Cyclic Durability of Thermal Barrier Coatings Subject to CMAS Attack

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Thermal barrier coatings (TBCs) are critical in modern gas turbine engines, increasing operating temperature, efficiency, and component life. Engines have reached temperatures at which ingested debris (CMAS) forms silicate melts that chemically and mechanically attack TBCs, leading to premature failure. New, CMAS-resistant coatings must be validated under conditions that recreate real-world TBC-CMAS interactions. No standardized testing to perform these analyses currently exists.

A cyclic thermal gradient rig with incremental CMAS deposition was developed based on modified literature designs. Tests performed using literature-based parameters showed TBC-CMAS interactions and failure morphology deemed not real-world representative by an engine manufacturer. The results were rationalized with the understanding that, in an engine, “cooling air” is relatively hot (~400 °C). Minimizing transient thermal gradients across the TBC coupon resulted in more representative test outcomes.

A second generation thermal gradient rig was developed with higher heat flux and sample throughput. This rig incrementally deposits CMAS powder, a feature not found on existing rigs. Heterogeneous CMAS was deposited onto an EBPVD YSZ TBC coupon. The CMAS layer had
intriguing non-uniformities in accumulation and chemical heterogeneity. This has implications for CMAS materials used for testing.

Engine manufacturers need to model TBC life reduction from CMAS attack for different engine parameters and CMAS environments. Preliminary experiments were performed that provided insight for such models. First, EBPVD YSZ coupons were cycled with varying CMAS dose rates. Over the range investigated, the lightest CMAS dose rate used 80% less CMAS to cause failure compared to the heaviest rate, disproving the concept of a “critical CMAS dose” for failure. Rather, failure is a mix of cycling and CMAS damage. As hot time and the number of thermal cycles increase, TGO growth and accumulated damage effectively reduce the toughness of the coating, making it more susceptible to spallation with less CMAS penetration. Second, differences between testing with homogeneous and heterogeneous CMAS were investigated on APS YSZ TBCs. While failures were similar, partial-life microstructures revealed differences in melting kinetics, which may have implications on how reactive TBC compositions interact with CMAS.
Cyclic Durability of Thermal Barrier Coatings Subject to CMAS Attack

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B.S., University of Maryland, Baltimore County, 2009

A Dissertation

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Doctor of Philosophy

at the

University of Connecticut

2018
Doctor of Philosophy Dissertation

Cyclic Durability of Thermal Barrier Coatings Subject to CMAS Attack

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2018
DEDICATION

In memory of George Barkley, mein Opa
ACKNOWLEDGEMENTS

First, I would like to thank Professor Eric Jordan for his years of support as my advisor, with constant ideas, encouragement, and a healthy balance of carrot and stick. Thanks also to Professors Maurice Gell and Mark Aindow for their feedback in developing this thesis.

I would also like to thank my lab mates through the years for their shared experience, knowledge, skills, and a helping hand when I just needed to hold these hoses upright, bend this strut to the left, and tighten this bolt just a little more… Mario Bochiechio, Chen Jiang, Rishi Kumar, Byung Jun, and Amadeusz Nasuta all contributed to the success of this research.

Thank you to the wonderful staff of IMS and C2E2. Shari Masinda and Nancy Kellerann were ever ready to deal with the next dozen purchase orders with a smile and just the right amount of sarcasm. Thank you to Mark Biron and Peter Menard for the Sisyphean effort of keeping the SEM running. Peter was also instrumental in the total demolition and renovation of our lab space, which was a personal education unto itself. Special thanks to Jeffrey Roth for his boundless energy, which could brighten even the most discouraging day.

A special acknowledgement is required for John Fikiet, who, with Amadeusz, constructed our test rigs. Without you, none of this would have been possible.

Finally, I’d like to thank my family for their love and support through this long process. I’d especially like to thank my wife, Maureen Harris, for her steadfast support, as well as her reminders that the only person making me do this was me.
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1 INTRODUCTION

1.1 Gas Turbine Engines and TBCs

The modern gas turbine engine (GTE) is a very complex piece of machinery, but it is, at heart, a heat engine [1]. As can be seen in the schematic below (Figure 1.1), air enters the GTE and is compressed through the intake and compression sections. It is then mixed with fuel and ignited in the combustion chambers. The hot combustion products are passed through several stages of turbine blades, which extract work from the gas. The gas is then exhausted back to the atmosphere, completing the thermal cycle.

![Schematic of a gas turbine engine](image)

*Figure 1.1 Schematic of a gas turbine engine (from [2])*

Like any heat engine, the efficiency of the GTE can be directly increased by increasing the maximum temperature of the thermal cycle, which is the operating temperature of the engine [3]. And the current global demand for more efficient GTEs is immense, especially for aero engines. In recent years, fuel costs have become the single largest expense for U.S. domestic carriers, representing about 40% of operational costs. At the same time, the increased demand for air travel worldwide could increase the CO₂ pollution associated with air travel by as much as 500% by 2050 [4]. Reacting to these factors, airlines and airplane manufacturers expect to buy an estimated $500
billion of newer, more efficient jet engines within the next decade, both for new aircraft and to retrofit older ones [5].

Over the last century, there have been numerous innovations that have allowed for engines to operate at increasingly higher temperatures, as seen in Figure 1.2. First, improvements to superalloy chemistry have decreased the oxidation rate and increased the creep resistance of the underlying metal. Improvements to processing, from directional solidification to single crystal casting, have also increased the resistance to creep and thermomechanical fatigue of GTE components. However, the introduction of advanced cooling schemes, such as internal cooling channels and film cooling, as well as thermal barrier coatings, have allowed for quantum leaps in engine operating temperature. Modern GTEs can, in fact, operate at temperatures well above the melting point of the metals that form engine structures.

![Figure 1.2 Allowable gas temperatures within GTEs over the last 50 years][1]

In the context of gas turbine engines, thermal barrier coatings (TBCs) are, as the name suggests, ceramic coatings that are used to protect hot section components from the extreme temperatures of the combustion gas. Miller suggests that the history of TBC research can be traced back to 1947, when researchers as the National Advisory Committee for Aeronautics (NACA,
present-day NASA) wrote a report discussing the use of ceramic coatings for turbine components. One of the earliest applications for TBCs was on the rocket engine nozzle of the X-15 test aircraft in 1960; ceramic coatings found several applications in rocketry in the next several decades [7]. Development progressed to the point that TBCs were introduced to commercial engines in the 1970s for combustors and 1980s for vanes [8]. Modern GTEs depend on TBCs to increase the usable life of hot section components: so much so that TBCs have become a “prime reliant” component of the engine design [9], [10]. This means that the expected useful life of the TBC, as well as potential sources for premature failure, must be carefully examined, both for safety and for economic considerations.

