errors [134]. The tool was used to quantify the differences between the micro-beam experiments and the FE analysis. The reaction force from the FE analysis was compared to the load from the experiments at the same displacement. The comparison was carried out for all trackable displacements for one test to generate an error. Eq. 4.1 describes the analysis.

\[
\text{Error} = \left[ \frac{\sum_{i=1}^{n} \left( \frac{F_{i}^{FE} - F_{i}^{exp}}{F_{i}^{exp}} \right) }{n} \right]^{1/2} + \left[ ... \right]_{\text{Beam}2}^{1/2} + \left[ ... \right]_{\text{Beam}3}^{1/2} + \ldots \quad \text{Eq. 4.1}
\]

where, \( F^{exp} \) is the experimental force and \( F^{FE} \) the reaction force from FE analysis, \( i \) the current number of force displacement pair; \( n \) the total number of data points compared.

The analysis was carried out for each test and the errors were summed up. The total error evaluated the fit of the modulus input. A number of moduli were input and the total errors
were calculated. Table 4.8 and Table 4.9 show the RMSE analysis for the straight beams and curved beams. The RMSE values for the straight beams are higher since they had seven tests and the curved beams had three tests in total. For the straight beams, the lowest error was generated by inputting 50 GPa as the compression modulus and 30 GPa as the tension modulus. For the curved beams, the compression modulus 47 GPa and tension modulus 28 GPa gave the smallest error. As a result, the top coat modulus for the straight beams and curved beams were determined. The load deflection comparison between the FE analysis and the experiments can be found in Figure 4.7 for the straight beams and Figure 4.8 for the curved beams.

Table 4.8: RMSE analysis of straight beams

<table>
<thead>
<tr>
<th>Ec</th>
<th>47</th>
<th>48</th>
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<tr>
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<tr>
<td>25</td>
<td>3.647</td>
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<td>3.121</td>
<td>3.486</td>
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Table 4.9: RMSE analysis of curved beams

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<tr>
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<td>1.773</td>
<td>1.921</td>
<td>2.212</td>
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The obtained top coat moduli were applied to model previously measured micro-beam bending result [111, 112] taken sections of the same burner rig bars. Two sets of micro-beam were manufactured as shown in Figure 3.11 for straight beams and Figure 3.12 for curved beams [111]. The beams were tested by placing the hook at the mid-span for each case. The results showed a tension/compression asymmetry [111, 112]. The meshed models for these beams were established using the method described previously. Figure 4.16 and Figure 4.17 show the model of the four beams. The dimensions for these beams are summarized in Table 4.10. Those beams have a higher radius of curvature at the corners and the bond coat is also thicker. Note that the curved cantilever beam has a varying bond coat thickness, which was captured and included in the model. The test and simulation results are shown in Figure 4.18 for the straight beams and Figure 4.19 for the
curved beams. The FE analysis results are in good agreement with the experimental results.

Figure 4.16: FE models for previous micro-beam bending experiments (a) straight bridge beam, (b) straight cantilever beam.
Figure 4.17: FE model for previously tested micro-beams (a) curved bridge, (b) curved cantilever.
Table 4.10: Beam geometry for the previous micro-beams

<table>
<thead>
<tr>
<th>Micro-beam</th>
<th>Beam length (µm)</th>
<th>Window height (µm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight bridge</td>
<td>1005</td>
<td>1010</td>
<td>150</td>
<td>50</td>
<td>110</td>
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<tr>
<td>Straight cantilever</td>
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<td>1004</td>
<td>150</td>
<td>50</td>
<td>110</td>
</tr>
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<td>Curved bridge</td>
<td>1002</td>
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<td>150</td>
<td>50</td>
<td>110</td>
</tr>
<tr>
<td>Curved cantilever</td>
<td>906</td>
<td>1002</td>
<td>150</td>
<td>50</td>
<td>110</td>
</tr>
</tbody>
</table>

Figure 4.18: Micro-bending and FE analysis for previously tested straight beams[111, 112].
4.5 Discussion of results

The tension and compression asymmetry of the EBPVD top coat observed in previous micro-bending experiments was confirmed in the current study. The micro-bending experiments conducted on the attached TBC revealed that the top coat is more compliant under tension than compression. Assuming a very simple bilinear stiffness response, the top coat modulus under tension and compression was determined to be 30 GPa and 50 GPa on the straight edges and 28 GPa and 47 GPa on the curved edges, respectively. As suggested by Johnson [120], the dependence of the EBPVD top coat modulus on stress is likely non-linear and complicated. Nevertheless, the tension and
compression asymmetry measured in this study is well described by the simple bi-modal modulus.

The physical explanation of the tension and compression asymmetry is undoubtedly based on the unique columnar microstructure of EBPVD top coat with vertical cracks and spaces between the individual columns. Relating the top coat microstructure to its micromechanical behavior, tension enhances the vertical spacing, while compression reduces it. Moreover, physical but unbonded contact points between columns would support compressive loads but not tensile loads, which would also lead to the top coat being stiffer in compression and more compliant in tension. Figure 4.20 shows the cross-sections of the entire top coat columnar morphology for the straight and curved surfaces. The dark contrast shows the location of the pores, which are distributed over the entire area along the thickness. Figure 4.21 focuses the top 50 µm of the top coat on the straight surface and highlights the presence of decent amount of pores and cracks between the columns. The moduli at these two places do not have big variation even though the substrate shapes are different. The porosity content was measured in each in Figure 4.20, and found to be close, which is consistent with the fact that the moduli were also similar.
Figure 4.20: EBPVD 7YSZ top coat microstructure along the edge of the wedge-shaped burner rig bar (a) straight edge; (b) curved edge.
Figure 4.21: Top 50 µm of EBPVD 7YSZ top coat on straight edge shows cracks and pores between the columns.

The porosity plays an important role in the stiffness response of the top coats [135]. The modulus of a porous material was empirically described by Sprigg [136], whereas the model developed by Wang [137] is more mechanics-based. Wang’s model considers a lattice structure of a cubic array with spherical particles intersecting the cubes, creating pores at the corner of the cube. The elastic response of the each lattice is predicted from the deformation of the particles when subjected to a load along a certain direction. Krstic et al. [138] predicts the modulus of nanocrystalline porous materials by incorporating an annular crack. They showed that the crack length versus the pore radius affects the modulus to a great extent. All of the three models predict that the porosity
decreases the modulus of the material. The three solutions were compared assuming a porosity of 10% in the top coat and that the modulus of the fully dense zirconia is 200 GPa [139]. Assuming the material constant in Springg’s solution to be 3.5, Springg and Wang’s solutions yield higher moduli of 193 and 176 GPa, respectively. In Kirstic’s solution, the crack was assumed to be five time longer than the radius of the pore, which forms a shape that resembles the vertical cavities in the top coat. Kirstic’s solution predicts a much smaller value (54.8 GPa), which is closer to the results in the current study. Aboudi [140] predicted the modulus of otherwise homogeneous solids with periodic rectangular cracks aligned to each other. The modulus in Mode I loading was a function of crack length and spacing. Assuming that the spacing between two parallel cracks in the top coat is 10 µm (width of a column), the length of the crack is also 10 µm and the head to toe spacing between two cracks is 5 µm, the modulus of the top coat is predicted to be 140 GPa. The comparison of the four solutions demonstrates that the shape of the pore/cracks does affect the predictions of the modulus. Of all the solutions, Kirstic’s prediction gives the closest match to the experimental results in the current study.

The tension/compression asymmetry of the EBPVD top coat was indicated by Wang et al.[87] who reported that different stiffness responses were observed when loaded at top coat free surface and bond coat interface in a three point bending of freestanding top coats. However Wang’s top coat was under both tension and compression because the neutral axis was located within the top coat, and no quantification or explanation of tension/asymmetry was given.
The apparent behavior of the top coat was approximated using bilinear stress-strain relation out of convenience. However, this type of material behavior is not physically sound, especially around the origin where the stress-strain relation changes abruptly. The actual material behavior of the top coat is not that simple, even though the measurement near zero stress is difficult. A transitional region tends to exist between tension and compression domain [141]. Continuous nonlinear stress strain behavior was proposed by Johnson [120] for EBPVD coating. He investigated the relationship between the in-plane modulus and residual stress of an EBPVD top coat using a resonance method [94]. Modulus of the top coat was found to increase nonlinearly as a function of compressive stress. The tensile behavior of the top coat was not measured due to the difficulty in imposing tension in the specimen. The maximum in-plane compressive strain in Johnson’s study was less than 0.1% and the tensile strain was less than 0.02%. The micro-bending method was able to investigate the top coat modulus under higher strains. A linear gradient of in-plane strain was created along the thickness of the beam during bending with the highest at the outmost fiber of the beam and decreases linearly along the thickness. For example, the straight bridge beam was subjected to 0.124% in-plane elastic tensile strain on the outmost fiber of top coat at the mid-span according to FE analysis. The cantilever test of beam 1 generated the highest 0.126% compressive strain in the outmost fiber of the top coat when loaded on the bond coat and the highest 0.133% tensile strain when loading on the free surface as indicated by FE analysis.

The magnitude of the elastic strain in the top coat during bending is compared to the thermal strain generated as the system cools down to ambient temperature. Assume
the thermal expansion coefficient for the top coat and the substrate is $10 \times 10^{-6}$ and $14 \times 10^{-6}$, respectively. The thermal strain is calculated to be 0.4% and compressive in nature assuming a temperature drop of 1000°C. The thermal strain is much larger than the bending strain and a higher modulus is possible if the stress-strain relation is nonlinear and increases with strain in the compressive region.

In summary, the current micro-beam bending method was able to assess tension and compression asymmetry of EBPVD top coat with the assistance of FE analysis. The method has shown robustness in obtaining the stiffness responses of the micro-beams and the developed FE models can be used to interpret the results and give a quantification of the moduli using root mean square method. The stiffness response of the previous micro-bending data was successfully predicted using the obtained moduli of $E_{\text{tension}} = 30$ GPa and $E_{\text{compression}} = 50$ GPa on the straight edge, $E_{\text{tension}} = 28$ GPa and $E_{\text{compression}} = 47$ GPa on the curved edge.
5.1 Turbine vane and micro-beam geometries

Extending the capability of the developed micro-bending technique, the EBPVD top coat of a PW2000 2nd stage turbine vane was evaluated at four specific locations to ascertain the variability of top coat modulus on components. The geometry of the substrate is different in shape and deposition condition. Figure 5.1 shows the cross-section of the turbine vane. Seven windows were created at the four different locations (A, B, D and D). Two beams were created at each location with one tested as bridge and another tested as cantilever, except for Location C at the leading edge. Due to area limitation, only one beam was accommodated at Location C and tested as a cantilever. The cantilever beams were created by cutting one end of bridge beams loose using a miniature cut-off wheel. Similarly to the burner rig bar study, the experimental results were modeled with FE analysis by matching the loading curve of each test.
Figure 5.1: Turbine vane cross-section was cut into two halves with micro-beams located at each half.

The exact geometries were measured for each micro-beam. Figure 5.2 and Figure 5.3 present the bridge beam and cantilever beam at Location A, which has the largest substrate radius of convex curvature (313 mm). The two beams sit on the trailing edge of the turbine vane as shown in Figure 5.1 and are 2 mm apart. Table 5.1 and Table 5.2 show the measurements of the two beams. The top coat thickness at this location was 275 µm. The bridge beam is 2 mm long and the cantilever 1.76 mm. The bond coat thickness on the beam is 50 µm for both beams and the corner radius is 45 µm. The window height could not be measured since the substrate was thin at this location and the EDM cut through the substrate to the cooling channel.
Figure 5.2: Bridge beam at Location A shows the top coat, bond coat and substrate.

Table 5.1: Geometry measurement of bridge beam at Location A

<table>
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<tr>
<th>Beam length (mm)</th>
<th>Window height (mm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
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<td>2.04</td>
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<td>275</td>
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<td>45.6</td>
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</tbody>
</table>

Loading position: 1.0 mm from both ends
Figure 5.3: Profile of cantilever beam at Location A shows the top coat, bond coat and substrate.

Table 5.2: Geometry measurement of cantilever beam at Location A

<table>
<thead>
<tr>
<th>Beam length (mm)</th>
<th>Window height (mm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
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Location B is at the position with the second lowest radius of convex curvature (17.3 mm). However, the top coat is the thickest (325 µm) at this location. The bridge and cantilever beams at this location are shown in Figure 5.4 and Figure 5.5. The substrate at this location is thicker, so the windows were cut to 1.5 mm tall and 2 mm wide. The length of the bridge beam is the same as the width of the window. The cantilever beam is 1.62 mm long and a slight deflection could be seen on the free end due to the release of 500 µm.
residual stress up cutting. The bond coat thickness was both 50 µm and the corner radius was 45 µm.

![Image]

Figure 5.4: Profile of bridge beam at Location B shows the top coat, bond coat and substrate.

<table>
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<tr>
<th>Beam length (mm)</th>
<th>Window height (mm)</th>
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Table 5.3: Geometry measurement of bridge beam at Location B

Loading position: 1mm from both ends
Figure 5.5: Profile of cantilever beam at Location B shows the top coat, bond coat and substrate.

Table 5.4: Geometry measurement of cantilever beam at Location B

<table>
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<td>1.55</td>
<td>325</td>
<td>50.4</td>
<td>45.6</td>
</tr>
</tbody>
</table>

Loading point: 1.40 mm at bond coat side. 1.50 mm on the top coat free surface

Location C is on the leading edge, which has the lowest radius of convex curvature (4.7 mm). The cantilever beam is shown in Figure 5.6, on which the top coat were slightly damaged from fabrication. A few top coat columns on the outer layer have spalled off. However, the majority of the top coat remained intact. Table 5.5 presents the
geometry measurements. The beam was 1.4 mm long with a 275 \( \mu \text{m} \) top coat and a 55 \( \mu \text{m} \) bond coat. The corner radius was 45 \( \mu \text{m} \) at the coupled end of the beam.

Figure 5.6: Profile of cantilever beam at Location C shows some damage on the top coat.

<table>
<thead>
<tr>
<th>Beam length (mm)</th>
<th>Window height (mm)</th>
<th>Average top coat thickness (( \mu \text{m} ))</th>
<th>Average bond coat thickness (( \mu \text{m} ))</th>
<th>Radius of curvature at corners (( \mu \text{m} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.42</td>
<td>1.51</td>
<td>275</td>
<td>55.7</td>
<td>45.2</td>
</tr>
</tbody>
</table>

Loading point: 1.34 mm at bond coat side. 1.5 mm on the top coat free surface

Location D is the only concave part of the vane that was evaluated. Its radius of concave curvature is 20.2 mm. The top coat at this location is relatively thin (200 \( \mu \text{m} \))
and supported by a 50 µm bond coat. The corner radius was 45 µm at the end of the beam. The bridge beam was 2 mm long and the cantilever beam was 1.66 mm.

![Figure 5.7: Profile of bridge beam at Location D shows a concave beam.](image)

<table>
<thead>
<tr>
<th>Beam length (mm)</th>
<th>Window height (mm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>1.53</td>
<td>200</td>
<td>56.3</td>
<td>45.2</td>
</tr>
</tbody>
</table>

Loading position: 1.00 mm from both ends
Figure 5.8: Profile of cantilever beam at Location D shows concave beam.

Table 5.7: Geometry measurement of cantilever beam at Location D

<table>
<thead>
<tr>
<th>Beam length (mm)</th>
<th>Window height (mm)</th>
<th>Average top coat thickness (µm)</th>
<th>Average bond coat thickness (µm)</th>
<th>Radius of curvature at corners (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.66</td>
<td>1.53</td>
<td>200</td>
<td>50.3</td>
<td>45.4</td>
</tr>
</tbody>
</table>

Loading point: 1.56 mm at bond coat side. 1.42 mm on the top coat free surface

The top coat microstructures at these locations were inspected in a TESCAN SEM and were found to be different in the four locations. Figure 5.9 to Figure 5.12 show the top coat microstructures at each location. The top coat columns at Location A forms 80° angle relative to the bond coat interface normal and appear much denser towards the bond coat interface as shown in Figure 5.9. Figure 5.10 presents the top coat at Location B,
where the top coat columns are perpendicular to the interface and are also somewhat denser closer to the bond coat interface. The top coat presented in Figure 5.11 shows high density of vertical cracks all the way to the bond coat interface at Location C. Figure 5.12 shows the top coat structure at Location D. The top coat columns at this location are also tilted to about 75° in the opposite direction from those in Location A and the overall density of the top coat was higher. The porosity content at these locations were also measured in the area enclosed by a dashed rectangle using ImageJ [142]. Table 5.8 shows the measurement results, showing Location C has the highest porosity content and Location D the lowest porosity content.
Figure 5.10: Top coat microstructure at Location B shows the columns are vertical.