1.2 The Challenge of CMAS

As the service temperature of engines has increased, new mechanisms for failure have developed. One challenge that has been introduced within the last thirty years has been that of CMAS, an acronym standing for Calcium-Magnesium-Aluminosilicates. Gas turbine engines ingest tremendous quantities of air during operation, and, especially during take-off and landing, there can be significant quantities of sand, dust, or particulates in that air. Figure 1.3 shows a military transport craft landing somewhere particularly sandy, illustrating just how much foreign matter may be collected by an engine.
While ingested debris has always presented erosion or impact damage risks to engine components, operating temperatures have become high enough that some debris melts and adheres to engine components. This introduces new damage mechanisms, especially to TBCs. How to model and predict this damage, as well as testing new, CMAS-resistant coatings, will require new testing methodologies.

1.3 Research Goals

The main purpose of this research effort has been to develop both a thermal gradient rig and the testing parameters necessary for representative thermal cycling of TBCs with CMAS contamination. In this case, “representative” means as similar to the CMAS accumulation and damage morphology seen in engines as is possible in the lab. There is, to date, no industry standard for the configuration of, nor the operational parameters for, a test rig to allow a lab-scale accelerated test to faithfully recreate CMAS-induced TBC failure in a GTE environment. Furthermore, since the lab-scale test must accelerate the rate of degradation compared to the real environment (potentially tens of thousands of hours), one runs the risk of generating spurious failure modes or mechanisms. This could lead to incorrect results, or even conditions under which
new coatings known to be more CMAS-resistant in field testing show worse performance than industry standard materials.

For these reasons, a majority of the effort behind this thesis went into designing, validating, and iterating the configuration and operating parameters of a thermal gradient rig. Test outcomes were examined by our industry sponsors and compared against their real-world engine experience, to which we were not privy. However, their feedback informed modifications and improvements to the rig and the testing parameters. Through the investigation of our test outcomes, we developed critical insights into how to construct and operate thermal gradients rigs with a fidelity and capability unmatched in the testing community. Furthermore, these rigs enabled fundamental experiments investigating how damage accumulates with CMAS and thermal cycling, and the impact of heterogeneous CMAS. To our knowledge, there are no current reports on thermal cycling in a gradient with heterogeneous CMAS in a temperature controlled environment.

We will show that these key insights and contributions include:

1) Given a rig with a low velocity flame, vertical orientation of the test rig allowed for an order of magnitude better temperature stability.

2) Attempting to replicate the rapid heating rate of a jet engine did not give realistic results. Minimizing the transient thermal gradient during heating of the test coupon, and modifying the rig to achieve this kind of heating, allowed for better test outcomes.

3) Designing a rig that utilized engineered thermal spray torches as the heat flux source allowed for more realistic deposition of molten and semi-molten CMAS oxides onto a TBC coupon.

4) The adhesion and melting behavior of a heterogeneous CMAS composition was fundamentally different from a homogenized CMAS material. This has direct implications in how reactive TBC compositions interact with the attacking CMAS.
5) The effect of CMAS dose rate, a critical parameter in modeling the degradation of coatings in real engine service, did not act independently of thermal cycling and bond coat oxidation. These damage mechanisms work synergistically to cause coating failure.
2 BACKGROUND AND MOTIVATION

2.1 Thermal Barrier Coatings

2.1.1 Anatomy of a TBC

In general, TBCs are composed of three conformal coating layers over the component to be protected. These three layers can be seen in Figure 2.1.

![Figure 2.1 Layers of a thermal barrier coating on a turbine blade [12]](image)

Starting from the right of the cross-sectional schematic is the hot gas path within a GTE. The outermost layer of the TBC, able to withstand the extreme temperature, is the ceramic top coat. This layer is manufactured from refractory ceramic materials with low intrinsic thermal conductivity. The extrinsic conductivity of the top coat is further reduced with an engineered, porous microstructure. Top coats can achieve temperature reductions on the order of 1 °C/μm, or about 300 °C for typical TBCs on aero-engine components [12]. The porous structure also increases the strain tolerance of the ceramic layer. As a relatively thin film on a thick substrate, the thermal expansion and contraction of the substrate is imposed on the top coat; because there is a mismatch in thermal expansion coefficient, this results in a thermal strain imposed on the coating. This strain is one of the leading damage mechanisms for the TBC. All current top coat materials
have a lower coefficient of thermal expansion than the underlying alloy. The increased strain tolerance from porosity is essential for long term coating durability.

The layer below the top coat is the bond coat, which is made from an oxidation resistant metal alloy. Bond coat materials are divided into two groups. The “MCrAlY” bond coats are a complex alloy of “M” (typically a nickel, cobalt and/or iron mixture) chromium, aluminum, and yttrium, sometimes including other alloying elements including hafnium and silicon. The other group are alloys of platinum, aluminum, and nickel [13]. As the name suggests, bond coats improve the adhesion strength and long term durability of the TBC. The bond coat promotes the formation of an adherent, compact, and uniformly slow-growing thermally grown oxide, or TGO. Current bond coats form an alumina TGO.

The TGO that develops between the top coat and the bond coat is unavoidable. Given the temperature and oxygen partial pressure in the combustion path, as well as the time-scales that a GTE component is expected to survive, any metallic compound will necessarily oxidize significantly. TBC engineers reduced the severity of this unavoidable oxidation by ensuring that primary TGO growth forms α-aluminum oxide. Compared to other relevant metal oxides, alumina is relatively tough and has the lowest oxygen diffusivity. So the TGO grows slowly, often rate-controlled by the diffusion of oxygen through the TBC to the bond coat, referred to as “inward growing” TGOs; however, some “outward growing” TGOs, controlled by diffusion of metal cations to the top coat-TGO interface, exist [14].

These three TBC layers, as well as the substrate below them, undergo many complex and evolving interactions during the thermomechanical cycling of gas turbine engine operation. This research effort focuses primarily on the ceramic top coat; when the acronym “TBC” is used below, it should be taken to refer only to the ceramic top coat.
2.1.2 TBC Materials

The industry standard TBC material used in GTEs is 6-8 weight percent yttria-stabilized zirconia (YSZ). In this composition range, YSZ forms a metastable tetragonal crystal structure that is phase stable between room temperature and current service temperatures, about 1200 °C [15]. Historically, selection of yttria as stabilizer and optimization of the yttria content were determined empirically based on thermal cycling performance [16]. Long after the development of YSZ, researchers subsequently identified a ferroelastic switching mechanism in this composition range as one source of YSZ’s comparatively high toughness [17]. YSZ also has a low intrinsic thermal conductivity, ~2.3 W·m⁻¹·K⁻¹. Another important factor is that YSZ has a high thermal expansion coefficient, ~11 ppm/°C; this is important because it reduces the misfit stresses associated with the thermal expansion and contraction of the superalloy substrate. For example, the mean coefficient of thermal expansion for Haynes 230 Alloy between 25 to 1000 °C is 16.1 ppm/°C [18]. A high thermal expansion coefficient is a key criteria for selection of TBC materials. All of these features have made YSZ the industry standard TBC material for many years.

However, the higher service temperatures of next-generation GTEs require TBC materials with lower thermal conductivity, phase stability at even higher temperatures, greater sintering resistance and, as will be discussed, better CMAS resistance. One class of next generation TBC materials are the rare-earth zirconates (REZ), with gadolinium zirconate (Gd₂Zr₂O₇, GZO) receiving the most attention [19]–[21]. GZO is phase stable in the cubic pyrochlore structure between room temperature and ~1550 °C, where there is an order-disorder transformation to fluorite [22]. GZO has a lower intrinsic thermal conductivity than YSZ [23], and researchers have shown that off-stoichiometric compositions can have even lower thermal conductivity, likely due
to increased phonon scattering [24]. GZO has been commercially developed as a TBC [23] and has been used in aero engine flight testing [25]. Another material being explored is yttrium-aluminum-garnet (Y₃Al₅O₁₂, YAG) [26]. YAG is a promising TBC material because of its very high temperature stability, high toughness, and potential for CMAS resistance.

2.1.3 TBC Depositions Methods

As stated earlier, TBCs are engineered to have lower extrinsic thermal conductivity and greater strain tolerance by utilizing controlled porosity. To date, there are two industry standard deposition processes, although other processes are being developed [27]–[29]. In the air plasma spray (APS) process, an oxide powder feedstock is injected into a plasma torch. The oxide particles rapidly melt in the plasma plume, which also accelerates the material toward the target substrate surface. The molten particles then “splat” onto the surface, rapidly solidifying together into an interlocking microstructure with complex porosity. Typical APS coatings have porosity in the 10-20% range and many transverse splat boundaries. Because of these microstructural features, APS YSZ coatings typically have a thermal conductivity around 1-1.5 W·m⁻¹·K⁻¹ [30]. APS coatings are thought to mechanically adhere to the bond coat, which is why APS bond coats are significantly roughened. Unfortunately, the tortuosity of the bond coat increases stress on the coating during thermal cycling, reducing the overall life of the coating [31].

The other common deposition method is electron beam physical vapor deposition (EBPVD). In the EBPVD process, substrates are heated, and typically rotated, in a high vacuum coating chamber. An ingot of the desired oxide is bombarded with an electron beam, ejecting vaporized material into the coating chamber. This material then settles onto the substrate, forming dense, columnar crystals. With optimal rotation speed, these crystals grow perpendicular to the substrate [32]. Compared to APS, these crystals are less mechanically interlocked with each other:
as a result, the coating is much more strain tolerant. The EBPVD process chemically adheres the TBC crystals to the bond coat, which also increases coating durability [33]. EBPVD coatings are tougher than APS because it is more difficult for a crack to propagate across the intercolumnar gaps. However, because the crystals are near fully dense, the thermal conductivity is higher, on the order of 1.5-2 W·m⁻¹·K⁻¹ [34]. The microstructures of APS and EBPVD YSZ are shown in Figure 2.2. The APS micrograph on the left highlights the rough TBC-bondcoat interface. The very top of the bondcoat can be seen as the straight, dark line at the bottom of the EBPVD micrograph on the right.

![Figure 2.2 Microstructure of the industry standard APS (a) and EBPVD (b) TBCs (adapted from [35])](image)

Comparing the two deposition processes, EPBPVD is more expensive in capital equipment costs [36] and manufacturing time: the process is relatively slow, with deposition rates of 4-10 microns/minute [33]. The faster deposition rates for APS [35] allow for very thick coatings to be reasonably produced, up to 1 mm for some stationary components and ground-based power GTEs [37]. Thus, EBPVD is typically reserved for rotating parts, where rotational stresses and greater chance of erosion necessitate more durable coatings.

One deposition process in development is solution precursor plasma spray (SPPS) [27][38][39]. SPPS uses much of the same thermal spray equipment as APS. However, a liquid chemical precursor solution replaces the traditional oxide powder feed stock. En route to the
substrate, the solvent is evaporated, or combusted in the case of an organic solvent, producing chemically homogeneous solid particles. These particles then melt and splat onto the substrate. This process has several advantages over APS. First, the shear forces of the plasma jet break the liquid into very fine drops, resulting in “ultrafine” splats, roughly an order of magnitude smaller than those for APS [35]. The smaller splat size increases mechanical adhesion, thus increasing coating durability and in-plane fracture toughness five-fold compared to standard APS [40]. Second, the SPPS process can be optimized to promote the formation of vertical cracks; these increase the strain compliance of the coating, analogous to the intercolumnar cracks of the EBPVD coating, while still maintaining lower thermal conductivity. This microstructure has proven to be significantly more durable than conventional APS YSZ in cyclic furnace testing [35]. Another processing innovation by Jiang et al. was the development of interpass boundaries: these layers of increased porosity significantly reduced the extrinsic thermal conductivity of YSZ TBCs, to around 0.62 W·m⁻¹·K⁻¹, without sacrificing the enhanced durability of SPPS coatings [41].