Figure 5.11: Top coat microstructure at Location C shows a higher porosity.
Figure 5.12: Top coat microstructure at Location D shows the columns are tilted.

Table 5.8: Porosity measurements at four locations

<table>
<thead>
<tr>
<th>Location</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.6</td>
</tr>
<tr>
<td>B</td>
<td>12.1</td>
</tr>
<tr>
<td>C</td>
<td>13.1</td>
</tr>
<tr>
<td>D</td>
<td>2.9</td>
</tr>
</tbody>
</table>

5.2 Micro-beam test results

Three micro-bridges and four cantilever beams were tested on these turbine vane cross-sections. The bridge beams were pulled from the bond coat side and the cantilever
beams were both pulled from the bond coat side and pushed from the top coat side. The exact locations of the hook during each test were included in Table 5.1 to Table 5.7. The cross-section was cut into two halves, and each half was first glued onto a fixture before testing. After the test, the fixture was immersed in acetone to release the specimen. The specimen was then re-attached to the fixture and another beam was aligned for testing. Figure 5.13 shows the top view of the attachment of the first half of the turbine vane cross-section designated from Figure 5.1. The first half was rotated in this figure such that the top coat shown as white layer is parallel to the edge of the figure. The bridge beam in Location A is aligned with the hook at the mid-span on the bond coat side, which is shown in the middle of the figure. The top piece is the hook and the bottom piece is the fixture. During the experiment, the bottom piece is moving downwards and the top piece sensed the load through the hook. Similar configurations were used to test other beams.
The results are presented from Figure 5.14 to Figure 5.17 for the four locations. All the loads were normalized by the width of the beams. Different load-deflection responses were observed for each beam due to variations in the geometry, boundary and loading conditions. Note that the tension/compression asymmetry was observed in the
experimental results of all the micro-cantilever beams. The beam was stiffer when top coat was placed in compression and more compliant when in tension. To determine the modulus of top coat at these locations, FE analysis was used due to the complex geometries and boundary conditions of the tested beams.

Figure 5.14: Load deflection results of micro-beams at Location A include a bridge test and two cantilever tests.
Figure 5.15: Load deflection results of micro-beams at Location B include a bridge and two cantilever tests.

Figure 5.16: Load deflection results of micro-beams at Location C show two cantilever tests.
Figure 5.17: Load deflection results of micro-beams at Location D show one bridge and two cantilever tests.

5.3 Determination of top coat modulus

A full scale model was built for the cross-sections of the turbine vane because the geometry is much more complex than those of the burner rig bar samples. Any simplification of the model would lead to misinterpretation of the top coat modulus. The two halves of the turbine vane were modeled individually since they were tested separately. Figure 5.18 shows the first half (trailing edge) of the turbine vane, on which sits two beams of Location A. Figure 5.19 shows the second half of the boundary vane, on which there are Locations B, C and D. Figure 5.20 and Figure 5.21 show the detailed FE model of the bridge and cantilever beams at this location. Note that the cantilever
beams had an initial deflection of 75 µm at the tip, which was caused by the release of the residual stress. A 20 µm mesh size was used for the model and the boundary conditions were applied in a way that mimics the gluing of the sample on the fixture. Fixed displacement was applied to the bridge and cantilever beams and the location of the loading point was taken in the geometry measurement (Table 5.2 to Table 5.7). The FE model of two beams at Location D is shown in Figure 5.22 for the bridge beam and Figure 5.23 for the cantilever beam. Figure 5.24 shows the FE model of the cantilever beam at Location C. Figure 5.25 and Figure 5.26 shows the FE models of bridge beam and cantilever beam at Location D.

Figure 5.18: Construction of the model for the first half includes the cooling channel.
Figure 5.19: FE model of the second half of the turbine vane includes the cooling channel.

Figure 5.20: FE mesh of the bridge beam at Location A with a point displacement loading at mid-span.
Figure 5.21: FE model of the cantilever beam at Location A shows the deflection of beam.

Figure 5.22: FE model of the Bridge beam at Location B shows displacement loading at the mid-span.
Figure 5.23: FE model of the cantilever beam at Location B shows the displacement loading.
Figure 5.24: FE model of the cantilever beam at Location C shows a curved beam with displacement loading towards the free end.
Figure 5.25: FE model of the bridge beam at Location D includes the curvature of the beam.

Figure 5.26: FE model of the cantilever beam at Location D includes the curvature.
The RMSE method was used to extract the modulus after comparing the results of the FE analysis and the micro-bending experiments. The Timoshenko solution was used to make an initial guess and the search area was expanded around it to find the best fit. Errors were calculated for each set of beams for one location. Table 5.9 to Table 5.12 show the calculation of RMSE for different pairs of tension and compression modulus. The moduli that best fits each data set is underscored and shown to produce the smallest error.

Table 5.9: RMSE analysis for micro-beams at Location A

<table>
<thead>
<tr>
<th>Et</th>
<th>Ec</th>
<th>27</th>
<th>28</th>
<th>29</th>
<th>30</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td></td>
<td>2.115</td>
<td>1.822</td>
<td>1.587</td>
<td>1.999</td>
<td>2.193</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>1.862</td>
<td>1.612</td>
<td>1.350</td>
<td>1.731</td>
<td>2.020</td>
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<tr>
<td>19</td>
<td></td>
<td>1.297</td>
<td>1.090</td>
<td>0.887</td>
<td>1.160</td>
<td>1.302</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>1.019</td>
<td>0.873</td>
<td>0.725</td>
<td>0.874</td>
<td>1.145</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td>1.210</td>
<td>1.016</td>
<td>0.847</td>
<td>1.024</td>
<td>1.346</td>
</tr>
</tbody>
</table>

Table 5.10: RMSE analysis for micro-beams at Location B

<table>
<thead>
<tr>
<th>Et</th>
<th>Ec</th>
<th>24</th>
<th>25</th>
<th>26</th>
<th>27</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td></td>
<td>1.527</td>
<td>1.302</td>
<td>1.121</td>
<td>1.438</td>
<td>1.587</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>1.333</td>
<td>1.140</td>
<td>0.939</td>
<td>1.232</td>
<td>1.454</td>
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<tr>
<td>15</td>
<td></td>
<td>0.898</td>
<td>0.739</td>
<td>0.583</td>
<td>0.793</td>
<td>0.902</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>0.684</td>
<td>0.572</td>
<td>0.619</td>
<td>0.573</td>
<td>0.781</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>0.831</td>
<td>0.682</td>
<td>0.632</td>
<td>0.688</td>
<td>0.936</td>
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</tbody>
</table>
Table 5.11: RMSE analysis for micro-beams at Location C

<table>
<thead>
<tr>
<th>Ec</th>
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<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>0.539</td>
<td>0.422</td>
<td>0.384</td>
<td>0.478</td>
<td>0.667</td>
</tr>
<tr>
<td>12</td>
<td>0.412</td>
<td>0.356</td>
<td>0.277</td>
<td>0.351</td>
<td>0.483</td>
</tr>
<tr>
<td>13</td>
<td>0.321</td>
<td>0.261</td>
<td>0.174</td>
<td>0.281</td>
<td>0.390</td>
</tr>
<tr>
<td>14</td>
<td>0.442</td>
<td>0.336</td>
<td>0.229</td>
<td>0.339</td>
<td>0.506</td>
</tr>
<tr>
<td>15</td>
<td>0.634</td>
<td>0.534</td>
<td>0.359</td>
<td>0.521</td>
<td>0.721</td>
</tr>
</tbody>
</table>

Table 5.12: RMSE analysis for micro-beams at Location D

<table>
<thead>
<tr>
<th>Ec</th>
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<th>59</th>
<th>60</th>
<th>61</th>
<th>62</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>1.124</td>
<td>1.029</td>
<td>0.945</td>
<td>0.874</td>
<td>0.898</td>
</tr>
<tr>
<td>34</td>
<td>0.833</td>
<td>0.801</td>
<td>0.815</td>
<td>0.847</td>
<td>0.855</td>
</tr>
<tr>
<td>35</td>
<td>0.514</td>
<td>0.494</td>
<td>0.432</td>
<td>0.508</td>
<td>0.514</td>
</tr>
<tr>
<td>36</td>
<td>0.841</td>
<td>0.814</td>
<td>0.793</td>
<td>0.801</td>
<td>0.780</td>
</tr>
<tr>
<td>37</td>
<td>1.200</td>
<td>1.168</td>
<td>1.173</td>
<td>1.159</td>
<td>1.165</td>
</tr>
</tbody>
</table>

5.4 Discussion of results

The top coat moduli were determined at the four specified locations on the turbine vane. The values of the modulus were comparable to the burner rig bar at location D (Tension: 35 GPa and Compression: 60 GPa). The moduli of the top coat on the burner
rig bar are 30 GPa (in tension) and 50 GPa (in compression) on the straight edges. The top coats on the curved edges are 28 GPa (in tension) and 47 GPa (in compression).