2.1.4 TBC Failure Mechanisms

Despite engineering efforts to maximize the life of the TBC, the extreme environment ensures that there are numerous life limiting factors. In Figure 2.3, Levi et al. neatly summarized these mechanisms as “intrinsic” and “extrinsic” spalling mechanisms [42].
Imagining the TBC system as perfectly flat, parallel strata, the following failure scenario would be any TBC’s eventual fate. As the TGO increases in thickness, the compressive stress stored within the TGO increases, and the strain energy increases with the square of the stress multiplied by the TGO thickness. At some critical TGO thickness and strain energy value, which depends on material properties and thermal trajectories, the energy stored within the TGO will be released in a spallation event [43]. This is the typical failure mode under some conditions, but there are numerous complications that change the expected TBC life and failure mode. For example, aluminum depletion of the bond coat leads to formation of oxides other than alumina and reduces the strength of the TGO [44]. Contaminants in the bond coat, typically yttrium, can lead to so called “stringers,” which are easy oxygen diffusion paths [45]. This leads to deleterious rapid and non-uniform TGO growth. Progressive evolution of the bond coat surface and increasing roughness (“rumpling”) imposes deformations on the ceramic top coat to irregular and elevated stresses [46]. Stresses are accommodated by cracking, and the cracks eventually link and cause coating spallation. In the case of APS TBCs, which start with a rough bond coat, rumpling and the associated cracking in the ceramic near the TBC-bondcoat interface are the dominant cause of
failure. The formation and linking of localized cracks is a complex process that is only beginning to be understood [47].

Because of the large number of interrelated variables, engine manufacturers have historically taken an extremely conservative approach to estimating the expected life of a TBC. This requires an engine overhaul schedule that discards or reconditions components long before their usable life is exhausted, at great cost to airlines and engine manufacturers. A number of models have been created to estimate the expected life of a TBC based on engine operating parameters, such as temperature and cycle duration [48]–[50]. As TBCs have become a “prime-reliant” component in modern GTE design, maximizing the usable life of TBCs has become an economic challenge that must be balanced against safety concerns.

Further complicating the modeling of TBC life are the more difficult to predict extrinsic failure modes. Extrinsic failure modes are usually caused by contaminants ingested by the GTE. The enormous volumes of air ingested during operation, as well as the long durations the engine is expected to operate, guarantee that a typical engine will ingest hundreds or thousands of kilograms of material during its lifetime. From a ground-based example, the GE MS9001 is a 300 MW gas turbine, which consumes on the order of 600 kg·s⁻¹ of air [51]. Even taking the EPA definition of “good” air having a maximum concentration of 54 μg·m⁻³ of PM10 dust [52], this engine would ingest a little over 2 kg of dust per day of operation. Ground-based turbines have particle filtration schemes to remove much of this dust from the air; in a turbofan, centrifugal forces will push larger particles away from the engine core. But, in either case, particulate matter will reach the engine core and damage components. Finer particles will cause TBC erosion, while coarser particles will cause impact damage. Another damage mechanism that has received
significant attention is the chemical and mechanical attack on the TBC by molten glassy deposits, so-called CMAS attack.

2.2 CMAS

CMAS, the acronym for Calcium-Magnesium-Aluminosilicates, was coined by Borom et al [53], who were analyzing deposits on land and aero turbines operating in geographically diverse areas. The damage was similar to that observed due to ingestion of volcanic ash [54], [55]. Molten material infiltrated the porosity of the TBC, leading to nearly complete spallation of the top coat. Similar damage can be seen in a more recent engine test in Figure 2.4, on the left-hand blades. The difference between blade sets will be discussed below. While volcanic eruptions can be avoided (despite the large economic costs [56]), the sources of CMAS appear to be much more ubiquitous. Therefore, the loss of expected TBC life has significant and enduring safety and economic impacts.

Figure 2.4 Turbine blades subjected to CMAS attack [25]
2.3 CMAS – TBC Interactions

2.3.1 CMAS and TBC Chemistry

The ratios of the main CMAS constituents, as well as content of minor constituents (iron oxide, alkaline and alkaline earth oxides, etc.) can vary widely by geography [53], [57]. Even minor changes in chemistry can greatly affect the material properties of the CMAS, including melt viscosity and tendency towards crystallization on cooling. For a given temperature, the viscosity of the melt could vary by orders of magnitude, depending on composition [58]. Under other conditions, CMAS can attack the TBC without even melting. In the investigation of deposits on ex-service turbine blades, Braue et al. observed silica-lean deposits on the surface of the TBC [59]. Despite having not melted or penetrated into the coating, solid state reactions degraded and sintered the TBC surface together, as shown in Figure 2.5.

![Figure 2.5 Micrograph of TBC-CMAS interaction zone from ex-service turbine blade [59]](image)

There are few examples in the open literature of the analysis of ex-service hardware, and fewer still that analyze CMAS attack. However, the typical form of the attack, in general terms, is as follows. The lowest temperature eutectic in the CaO – SiO₂ – Al₂O₃ ternary melts at 1170 °C [60]. Above this temperature, CMAS deposits will form a silicate melt pool, penetrating the porous TBC. The top coat material dissolves into the melt. In the case of YSZ, the melt reaches local saturation of zirconia, but not yttria [61]. This leads to the reprecipitation of destabilized zirconia,
typically forming small globular grains of zirconia near the TBC surface; an example of this formation on an EBPVD TBC can be seen in Figure 2.6. Upon cooling, some or all of the CMAS may crystallize [62].

![Image of chemical attack of EBPVD YSZ](image)

Figure 2.6 Chemical attack of EBPVD YSZ: pristine columns (a) become small spheroid particles (b), while the cross section (c) and (d) show penetration of CMAS into the TBC and YSZ diffusing out into the melt [61]

Given the large variability of CMAS compositions described in the literature, both from real-world deposits and model chemistries, some researchers have attempted to condense the chemical complexity using the concept of optical basicity [63]. Indeed, it has been shown that most CMAS compositions have very similar optical basicity, given the highly “acidic” nature of silica [64]. Optical basicity can also be used to rationalize the reactivity of TBC materials with the melt, with the potential for identifying top coat materials that might be less reactive with CMAS.

2.3.2 Thermomechanical Damage

While the dissolution of the TBC into the CMAS melt is a serious problem, the mechanical damage due to melt infiltration into the TBC porosity is more immediately destructive. As stated earlier, the porous splat structure (APS) or intercolumnar gaps (EBPVD) are what allow the coating to accommodate the stresses created by the thermal expansion mismatch between the TBC
and the substrate as the engine heats and cools. The CMAS melt penetrates into these gaps in the coating and solidifies on cooling. This drastically increases the effective elastic modulus of the infiltrated coating, and thus the elastic energy stored within the coating [65]. This is the leading driver of bulk failure of TBC coatings in the field; the coating spalls from the substrate before dissolution removes the coating [25].

The thermomechanical stresses experienced by a TBC during cooling are quite complex. At temperature, the coating relaxes due to creep, becoming essentially stress free [66]. The magnitude of the compressive strain that the TBC sees during cooling is imposed by the substrate: as a thin coating on a thick substrate, it is simply along for the ride. However, the TBC system operates in a gradient; the coating is hotter than the substrate. The extra thermal contraction of the coating partially mitigates the compressive stress. Further complicating matters is the fact that this is a multiple layer system: the TGO and the bond coat also can influence the stresses and failure mode in the system. The addition of CMAS only increases the difficulty in modeling the stress distribution by introducing what is effectively a CMAS-TBC composite layer.