High variability of modulus values was found comparing the four locations. Table 5.13 shows the result summary for the top coat modulus determined at the four locations. The concave substrate of the turbine vane produced a higher modulus than the convex locations. The top coat modulus is also dependent on the radius of curvature of the substrate. The top coat modulus on the highest radius of curvature is bigger than the other two locations with a lower radius of curvature on the convex locations of the turbine vane. The smallest modulus was found for the top coat at Location C, where the substrate is highly curved.

*Table 5.13: Top coat modulus on the turbine vane*

<table>
<thead>
<tr>
<th>Radius of curvature (mm)</th>
<th>Location</th>
<th>Depth(μm)</th>
<th>Concave/Convex</th>
<th>Porosity (%)</th>
<th>E_tension (GPa)</th>
<th>E_compression (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-313</td>
<td>A</td>
<td>275</td>
<td>Convex</td>
<td>6.6</td>
<td>20</td>
<td>29</td>
</tr>
<tr>
<td>-17.9</td>
<td>B</td>
<td>325</td>
<td>Convex</td>
<td>12.1</td>
<td>15</td>
<td>26</td>
</tr>
<tr>
<td>-4.7</td>
<td>C</td>
<td>275</td>
<td>Convex</td>
<td>13.1</td>
<td>13</td>
<td>20</td>
</tr>
<tr>
<td>20.3</td>
<td>D</td>
<td>200</td>
<td>Concave</td>
<td>2.9</td>
<td>35</td>
<td>60</td>
</tr>
</tbody>
</table>

The top coat thickness and microstructure observed at the four locations are also different and the measured modulus scaled with substrate curvature and top coat porosity. The top coat at Location D has the lowest thickness and porosity content being the densest, which produced the highest modulus. The top coat at Location C has the smallest
modulus and the greatest volume fraction of pores was identified. It is worth noting that
the burner rig top coats did not scale with substrate curvature. This suggests that
deposition condition as well as substrate curvature have a role in determining top coat
microstructure and properties. Moreover, the top coat columns at Location A and D
forms an angle with respect to the normal of the top coat/bond coat interface. A rational
explanation can be made based on the processing condition. During EBPVD process, the
vaporized ions travel in a straight line from the source to the parts. Both the burner rig bar
and the vane were rotated during deposition, but the burner rig bar was more symmetric
and the line-of-sight to the surface was much more complicated for the vane.

The microstructure of the top coat is dependent on the rotation of the substrate
and vapor incident angle (VIA) [135, 143, 144]. The substrate rotation was shown to
create a graded top coat microstructure, whereas the microstructure of the top coat
produced on a stationary substrate was more uniform. Higher substrate rotation was
found to create a more porous top coat than the lower speed during deposition [145]. VIA
is defined as the angle between the coating vapor flux and the substrate surface normal.
Deposition from an oblique angle produces titled top coat columns such as can be observed in locations A and D. VIA can affect the porosity in the top coat and it was
found that the porosity produced from oblique VIA is higher than normal incidence on
flat and stationary substrate [146]. The current study showed that the porosity in the top
coat was closely related to the modulus. However, little was known about the effect of
substrate geometry during deposition to the porosity of the EBPVD top coat. Based on
the top coat microstructure observed in the turbine vane, it is assumed that the line-of-
sight also plays a major role in determining the top coat microstructure, especially the porosity.

Anisotropic elasticity was used to understand the tilting of the top coat columns for locations A and D. The columns were tilted to 80 degrees at location A and 75 degrees at location D towards the bond coat interface. Using the out-of-plane modulus of 150 GPa and the in-plane moduli of 29 GPa for compression and 20 GPa for tension at location A, the modulus along the top coat columns was calculated to be 134 GPa and the modulus perpendicular to the columns was 20.8 GPa for tension and 29.8 GPa for compression, respectively. The modulus along the top coat columns (75 degrees) at location D was also calculated to be 133 GPa and perpendicular to the columns, the moduli was calculated to be 59.1 GPa for compression and 35.7 GPa for tension. The modulus along columns decreases by 10% and the modulus perpendicular to the columns has minimum variation. The calculation shows that the titling of the columns does not change the top coat modulus to a significant extent.

Tension and compression asymmetry of the top coat was also observed. The modulus in tension is roughly half of the modulus in compression. As with the burner rig bars, the tension/compression asymmetry appears to be related to the microstructure of the top coat. Pores and vertical spacings were observed between the top coat columns (Figure 5.9 to Figure 5.12). Tension enlarges the pore and opens up the cracks, resulting in a compliant top coat. On the other hand, compression reduces the pores size and close the cracks, leading to a stiffer top coat.
Chapter 6: Elastic response of freestanding EBPVD 7YSZ top coats

6.1 Geometry of Freestanding EBPVD 7YSZ top coats beams

A total of 10 freestanding top coat beams of different thicknesses were prepared to measure the depth dependency of the EBPVD 7YSZ top coat modulus. Four of them were 152 μm thick, three were 100 μm and the other three were 67 μm. The length and the radius of curvature of the beams were measured for each beam. Since the beams were curved, the length was measured to the closest distance from one end to the other. The curvature was measured by fitting an arc along the concave top coat free surface using ImagePro software. Table 6.1 to Table 6.3 give the length, width and radius of curvature for each beam tested. The width of each beam was taken as the average of three measurements along the length. The curvature developed upon detachment means that there was residual stress in the top coat. The distance between the two outer pin measured from the centroids is 4.3 mm, so the aspect ratio of all the beams are high enough to use Euler-Bernoulli solution to extract the top coat modulus.
Table 6.1: Dimension measurement of 152 μm thick beams

<table>
<thead>
<tr>
<th>Beam number</th>
<th>Length (mm)</th>
<th>Width (μm)</th>
<th>Radius of curvature at top coat free surface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.3</td>
<td>600</td>
<td>33.4</td>
</tr>
<tr>
<td>2</td>
<td>6.5</td>
<td>631</td>
<td>35.3</td>
</tr>
<tr>
<td>3</td>
<td>8.6</td>
<td>600</td>
<td>33.7</td>
</tr>
<tr>
<td>4</td>
<td>5.9</td>
<td>538</td>
<td>31.4</td>
</tr>
</tbody>
</table>

Thickness: 152 μm

Table 6.2: Dimension measurement of 100 μm thick beams

<table>
<thead>
<tr>
<th>Beam number</th>
<th>Length (mm)</th>
<th>Width (μm)</th>
<th>Radius of curvature at top coat free surface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.8</td>
<td>467</td>
<td>21.5</td>
</tr>
<tr>
<td>2</td>
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</tr>
<tr>
<td>3</td>
<td>5.6</td>
<td>721</td>
<td>25.1</td>
</tr>
</tbody>
</table>

Thickness: 100 μm

Table 6.3: Dimension measurement of 67 μm thick beams

<table>
<thead>
<tr>
<th>Beam number</th>
<th>Length (mm)</th>
<th>Width (μm)</th>
<th>Radius of curvature at top coat free surface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.8</td>
<td>390</td>
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</tr>
<tr>
<td>2</td>
<td>7.1</td>
<td>485</td>
<td>24.5</td>
</tr>
<tr>
<td>3</td>
<td>5.6</td>
<td>480</td>
<td>25.1</td>
</tr>
</tbody>
</table>

Thickness: 67 μm
The top coat was also thermally exposed to study the effect of top coat sintering. One burner rig bar cross-section was heat treated with top coats still attached to the bond coat and substrate. The thermal exposure was carried out at 1100°C at ambient air atmosphere for 8 hours. Two freestanding top coat beams were obtained after the heat treatment. No thinning was performed, so the thickness of the top coat beams remained 150 µm. The dimensions of the two beams are in Table 6.4. The difference in radius of curvature between the as-deposited top coat beams and the thermally exposed beam are not obvious. Since there were only two beams, no conclusion could be drawn.

<table>
<thead>
<tr>
<th>Beam number</th>
<th>Length (mm)</th>
<th>Width (µm)</th>
<th>Radius of curvature at top coat free surface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.3</td>
<td>713</td>
<td>35.9</td>
</tr>
<tr>
<td>2</td>
<td>7.7</td>
<td>678</td>
<td>32.1</td>
</tr>
</tbody>
</table>

Thickness: 150µm

Three CMAS infiltrated top coat beams were also prepared. The top coat was measured to be denser after infiltration and an observation of the cross-section in SEM shows that the vertical spaces between the columns has been filled (Figure 6.1). Extra CMAS was also observed near the bond coat interface, which increased the overall thickness of the sample [125]. The total thickness of top coat plus CMAS was measured to be ~165 µm. Other dimensions of the three beams are shown in Table 6.5.
Figure 6.1: CMAS infiltrated EBPVD 7YSZ top coat shows a dense top coat and residual CMAS on bond coat side of the top coat.

<table>
<thead>
<tr>
<th>Beam number</th>
<th>Length (mm)</th>
<th>Width (µm)</th>
<th>Radius of curvature at top coat free surface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>6.2</td>
<td>422</td>
<td>34.4</td>
</tr>
<tr>
<td>2</td>
<td>5.8</td>
<td>444</td>
<td>33.8</td>
</tr>
<tr>
<td>3</td>
<td>5.5</td>
<td>322</td>
<td>30.5</td>
</tr>
</tbody>
</table>
6.2 Results of three point bending tests

The freestanding top coat beams were subjected to three point bending and the load-displacement curves were used to determine their modulus. Each beam was first loaded with the central pin on the top coat free surface and the outer pins on the bond coat side, which place the top coat free surface in compression. The beams were flipped to place the outer pins on the top coat free surface and the central pin on the bond coat side, which imposed tension on the top coat free surface (Figure 3.39). The loading and outer pins were not moved during flipping of the beams to ensure consistency. At least two beams of the same type were tested to measure the variability of the top coat material and repeatability of the test methodology. DIC was used to measure the mid-span deflection relatively to the outer pins. Load-deflection curves were obtained for each beam.

The four 150 µm as-deposited top coat beams were loaded to only 0.075 N to avoid damaging them and then unloaded. Figure 6.2 to Figure 6.5 present the load-deflection of the four 150 µm top coat beams. The deflection was measured at the mid-span. The dotted line (denoted as TC) is the load-deflection curve when loading on the top coat free surface and the solid line (denoted as BC) is when loading on the bond coat side. To avoid confusion, the mid-span refers to the middle of test span instead of the beam length. The load was normalized by the widths of the beams for direct comparison since the widths were different from one beam to another.
Figure 6.2: Load-displacement of 150 um beam 1 loaded at bond coat and top coat sides.

Figure 6.3: Load-displacement of 150 um beam 2 loaded at bond coat and top coat sides.
Figure 6.4: Load-displacement of 150 um beam 3 loaded at bond coat and top coat sides.

Figure 6.5: Load-displacement of 150 um beam 4 loaded at bond coat and top coat sides.
A few consistent observations were made from the load deflection of the four beams: First, the beams show a difference in terms of stiffness response by locating the central pin at top coat free surface and bond coat side. The beam is stiffer when the central pin was on the top coat surface while it is compliant when it is on the bond coat side. Second, the load and unload processes follow a different path showing a small amount of viscoelastic behavior. Third, there was always a small offset (<1 µm) of the deflection upon full unloading indicating a permanent deformation. The offset was always bigger when the central pin on the bond coat side than when it was on the top coat side. The analytical three point bending solution (Eq. 3.10) was used to extract the modulus of each test and is rearranged to show the calculation of modulus as:

\[ E = \frac{FL^3}{48WI} \]

where \( F \) is the applied load; \( L \) is the span length between the two outer pins; \( W \) is the mid-span deflection; \( I \) is the second moment of inertia, which is calculated as \( bh^3 / 12 \) (\( b \) is the width and \( h \) is the thickness). Since the load has already been normalized by the width and the slope of the load-deflection curve further normalized the load by t deflection. The calculation of modulus can be simplified to the following equation:

\[ E = \frac{KL^3}{4h^3} \]

Where \( K \) the slope is measured for each test; \( h \) is the thickness of the top coat. Table 6.6 gives the measurement of the slope for each test. \( K_{TC} \) is the slope of the load-deflection when loading on the top coat free surface and \( K_{BC} \) is the slope when loading on the bond.
coat side. \( L \) and \( h \) are also given. The modulus of the top coat was calculated for each test. Consistent top coat moduli were obtained for all the four beams. The top coat modulus is higher when loading on the top coat free surface than on the bond coat side.

\[ \text{Table 6.6: As-deposited 152 \( \mu \text{m} \) top coat modulus} \]

<table>
<thead>
<tr>
<th>Beam number</th>
<th>( K_{TC} ) (per unit width)</th>
<th>( E_{TC} ) (GPa)</th>
<th>( K_{BC} ) (per unit width)</th>
<th>( E_{BC} ) (GPa)</th>
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<tr>
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<tr>
<td>4</td>
<td>0.01075</td>
<td>61</td>
<td>0.00945</td>
<td>54</td>
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</tbody>
</table>

Span length = 4.3 mm; Loading pin at Mid-span

Three beams were polished back to 100 \( \mu \text{m} \) and tested in the same way. The results are shown in Figure 6.6 to Figure 6.8. The maximum load reached was half of that for 152 \( \mu \text{m} \) beams and the discrepancy of the load-deflection curves loaded on opposite sides is significantly smaller. The two load-deflection curves align relatively well with one another regardless of which side the center pin was on. A second difference was the decrease in the residual deformation; it was observed that the deviation was small upon unloading for the beams made from the bottom 100 \( \mu \text{m} \) of the top coat. The modulus for these beams was calculated in Table 6.7 and the results are consistent. The modulus of the 100 \( \mu \text{m} \) beams is higher than those of the 152 \( \mu \text{m} \) beams in all the two loading positions on the samples. In addition, the modulus does not show a difference upon loading the sample on the top coat free surface or on the bond coat side.
Figure 6.6: Load-deflection of 100 µm beam 1 loaded at bond coat and top coat sides.

Figure 6.7: Load-deflection of 100 µm beam 2 loaded at bond coat and top coat sides.
Figure 6.8: Load-deflection of 100 µm beam 3 loaded at bond coat and top coat sides.

Table 6.7: As-deposited 100 µm top coat modulus

<table>
<thead>
<tr>
<th>Beam number</th>
<th>( K_{TC} ) (per unit width)</th>
<th>( E_{TC} ) (GPa)</th>
<th>( K_{BC} ) (per unit width)</th>
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<td>0.00330</td>
<td>66</td>
<td>0.00330</td>
<td>66</td>
</tr>
</tbody>
</table>

Span length = 4.3 mm; Loading pin at Mid-span

A set of three other beams were polished down to 67 µm. Figure 6.9 to Figure 6.11 show the load-deflection curves for the three beams. The maximum load reached was even smaller at about 0.01 N due to the shallower thickness than the first two types
of beams. Similarly to 100 µm thick beams, the difference in load-deflection curves between loading on the top coat free surface and the bond coat side is insignificant the 67 µm thick beams. There is an overlapping of the loading and unloading curve. Table 6.8 presents the modulus for the 67 µm beams. The difference between loading on the top coat free surface and bond coat side remain small. The modulus is higher than those of the 100 µm and 152 µm beams. A depth dependency of the top coat modulus was suggested by Zhao and Xiao [147] using nano-indentation, which decreased along the thickness from bond coat interface to top coat free surface. However, it is difficult to probe the macroscopic modulus of the top coats at various thicknesses. This result of this study has showed a depth dependency of the EBPVD 7YSZ top coat modulus.