The most complete analysis to date of the relevant thermomechanics and fracture mechanics was produced by Evans and Hutchinson [67]. They condensed the governing equations and material properties for a simplified TBC system into a map that essentially predicts delamination based on CMAS infiltration depth and cooling trajectory. An example map is shown in Figure 2.7.
A walk-through of the map is necessary. At time \( t = 0 \), the TBC-substrate system is at steady state with some thermal gradient between the temperature at the surface (\( T_{\text{sur}} \)) and some lower temperature at the TBC-substrate interface (\( T_{\text{sub}} \)). Then the system begins cooling towards ambient. The \( x \)-axis (\( \Delta T_{\text{substrate}} \)) represents the amount that the substrate has cooled at any time \( t \), and the \( y \)-axis (\( \Delta T_{\text{sur}/\text{sub}} \)) represents how much more the surface of the TBC has cooled compared to the substrate. Thus, any cooling trajectory superimposed on Figure 2.7 starts at the origin (at \( t = 0 \)) and will end at the \((x, y)\) point \( (T_{\text{sub}}, T_{\text{sur}} - T_{\text{sub}}) \). Note that \( T_{\text{sur}} - T_{\text{sub}} \) is the initial thermal gradient. For example, in an isothermal furnace test, where \( T_{\text{sur}} = T_{\text{sub}} \) for all times \( t \) (during both heating and cooling), the cooling trajectory would follow directly along the \( x \)-axis, because \( \Delta T_{\text{sur}/\text{sub}} \) would be 0 for all times \( t \). For any non-zero steady state gradient, the endpoint of the cooling trajectory will end at the point where \( x \) equals the initial substrate temperature and \( y \) equals the steady state gradient. The \( h/H \) lines represent the CMAS penetration depth, normalized to the coating thickness, i.e. \( h/H = 0.5 \) for a coating penetrated to half its thickness. The region outside the two lines for a given \( h/H \) value (shaded for \( h/H = 0 \)) represent regions in temperature space where deep delamination will occur should a given cooling trajectory enter that region at any time during cool down.
The key conclusions that can be drawn from the map are as follows. First, deeper CMAS infiltration is more likely to cause CMAS spallation. Second, that for a given CMAS infiltration depth, the cooling trajectory will determine whether or not the coating will fail. If the surface cools too fast relative to the substrate (the upper left-hand corner of the map), spallation will occur early during cooling. If the steady state gradient is too low (the lower right-hand corner), the coating will fail at the end of cooling, when the system is near room temperature. Finally, and the most critical for testing CMAS-TBC interactions, is that isothermal testing, such as that carried out in conventional furnaces, will likely cause delamination for any test run hot enough to melt CMAS (above ~1170 °C). Indeed, researchers investigating basic CMAS-TBC interactions using furnace tests have either utilized alumina substrates to get around this problem (greatly reduced thermal mismatch) [61], [68], or they carry out their post-test analysis on the spalled fragments of the TBC, typically after the first cycle [69]. Alumina substrates are an effective solution for studying the basic chemistry of CMAS-TBC interactions, but not for understanding how CMAS will affect the expected life of real engine components. And one-cycle experiments do not allow for engine-representative cyclic testing.

2.4 Mitigation Strategies

Based on the first key insight from above, preventing CMAS penetration into the coating, or at least reducing its depth, has been the main research focus for creating CMAS-resistant TBCs. A few researchers have attempted to add a non-wetting or impermeable coating on top of the existing TBC [70], [71], but these efforts have been largely unsuccessful. Key challenges have been to deposit a continuous layer on top of a discontinuous (porous) surface, and to have this layer survive thermal cycling for any significant duration.
Most research has explored new TBC ceramics that will react with the CMAS to create a sealing layer near the surface, preventing further infiltration. Aygun et al. developed a modified YSZ TBC doped with 20 mol% Al$_2$O$_3$ and 5 mol% TiO$_2$, deposited using SPPS [72]. The SPPS process allowed for the alumina and titania to be metastably and homogeneously distributed in the YSZ. In furnace exposures to CMAS, this doped YSZ reacted with the melt to form anorthite and arrested CMAS penetration to about 25% coating thickness, compared to complete penetration of conventional YSZ. The authors demonstrated that both the alumina and titania were necessary for the CMAS arrest. The alumina changed the melt chemistry to a more readily crystallized composition (anorthite), but crystallization did not occur without the titania acting as a nucleating agent. Subsequent work from the same group showed that their doped YSZ could also be created utilizing the more conventional APS process and a custom spray-dried powder [73].

Many researchers have demonstrated the CMAS resistance of the rare-earth zirconates, which were mentioned in Section 2.1.2 for their higher temperature capability and lower intrinsic thermal conductivity. Dissolution of REZ ceramics into the CMAS melt results in the rapid precipitation of apatite grains with nominal chemistry Ca$_2$RE$_8$(SiO$_4$)$_6$O$_2$. This reaction phase has proven effective at arresting CMAS infiltration in both EPBVD [74] and APS [75] GZO coatings. Other REZ have been explored in the literature [76]–[78]; Krause et al. have demonstrated that yttrium-zirconate reacts to form a slightly different apatite, Ca$_4$Y$_6$(SiO$_4$)$_6$O$_2$, theoretically arresting more CMAS per rare-earth oxide consumed than GZO [79]. Beyond lab-scale experiments, GZO coatings have clearly demonstrated their improved CMAS durability in some engine flight testing, as shown in Figure 2.4 [25]. An engine was operated in an environment that subjected it to CMAS attack. Some blades were coated with standard YSZ, while others had GZO. The GZO TBCs
clearly fared better. The full details of these experiments have not been publicly released, so little else is known about the experiment behind this photograph.

Unfortunately, REZ coatings like GZO have several drawbacks compared to conventional YSZ. First, GZO materials are not thermodynamically compatible with an alumina TGO [80], forming GdAlO$_3$, which undermines the TGO integrity. This has necessitated the deposition of an inner layer of YSZ for REZ TBCs [81], which increases the manufacturing cost and complexity of the TBC. GZO and other REZs have a lower fracture toughness than YSZ [82], making them more susceptible to erosion or foreign object damage. The increased rare-earth content of the ceramic compared to YSZ means that the feedstock is more expensive. As with any engineering change, there must be a cost-benefit analysis to determine the conditions under which the increased CMAS resistance trades positively against the increased cost, complexity, and lower toughness. Thus, it becomes essential to be able to quantify how much more durable any new coating material is in the face of CMAS attack compared to conventional YSZ.