![Graph showing load-deflection of 67 µm beam](image)

*Figure 6.9: Load-deflection of 67 µm beam 1 loaded at bond coat and top coat sides.*
Figure 6.10: Load-deflection of 67 µm beam 2 loaded at bond coat and top coat sides.

Figure 6.11: Load-deflection of 67 µm beam 3 loaded at bond coat and top coat sides.
Table 6.8: As-deposited 67 μm top coat modulus

<table>
<thead>
<tr>
<th>Beam number</th>
<th>$K_{TC}$ (per unit width)</th>
<th>$E_{TC}$ (GPa)</th>
<th>$K_{BC}$ (per unit width)</th>
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<td>83</td>
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Span length = 4.3 mm; Loading pin at Mid-span

The maximum loads reached in all the tests were relatively conservative to maintain the elastic behavior region and minimize damage. The inelastic region of the top coat was also probed by increasing the maximum load for a few additional tests. Two as-prepared 152 μm beams were tested by increasing the maximum loads to about 0.1 and 0.2 N, respectively. The results were compared with that of Beam 1 presented in Figure 6.2. One cycle of loading was performed for each sample and the two orientations were tested. Figure 6.12 presents the load-deflection of the beams when central pin loaded on the top coat free surface and Figure 6.13 presents the results when central pin loaded on the bond coat side. The loading part of the curves is in good agreement showing the consistency of the material behavior. However, the higher loads resulted in a deviation from linear elastic loading. The residual deformation is greater for the sample that experienced the higher load and these observations are consistent regardless of which side of the samples was loaded. The trend of the stiffness response of the top coat beams was also in accordance with the previous test results showing the top coat to be stiffer when central pin loaded on the top coat free surface than it was from the bond coat side.
However, the area encapsulated within the load deflection curve is also smaller when central pin loaded on the top coat side with smaller residual deformation.

**Figure 6.12:** 150 µm top coat beams were loaded at top coat free surface to higher loads.

**Figure 6.13:** 150 µm top coat beams were loaded at the bond coat side higher loads.
The modulus of the CMAS infiltrated freestanding top coat was also evaluated to quantify the effect of the CMAS contamination. A total of three beams were assessed by both loading on the top coat free surface and bond coat side. Figure 6.14 to Figure 6.16 presents the load-deflection results with one loading cycle for each test. The load-deflection curves of these tests have much higher slopes than those of the as-deposited top coats indicating a much more rigid top coat. The loading and unloading curves align with each other and there is almost no difference between loadings on the top coat free surface versus loading on the bond coat side. The slope of the loading curve was fitted to calculate the modulus for each beam. The modulus of the CMAS infiltrated top coat is much higher than those of the as-deposited top coats. The small scatter in the results could be caused by the non-uniform infiltration of CMAS from one location to the other or the different amount of residual CMAS in the bottom part of the top coat shown in Figure 6.1, but the influence of CMAS penetration is clear.
Figure 6.14: Load-deflection response of CMAS infiltrated top coat beam 1 loaded on two sides.

Figure 6.15: Load-deflection response of CMAS infiltrated top coat beam 2 loaded on two sides.
The modulus of CMAS infiltrated top coat manufacture by EBPVD technique was mainly estimated due to lacking of experimental evaluations and the values have a wide range. Levi et al. [148] estimated the CMAS infiltrated modulus to be 90 GPa and Mercer’s hypothesis of the modulus is 200 GPa [67]; Jackson et al. [149] used simple Reuss rule-of-mixtures model to calculate the modulus. Depending on the material of infiltration, the calculation of top coat modulus varies from 70 to 180 GPa. This study has shown that the CMAS infiltration raised the modulus of EBPVD top coat to 182±14 GPa, which is close to the upper bound of the estimates.

Figure 6.16: Load-deflection response of CMAS infiltrated top coat beam 3 loaded on two sides.
To quantify the effect of thermal exposure, two post-heat treatment top coat beams were tested and the results are shown in Figure 6.17 and Figure 6.18. The most obvious finding is that the two beams are much more compliant than the previously tested beams. Large deformations were witnessed at the mid-span deflects, while the maximum load reached are only slightly lower. The unloading curves were discontinuous showing a huge load drop and a big offset when the beams were fully unloaded, which is an indication that damage was caused in the beam. The modulus was calculated using the loading curve and is presented in Table 6.10, which has dropped significantly as compared to the as-deposited top coats. The modulus when loaded on the bond coat side is only half of that when loaded on the top coat free surface.

<table>
<thead>
<tr>
<th>Beam number</th>
<th>$K_{TC}$ (per unit width)</th>
<th>$E_{TC}$ (GPa)</th>
<th>$K_{BC}$ (per unit width)</th>
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<tr>
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<td>0.04171</td>
<td>183</td>
</tr>
</tbody>
</table>

Span length = 4.3 mm; Loading pin at Mid-span
Figure 6.17: Load-deflection of thermally exposed top coat beam 1 loaded on two sides.

Figure 6.18: Load-deflection of thermally exposed top coat beam 2 loaded on two sides.
The effect of EBPVD top coat sintering on the modulus was reported in the literature. Vecchione et al. [83] reported, using nano-indentation, that the modulus of EBPVD YSZ top coat increased from 81 to 88 GPa after 80 hours of isothermal exposure under 1100°C. Guo and Kagawa [84] also found that the thermal exposure increased the top coat modulus due to sintering using nano-indentation. Pfeiffer et al. [88] reported that the modulus of EBPVD top coat increased initially from 20 to 80 GPa and then decreased to 40 GPa as a function of thermal exposure time, using a four point bend technique, which is also observed by Wang et al. [87] using a three point bending of freestanding EBPVD top coat. However, the experimental data in this study clearly shows that the modulus drops substantially after thermal exposure.

<table>
<thead>
<tr>
<th>Beam number</th>
<th>K_{TC} (per unit width)</th>
<th>E_{TC} (GPa)</th>
<th>K_{BC} (per unit width)</th>
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<td>0.00257</td>
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<td>7</td>
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</tbody>
</table>

6.3 Discussion of results

The 150 µm freestanding top coat also exhibits a tension and compression asymmetry with a smaller difference as compared to those of the attached top coat. The top coat is stiffer when loaded on the top coat free surface as opposed to loaded on the bond coat side. The tension and compression asymmetry was not very obvious in the
stiffness response of the thinned top coat. The experimental results for the two thinner beams (100 and 67 µm) show that the load-deflection curves nearly overlapped from placing the central pin at the top coat side and the bond coat side. The smaller difference is originated from the mixed loading state through the thickness of the freestanding beams subjected to bending. By contrast, the attached top coat is entirely under pure tension or compression because the neutral axis is located outside the top coat. As experimentally measured, the neutral axis of the freestanding beam is located at 90 µm away from the top coat free surface, so approximately 3/5 of top coat is under either tension or compression, while the other 2/5 is loaded oppositely. A second reason leading to a reduced tension and compression asymmetry is the release of the residual stress upon detachment from the substrate. The release of the residual stress led to the development of curvature that reduced the spacing of the columns near the top coat free surface. During testing, the spaces were either to be reopened or further closed up, which causes the reduction of the asymmetry.

The test results for the freestanding top coat beams shows that the modulus is not constant over the entire thickness of the top coat, but rather it increases towards the bond coat interface. The observation appears to be related to the columnar microstructure of the TBC top coat that incorporates a gradient in both column diameter and porosity content. The porosity measured on the attached top coat cross-section in Figure 3.34 corroborates this line of reasoning. As is shown, the porosity content in the top coat drops when approaching the bond coat interface; the top coat becomes denser towards the interface. The depth dependence of the modulus and the location of the neutral axis in the
beam both support this observation. The neutral axis was measured to be 60 µm away from the bond coat side, while the entire top coat thickness is 150 µm, which means the top coat is more rigid near the bond coat side. The gradient of EBPVD top coat microstructure was also mentioned by Strangman [150], where the density of the top coat, hence the modulus, decreases away from the bond coat. The formation of the graded microstructure was reported by Kaysser et al. [151] to result from the rotation of the substrate during deposition. Without rotation, the sizes of the columns were uniform along the thickness. Increasing the rotational speed of the substrate forms the columns that vary in diameter from the bond coat interface to the free surface.