2.5 CMAS Durability Testing of TBCs

To date, there have been several methods used to characterize the interaction between TBCs and CMAS. Many important investigations into the chemical reactions between CMAS and TBC materials have been carried out under isothermal conditions, i.e. in a furnace [83]–[85]. But, as demonstrated by Evans and Hutchinson, the thermal gradient across the TBC is necessary to accurately replicate the thermomechanical interaction between CMAS and TBCs. Without the gradient, CMAS-contaminated coatings that could survive significantly more engine cycling will prematurely fail.
As mentioned earlier, engine manufacturers have some experience comparing the life of TBC systems in an actual jet engine operating in the presence of CMAS-forming contaminants. There have also been detailed examinations of engines that have inadvertently flown through volcanic ash clouds [86]. However, neither of these methods are practical for controlled experimentation. Dunn describes experiments utilizing ground-based test engines and a dust injection system to control contaminant ingestion [87]; NASA has performed similar experiments on an on-wing engine due for overhaul, as seen in Figure 2.8 [88]. But an experiment of this scale is outside the grasp of most researchers. Using an actual engine is costly, difficult to accelerate, and the experimenter is bound by the operating parameters of the specific engine utilized.

Several laboratory-scale test rigs have been described in the literature. Jensen et al. developed a rig to study how CMAS and volcanic ash erode and/or accumulate onto GTE components [89]. A large vertical burner heated air to engine temperatures, while a controlled dose of contaminant was entrained and heated in the gas path. This contaminated gas then impinged on engine hardware or test coupons. The nature of this rig, however, precludes accelerated thermal cycling of TBC coupons. Multiple research groups have constructed so called thermal gradient rigs specifically for rapidly thermally cycling TBC coupons. The basic concept

Figure 2.8 NASA studies the effect of ash ingestion on a GTE directly [88]
behind these test rigs is to heat the TBC surface of the test coupon while actively cooling the back of the substrate, typically with compressed air. Researchers at NASA Glenn [90] and UCSB [91] have utilized CO$_2$ lasers as the heat flux source. Others, including groups at Jülich [92], OSU [93], and Sensor Coating Systems [94] have used oxy-fuel torches of various design.

Some of these test rigs have also included provision for simulating CMAS contamination. A number of methods have been used, such as pre-depositing a paste of CMAS or a sintered pellet [91]. Others used a paint sprayer and suspended CMAS glass frit [95] or a chemical precursor solution coaxially fed into the flame [96].

While an ISO standard has been created for the thermal cycling of TBC coupons [97] in a gradient, it is vague on recommended operating parameters of a test rig. It does not describe appropriate heating and cooling rates, dwell times, or what might indicate an incorrect sample failure. It also does not include any description of a CMAS contamination scheme. Furthermore, there has been no open research comparing the results of any of these lab-scale tests with failure results on in-service components to ensure that the experiments are recreating realistic engine failure in the lab. There are also limitations in what kind of experiments may be performed using the rigs described. For example, any pre-deposited paste cannot be used to test incremental addition of CMAS with every thermal cycle, which is necessary to capture any dose rate effects. Chemical precursor solutions, while easy to develop and spray at a sample, are chemically dissimilar from actual sand, so there are nuances to the reaction process that may be lost. The precursor solution is likely to favor simple oxides, while there are many more complex oxides heterogeneously distributed in actual sand. Real world materials will have particle size distributions which would be difficult to control in the liquid precursor solution reaction. These differences may affect how the CMAS adheres to the coating and how it melts.
2.6 Research Motivation

The fundamental goal of this project is to develop a test rig and operational parameters to test the cyclic durability of TBC coupons in a thermal gradient with incremental addition of CMAS contamination. The important features of testing that need to match engine experience are the failure mode of TBC systems subject to CMAS attack, the extent of CMAS accumulation, infiltration, and attack before failure, and the relative performance of various coating systems. Because of the potential size of test matrices to study different coatings, CMAS compositions, CMAS dosing rate, and thermal conditions, one of the requirements for the project was to develop a rig that could affordably test multiple samples at the same time.

With such a rig, countless different experiments are possible: the effect of CMAS dose rate on TBC life, the relative performance of different coating systems, the effect of two-phase CMAS mixtures on infiltration kinetics, and the relative “aggressiveness” of different compositions from different geographical regions are a few of the possible avenues of experimentation, some of which are explored in this work.
3 METHODS

3.1 Materials Characterization Techniques

3.1.1 Microstructural and Elemental Composition Evaluation

The microstructure and elemental composition of TBC coupons and CMAS contaminants were routinely examined. To ensure specimen integrity, especially if a TBC coupon was damaged from cycling, samples were first mounted in a low-viscosity two part epoxy (EpoxySet, Allied High Tech) and allowed to fully cure. The mounted sample was then sectioned using a high-speed sectioning saw (Accutom-50, Struers), and the cross section was mounted again in epoxy. The cross section was then polished using standard metallographic techniques to a 1-micron finish, then sputter-coated with, typically, 80%/20% gold/palladium (E5100 SEM Coating Unit, Polaron). These samples were examined in an FEI Quanta 250 FESEM with EDXS (EDAX).

The surface of some TBC coupons and loose CMAS powders were also examined by SEM and EDXS. These samples were placed in the SEM with either no sample preparation or, to reduce charging in some cases, sputter-coated with the gold/palladium mixture.

3.1.2 Phase Identification

To identify the phases of TBC and CMAS materials, X-ray diffraction patterns were collected using either a Bruker D2 Phaser or D8 Advance. In either machine, copper K-alpha radiation was used, and the pattern was typically collected from 10 to 90 2θ in 0.02 degree increments. Patterns were identified using Bruker’s EVA software.

3.1.3 Calorimetry

The melt onset of CMAS compositions and their chemical precursor solutions were investigated using DSC-TGA (Q600, TA Instruments). Samples were placed inside alumina
crucibles with vented platinum lids and heated at 10 °C/min to 300 °C to drive off any water, then heated at 2.5 °C/min to 1300 °C.

3.2 Test Materials

3.2.1 TBC Coupons

The basic TBC coupon used in this work is shown in Figure 3.1. It is a superalloy disk, one inch in diameter and 1/8” thick (Ø 2.54 cm x 0.3 cm), with a bond coat and ceramic top coat on one face of the disk.

![Figure 3.1 Typical TBC coupon](image)

Four types of TBC were used in this work. An engine manufacturer provided APS and EBPVD YSZ TBCs on an unspecified bond coat and alloy. They also provided bond-coated superalloy substrates with no top coat. A bi-layer top coat was designed and thermally sprayed onto these substrates in the UConn Thermal Spray Laboratory: an APS YSZ inner layer with an outer layer of SPPS GZO. The development of SPPS GZO has been described elsewhere [98]. As stated previously, the APS inner layer is necessary due to the chemical incompatibility between the alumina TGO and GZO. The inner layer was deposited by APS because the bond coat was found to be too rough for SPPS YSZ. The spray parameters for both the APS YSZ and SPPS GZO can be found in Table 3.1. For the isothermal furnace testing described in section 3.4, APS YSZ
coupons were used from a different manufacturer, Solar Turbine. These were, however, similar to the other APS YSZ specimens.

Table 3.1 Spray parameters for bi-layer TBC coupons

<table>
<thead>
<tr>
<th>Spray Parameter</th>
<th>APS YSZ Inner Layer</th>
<th>SPPS GZO Outer Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Gun</td>
<td>Metco 9MB</td>
<td>Metco 9MB</td>
</tr>
<tr>
<td>Gun Nozzle</td>
<td>GH</td>
<td>GH</td>
</tr>
<tr>
<td>Plasma Current/Voltage (V)/(A)</td>
<td>600/67</td>
<td>650/70</td>
</tr>
<tr>
<td>Feedstock</td>
<td>Metco 204-XCL</td>
<td>Aqueous gadolinium nitrate (Inframat) /zirconium acetate (MEL) mixture</td>
</tr>
<tr>
<td>Delivery System</td>
<td>Metco 4MP Powder Feeder</td>
<td>SPPS Delivery System with BETE Fog Nozzle (FC4/AC1501 Fluid/Air Caps)</td>
</tr>
<tr>
<td>Feed Rate</td>
<td>4.5-5.0 lb/hr</td>
<td>22 mL/min</td>
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<tr>
<td>Scan Speed (mm/s)</td>
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<td>450</td>
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<tr>
<td>Scan Width (mm)</td>
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<td>400</td>
</tr>
<tr>
<td>Raster Size (mm)</td>
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<tr>
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<td>15</td>
</tr>
<tr>
<td>Coating Passes</td>
<td>3</td>
<td>25</td>
</tr>
</tbody>
</table>

A cross section sample of each TBC system was prepared and analyzed as described in 3.1.1 to document the as-sprayed microstructure. The X-ray diffraction pattern of each sample was also collected in the as-sprayed state, as described in 3.1.2.

3.2.2 CMAS Compositions and Precursor Development

Two CMAS compositions were used in this work: their constituents are listed in Table 3.2, normalized to mole percent cation (AFRL-03 only). The first composition, designated “CMAS-1,” was a proprietary mixture provided by an engine manufacturer. Some representative powder was also provided. The powder itself was not used in any experiments: the CMAS-1 composition
was only used in the form of a precursor solution. The second composition, designated “AFRL-03,” is a commercially available test dust (AFRL-03 Test Dust, Powder Technology, Inc.) meant to simulate CMAS-forming sand compositions in the South-west Asia region [99]. It is made by pulverizing natural minerals – namely quartz, gypsum, aplite, and dolomite – and food-grade sodium chloride. Some of the as-delivered AFRL-03 was examined by SEM and EDXS to determine particle morphology and chemical heterogeneity. The particle size distribution was provided by the manufacturer. Although these CMAS compositions are reported here in mole percent cation, it is important to note that both derive most of their calcium from calcium sulfate.

Table 3.2 CMAS compositions, normalized to mol% cation

<table>
<thead>
<tr>
<th>Cation</th>
<th>CMAS-1</th>
<th>Cation</th>
<th>AFRL-03</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Descending Concentration</td>
<td>Si</td>
<td>59</td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td>Ca</td>
<td>20</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>Na</td>
<td>9</td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td>Mg</td>
<td>6</td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td>Al</td>
<td>5</td>
</tr>
<tr>
<td>K</td>
<td></td>
<td>K</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>Fe</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Based on these nominal compositions, liquid precursor solutions were prepared. The ingredients used to produce each CMAS constituent are listed in Table 3.3. The purpose of these solutions was to provide a route by which CMAS can be deposited onto TBC coupons in a controlled fashion, which was done using several methods. Upon heating, these precursor solutions evaporate, leaving behind nitrate salts and other precipitates. These nitrates then thermally decompose into the desired oxides. Solutions were typically produced at a concentration
of about 1 wt% CMAS. That is, upon decomposition of 100 mg of solution, there are sufficient metal cations to produce 1 mg of CMAS oxides, assuming the formation of simple oxides and calcium sulfate.

Table 3.3 Ingredients for precursor solutions

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Precursor Ingredient(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO$_4$ · 2 H$_2$O</td>
<td>Calcium Nitrate, L-cysteine</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium Nitrate</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium Nitrate</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Aluminum Nitrate</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Ludox® AM Colloidal Silica</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Iron Nitrate</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>Potassium Nitrate</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Titanium Sulfate</td>
</tr>
<tr>
<td>NaO</td>
<td>Sodium Nitrate</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
</tr>
</tbody>
</table>

3.3 CMAS Characterization and Comparison with Precursors

In order to compare the CMAS compositions and the chemical precursor solutions intended to recreate them, the experiments described below were carried out.

3.3.1 Calorimetry

The melt onset of the CMAS powders and their precursor solutions were analyzed using DSC, as described in 3.1.3. The precursor solutions were evaporated in a drying oven (APT.line, Binder) at 60 °C, and the residue was utilized.
3.3.2 Phase Evolution

Ideally, the precursor solutions would yield the same phases as those found in the original CMAS compositions. To determine to what extent that was true, the X-ray diffraction patterns were collected, as described in 3.1.2, of:

- The as-received powders
- The powder after calcination
- The powders after melting and cooling
- The evaporated precursor
- The precursor after calcination
- The precursor after melting and cooling

The calcination and melting heat treatments were carried out in a box furnace (1700 Series, CM Furnace). Calcination was at 900 °C for one hour, and melting was at 1300 °C for one hour. In both cases, heating and cooling were both carried out at 5 °C/min.