The top coat modulus was extracted from the load deflection responses with the assumption that no TGO is present. To quantify the influence of a TGO layer, the location of the neutral axis for the freestanding top coat specimens was calculated both with and without TGO. The top coat was assumed to include three layers with gradient moduli of 60, 67 and 87 GPa from the top coat free surface to the bond coat interface. The thicknesses for the three layers were 50, 33 and 67 µm, respectively. In the case of including a fourth layer of TGO, its modulus was assumed to be 360 GPa and with a thickness of 1 µm. Assuming that all the layers are homogeneous and isotropic, the position of the neutral axis was analytically calculated to be 67 µm (without TGO) and 66 µm (with TGO) away from the bond coat interface. The position of the neutral axis in the top coat beams has insignificant with the inclusion of a thin TGO layer during calculation, because of its small thickness (<1 µm) compared to the 150 µm thick top coat. The predicted position of the neutral axis agrees well with the measurement which shows that
the neutral axis is located 60 µm away from the bond coat interface. The match between the analytical calculation and the experimental results indicates the accuracy of modulus measurement on the freestanding top coats.

The results from the three point bending experiments further indicates that the top 50 µm top coat dominates the tension and compression asymmetry. The load deflection responses for the 150 µm top coats depend on the location of the central pin. The beam is stiffer when the pin is located at the top coat free surface, whereas the top coat is more compliant when the pin is placed at the bond coat interface. The difference in the stiffness responses of the top coat disappears in the load deflection of the top coats thinned down to 100 and 67 µm. The disappearance of the tension and compression asymmetry in the 100 and 67 µm indicates the material is more homogeneous at these two depths, whereas the top 50 µm contributes more to the tension and compression and is assumed to be more porous.

Anelastic behavior of the top coat was observed in the load deflection responses of the 150 µm top coat specimens, in which the unloading curves deviate from loading. The anelastic behavior of the top coat was enhanced when the top coat experienced higher loads. A permanent offset of deflection was found upon unloading. The higher the load, the bigger the offset was. The observed offset when the central pin located on the bond coat interface was high than the central pin located on the top coat free surface. Nonlinear load deflection was also observed and became obvious beyond 0.2 N, in which the slope of the load deflection curve dropped. The offset of deflection and the
nonlinearity of the load deflection curve indicate the microstructure damage in the top coat.

The strain in the outmost fiber on the top coat free surface was calculated and compared with the measured value at the same load of 0.15 N. The strain was calculated to be $6.2 \times 10^{-6}$ when the outmost fiber of the top coat was under compression with the central pin on the top coat free surface. The position of the neutral axis was calculated to be 66 µm away from the bond coat interface in the case of TGO presence. The top coat modulus used in calculation was 60 GPa from the three point bending result. The measured strain at 5 µm below the top coat free surface was $8 \times 10^{-4}$, which is much larger than the calculated value. The discrepancy between the calculated and measured strain indicates that the modulus of the top coat close to the free surface is much lower than averaged value of 60 GPa, showing that the top coat is the most compliant along the thickness.

Contrary to what was expected, thermal exposure were found to significantly reduce the modulus of the EBPVD 7YSZ top coat. The top coat is more compliant than the substrate, hence it tolerates the expansion and contraction of the substrate subjected to thermal cycling. In this case, it is reasoned that the expansion of the substrate at elevated temperature induced tensile strain the top coat which facilitates the propagation of the vertical cracks. As the sample cools down, permanent damage has been caused in the top coat, which leads to the reduction of the stiffness responses. Another possible explanation could be that sintering led to vertical separation through the top coat. In this case size
scale would be important. Macroscopic deformation imposed by bending would sense the effect of the vertical separations within the top coat.

The tension and compression asymmetry was also significantly enhanced accompanied by the overall drop of modulus due to local cracking as compared to the as-deposited top coats. The thermally exposed top coats are much stiffer when loaded on the top coat free surface than from the bond coat side. This observation could be explained by the propagation of the cracks in the top coat from thermal exposure while still attached on the substrate. The CTE mismatch between the top coat and the substrate led to a tensile stress in the top coat during high temperature exposure. The tensile stress induced propagation of the crack, which made the beam more compliant.

The CMAS infiltrated top coat showed a substantial increase in the top coat modulus. The average modulus was evaluated to be 186 GPa when loaded on the top coat free surface and it was 181 GPa when loaded from the bond coat side. The infiltrated CMAS filled up the cracks in the top coat increasing the density, resulting in an increase in the modulus. Accordingly, the tension and compression asymmetry also disappeared as the top coat becomes homogeneous.
Chapter 7: Summary and future work

7.1 Summary of current characterization of EBPVD 7YSZ top coats

The EBPVD 7YSZ top coat modulus was characterized in this study as a function of substrate geometry, coating thickness, thermal exposure, and CMAS contamination. The characterization was carried out on commercial top coats deposited on burner rig bars and on a real turbine vane, both provided by Pratt & Whitney. The top coat modulus was determined experimentally in both attached and freestanding configurations. Two techniques were employed: a novel micro-beam bending geometry with unique sample design to evaluate the attached top coat modulus and a three-point bending configuration to assess the freestanding top coats. The determination of modulus was accomplished via FE simulations of the attached top coats using a parametric analysis. The analytical Euler-Bernoulli beam bending solution was utilized to extract the modulus of the freestanding top coats. A resonance frequency and curvature method was also introduced to evaluate the top coat modulus and residual stress using APS 8YSZ top coats as an example. The operating procedure for this was documented for future reference. A summary of the key findings of this study is as follows:

1. A tension/compression asymmetry in EBPVD 7YSZ top coats was confirmed and quantified. Earlier micro-beam bending experiments reported that the top coats were stiffer when loaded in compression and more compliant when loaded in tension. The current micro-bending study
confirmed the observation and determined the representative values for both tension and compression. Experiments carried on burner rig bars yielded values of 30 GPa and 50 GPa on the straight surfaces, and 28 GPa and 47 GPa on the curved surfaces, respectively. Micro-bending specimens cut from an as-deposited commercial turbine vane yielded a slightly wider range of moduli (13 ~ 60 GPa). In general, the tension modulus was found to be about half of the compression modulus. The tension/compression asymmetry is likely due to the columnar microstructure of the EBPVD top coats with vertical cavities and pores in between. Tension causes the vertical spaces to open up, while compression leads to denser and stiffer top coat.

2. The modulus of the top coat on the turbine vane was found to depend on the geometry of the substrate and the deposition conditions. The top coat modulus is higher on the convex side than the concave side. Moreover, the top coat modulus is higher in curvature regions and lower on a highly curved substrates. This variation of the top coat modulus has been associated with differences in the microstructure. The top coat on the convex side of the substrate contains the least porosity. The top coat on the highest curvature substrate has the highest porosity and is most compliant. The substrate dependency of the top coat modulus was not apparent on the straight and curved edges of the burner rig bar samples, where similar microstructure and modulus were observed. This observation points to the importance of processing geometry and conditions.
3. Top coat modulus was found to be dependent on the depth at which it was evaluated. The tests of freestanding top coats showed that the modulus is highest close to the bond coat side and lower close to the top coat free surface. The change in the porosity through the thickness accompanies this finding; the top coat close to the bond coat has lower porosity and is denser. The moduli of freestanding top coats are slightly higher than the attached ones and the tension/compression asymmetry is reduced, which can be explained by the difference in the deformation of the top coat. The entire top coat is under either tension or compression since the neutral axis is outside the top coat in the attached case. The neutral axis in the freestanding top coat was measured to be at 90 µm away from the free surface. The top coat was under both tension and compression during bending. Since the top coats were more rigid under compression. The modulus is higher in the case of bending freestanding top coats.

4. Thermal exposure substantially reduced the top coat modulus. The modulus of the freestanding top coat after thermal exposure (8 hours, 1100°C, at ambient air atmosphere) was only ~1/3 of the as-deposited value when center loaded at the top coat free surface. It dropped to ~1/8 of the as-deposited counterpart when loaded on the bond coat side. The top coats were still attached to the bond coat and substrate during thermal exposure and thermal stress may create vertical separations, which reduce the top coat modulus.
Furthermore thermal exposure caused sintering of the top coat that separated some of the columns and reduced the modulus.

5. The CMAS infiltrated coat possessed much higher moduli, which were three to four times of the as-deposited value. The CMAS infiltration was driven by capillary and the molten CMAS followed the free path between the columns and filled up the spaces at high temperature. Once cooled down, CMAS solidified and led to much denser and more homogeneous top coats. The CMAS infiltration altered the top coat microstructure resulting in the loss of the tension/compression asymmetry.

6. A resonance frequency and curvature technique have been introduced to evaluate the top coat modulus and residual stress as a function of depth. The advantages of the technique are three-fold: it measures the top coat modulus when still attached on the substrate, which represents the working state of the coating; the sample is relatively large so the results are more representative of the overall macroscopic coating; and the test is easy to set up and run. Preliminary tests indicated that the resolution of the oscilloscope and the sample temperature influence the testing results to a significant extent. Improved consistency and accuracy of the test results could be achieved if the two factors were controlled. A high resolution oscilloscope can lead to determination of the resonance frequency with better accuracy. To better
control the sample temperatures, two methods are proposed: (i) better control of the ambient temperature with minimum fluctuation and let the sample temperature equilibrate; (ii) calibrate the temperature and the resonance frequency to account for modulus change of the substrate when the samples are evaluated at different ambient temperatures.

7.2 Opportunities for future work

7.2.1 Effect of thermal exposure

We observed significantly lower modulus for thermally exposed freestanding top coats. The finding deserves further attention to fully understand the mechanisms. The sintering of the top coat occurs locally when necking develops between the columns. The local modulus of the top coat increased as observed using nano-indentation. However, the top coat modulus on a global scale is expected to be more strongly affected by the change in the stochastic vertical separations between the columns.

2D and perhaps 3D microstructure characterization and statistical analysis can help determine the density and location of the change in the vertical separations in the thermally exposed top coat as compared to the as-deposited state. The quantified change could then be used to explain the change in the modulus of the top coat at a mesoscopic level.
7.2.2 Residual stress measurements

The existence of the residual stress was indicated by the development of curvature in the freestanding top coats. Since the residual stress greatly influences the strain energy, which leads to the spallation of top coat, to determine the residual stress in the top coat should not be overlooked. One promising option is to evaluate the residual stress with laser sectioning and DIC. Another is to use detailed curvature technique. Both are both destructive methods which can change the internal force equilibrium and cause a shape change. Laser sectioning is precise in removing the material and the use of high resolution DIC facilitates measurement of the associated strain release. Residual stress can be back calculated if the modulus is known. The curvature method combined with the resonance frequency technique measures substrate curvature change and modulus associated with the thinning of the top coat. Analytical equations are available to calculate the residual stress of the coating. However, the substrate is much more rigid that top coat and the primary challenge is that the change in the substrate curvature can be very small, requiring a high resolution surface profile measurement technique.

7.2.3 Extension to other engine hardware

The top coat modulus on a turbine vane is not uniform. This is likely true in other TBC coated engine components such as combustor panels and turbine blades. The combustors are circular and the shape of the turbine blades is highly complex with curved surfaces. The service condition at the different places of the blade surface differ greatly
due to different stresses, strains, and temperatures[152], which exhibit different failure modes. For example, CMAS infiltration is more severe in the hottest sections of the turbine blades, especially on the pressure surface. The failure prediction at these places requires the input of a local modulus. The micro-bending technique provides an opportunity to assess the top coat modulus at different locations on the components. To gain more insight in the top coat modulus and substrate geometry relations, samples with a variety of shapes should be evaluated. The service condition of the turbine components also highlights the importance of understating the top coat modulus evolution as a function of service life, in order to be used for life prediction.

This study mainly focuses on the investigation of the top coat modulus in the radial direction of the samples with the assumption of equal in-plane modulus. Johnson et al.[94] reported that the moduli of the EBPVD top coat at the two in-plane directions were different. Accordingly, the transverse orthotropy of the top coat needs to be further validated by evaluating the top coat modulus along the longitudinal direction of the parts.

In closing, the developed micro-beam techniques provide a much needed toolset for the community to evaluate the top coat modulus. It was demonstrated that the techniques were robust to understanding the effect of both the deformation dependency and the microstructural variations in the top coat modulus in this study. Little was known about the relations between the EBPVD top coat modulus and the substrate geometries. This study have enhanced our understanding of TBC properties. Opportunity for further increasing our understating and incorporating the measuring elastic response in failure models appear promising.
Reference


[125] W. Jackson. Personal communication. 2014.


Appendix: UMAT user subroutine

The UMAT subroutine define a constitutive relation between the stress and strain by composing the stiffness matrix in either 2D or 3D material model. User subroutine is attached to the main input file during calculation on the platform of ABAQUS. The following UMAT subroutine defines a 2D transversely orthotropic material with different tension and compression modulus in a plane stress condition. Sight modification to the stiffness matrix by including the third dimension could be done to switch to plane strain or a full 3D consideration. The main body of the subroutine used in the FE analysis of the current study is as follows:

```fortran
SUBROUTINE UMAT(STRESS, STATEV, DDSDE, SSE, SPD, SCD,
  1 RPL, DDSDDT, DRPLDE, DRPLDT,
  2 STRAN, DSTRAN, TIME, DTIME, TEMP, DTEMP, PREDEF, DPRED, CMNAME,
  3 NDI, NSHR, NTENS, NSTATV, PROPS, NPROPS, COORDS, DROT, PNEWDT,
  4 CELENT, DFRGRO, DFRGRI, NOEL, NPT, LAYER, KSPT, KSTEP, KINC)
C
INCLUDE 'ABA_PARAM.INC'
C
CHARACTER*80 CMNAME
DIMENSION STRESS(NTENS), STATEV(NSTATV),
  1 DDSDE(NTENS, NTENS), DDSDDT(NTENS), DRPLDE(NTENS),
  2 STRAN(NTENS), DSTRAN(NTENS), TIME(2), PREDEF(1), DPRED(1),
  3 PROPS(NPROPS), COORDS(3), DROT(3, 3), DFRGRO(3, 3), DFRGRI(3, 3)
  4 DIMENSION DSTRES(NTENS), D(2)

IF (STRAN(1) .LT. 0.D0) THEN
  E = PROPS(1)
ELSE
  E = PROPS(2)
END IF
```

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M = PROPS(3)
ENU = PROPS(4)

C---- STORE LAME CONSTANTS IN D(1) & D(2)
D(1) = ENU*E
D(2) = (E*ENU)/M

C---- FORM LINEAR ELASTIC STIFFNESS MATRIX (6x6)
DO I = 1,3
    DO J = 1,3
        DDSDDE(I,J) = 0.D0
    END DO
END DO

DDSDDE(1,1) = E/(1.D0-ENU*D(2))
DDSDDE(1,2) = D(1)/(1.D0-ENU*D(2))
DDSDDE(2,1) = D(1)/(1.D0-ENU*D(2))
DDSDDE(2,2) = M/(1.D0-ENU*D(2))
DDSDDE(3,3) = 0.5D0*E/(1.D0+ENU)

C---- COMPUTE STRESS INCREMENTS FROM STRAIN INCREMENTS
DO I=1,3
    DSTRES(I) = 0.D0
    DO J=1,3
        DSTRES(I) = DSTRES(I) + DDSDDE(I,J)*DSTRAN(J)
    END DO
END DO

C---- UPDATE THE STRESS & Sp. ELASTIC STRAIN ENERGY (SSE)
DSSE = 0.D0
DO I=1,3
    STRESS(I) = STRESS(I) + DSTRES(I)
    DSSE = DSSE + ( STRESS(I) + 0.5d0*DSTRES(I) ) * DSTRAN(I)
END DO

SSE = SSE + DSSE

RETURN
END
Curriculum vitae

Binwei Zhang was born in Shanghai, China in September 1982, to Ruxiang Zhang and Xiaofeng Liu. He graduated from Tsinghua high school in Shanghai, China in 2000. He attended Shanghai institute of technology and earned a degree of Bachelor of Science in Material Science and Engineering with a concentration in metallurgical engineering in 2005. Upon graduation, he worked as a manufacturing engineer at Baosteel, stainless steel branch. He came to U.S. in the summer of 2007 to study under a master’s program in the department of Civil Engineering at West Virginia University. His research focused on development of Nondestructive methods to monitor the integrity of thermal barrier coating (TBC) systems. He joined Professor Kevin Hemker’s group in August 2010 and worked on the experimental characterization of TBC constituents. In August of 2015, he completed his Doctor of Philosophy degree in Mechanical Engineering.