3.4 Isothermal Furnace Testing

While one of the main objectives of this thesis was to develop thermal gradient rigs for carrying out CMAS durability testing, there was a need to perform some testing while the first generation rig was still in development. The goal was to develop an isothermal test that would demonstrate the improved cyclic durability of a GZO TBC compared to YSZ TBCs when CMAS was introduced. Since most methods of pre-depositing CMAS on a TBC would cause spallation within the first several cycles of an isothermal furnace test, a new method was developed to incrementally add small doses of CMAS to the TBC during cycling.
TBC coupons (Solar APS YSZ and UConn-developed bi-layer GZO/YSZ) were placed in a bottom-loading box furnace (1700 series, CM Furnace), and thermally cycled using a one hour cycle: 5 minute ramp to 1180 °C, 45 minute dwell, and 10 minutes forced air quench (Figure 3.2).

![Graph of substrate temperature over time](image)

*Figure 3.2 Heating cycle for isothermal furnace testing*

Five minutes into the quench, when the sample temperature was approximately 300 °C, the samples were sprayed with 1 wt% CMAS-1 precursor solution using a medical atomizer (MADomizer, LMA), shown in Figure 3.3. This atomizer produces a metered dose of 0.1 mL liquid per spray, and the samples were sprayed twice per thermal cycle. Thus, each sample was sprayed with approximately 2 mg of CMAS per cycle. The life of these samples, defined as 40% visible surface damage, was compared against baseline samples with no CMAS spray and samples sprayed with de-ionized water. Cross sections of failed specimens were investigated using the techniques described in 3.1.1.
3.5 Modeling of Transient Temperature Distributions

During the development of the first generation gradient rig, an estimate of the transient temperature distribution across the TBC coupon, from the surface of the ceramic top coat through to the back of the superalloy substrate, was modeled using a one-dimensional explicit finite difference method. In brief, the transient temperature distribution through a flat, planar, infinitely thick plate is given by the heat equation (3.1).

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$  \hspace{1cm} (3.1)

In the finite difference method, space and time are discretized into finite increments. The body in question is divided into slices or nodes, each with its own set of unique material properties. The calculation for the heat flowing into and out of each node is assumed to be linear in space, and the accumulation of heat in the node is linear in time. One formulation for the explicit finite difference method, incorporating both variable node thickness and variable material properties is given by equation (3.2). Table 3.4 explains the notation.
\[ T_{i}^{k+1} = T_{i}^{k} + \frac{1}{M_{i}} \left[ \frac{2K_{i-1} \Delta X_{i}^{-}}{K_{i} \Delta X_{i}^{-} + K_{i+1} \Delta X_{i}^{+}} \right] [T_{i-1}^{k} - T_{i}^{k}] + \frac{1}{M_{i}} \left[ \frac{2K_{i+1} \Delta X_{i}^{+}}{K_{i} \Delta X_{i}^{-} + K_{i+1} \Delta X_{i}^{+}} \right] [T_{i+1}^{k} - T_{i}^{k}] \]

\[ M_{i} = \frac{\Delta X_{i}^{2}}{\alpha_{i} \Delta t} \]

Table 3.4 Notation in finite difference equation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{i}^{k+1})</td>
<td>Temperature (°C or K) – superscript is the time step, subscript is the node element</td>
</tr>
<tr>
<td>(K_{i})</td>
<td>Thermal conductivity of the node (\left(\frac{W}{m \cdot K}\right))</td>
</tr>
<tr>
<td>(\Delta X_{i})</td>
<td>Thickness of material represented by the node (m)</td>
</tr>
<tr>
<td>(\alpha_{i})</td>
<td>Thermal diffusivity of the node (\left(\frac{m^{2}}{s}\right))</td>
</tr>
</tbody>
</table>

Given the initial condition of each node and two boundary conditions, this equation can be used iteratively to determine the temperature at each node and at each time step. For stability reasons, \(M\) must be greater than 2, which sets boundaries on what time and space increments can be selected based on material properties of each node \(\alpha_{i}\). The code to iteratively solve the equation and record values was written in MATLAB. In this case, the front and backside temperature data from the rig were used as the boundary conditions at each time step. Because the data recording from the pyrometers was, at best, 10 Hz, the surface temperatures at any given time step were set as the linear interpolation between recorded data points. The material properties assumed and the node dimensions are given in Table 3.5. The thickness of the top coat and bond coat were measured in the SEM. Because the TGO layer is very thin, especially early in the coating cyclic life, its contribution to the temperature distribution was assumed to be negligible.
Table 3.5 Parameters used for finite difference model

<table>
<thead>
<tr>
<th>Layer</th>
<th>Parameter</th>
<th>Value for APS YSZ TBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic Top coat</td>
<td>Thermal conductivity ( \frac{W}{m \cdot K} )</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Thermal diffusivity ( \frac{m^2}{s} )</td>
<td>3.97x10^{-7}</td>
</tr>
<tr>
<td></td>
<td>Thickness (m)</td>
<td>380x10^{-6}</td>
</tr>
<tr>
<td></td>
<td>Mesh size (m)</td>
<td>10x10^{-6}</td>
</tr>
<tr>
<td>Bond Coat</td>
<td>Thermal conductivity ( \frac{W}{m \cdot K} )</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Thermal diffusivity ( \frac{m^2}{s} )</td>
<td>6.32x10^{-6}</td>
</tr>
<tr>
<td></td>
<td>Thickness (m)</td>
<td>150x10^{-6}</td>
</tr>
<tr>
<td></td>
<td>Mesh size (m)</td>
<td>25x10^{-6}</td>
</tr>
<tr>
<td>Substrate</td>
<td>Thermal conductivity ( \frac{W}{m \cdot K} )</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td>Thermal diffusivity ( \frac{m^2}{s} )</td>
<td>4.34x10^{-6}</td>
</tr>
<tr>
<td></td>
<td>Thickness (m)</td>
<td>3.2x10^{-3}</td>
</tr>
<tr>
<td></td>
<td>Mesh size (m)</td>
<td>200x10^{-6}</td>
</tr>
<tr>
<td></td>
<td>Time step (s)</td>
<td>2x10^{-5}</td>
</tr>
</tbody>
</table>

For this analysis, time and space dimensions were set such that M was greater than 4 for each layer of the TBC. To confirm that this mesh was sufficiently fine, one test case and one rig run were repeated with a mesh half as thick (requiring the time step to be reduced to 5x10^{-6} seconds to maintain M values), and the results were compared, showing minimal change in results. The steady state interface results for the test case are shown in Table 3.6 below, compared also with the results using the 1D steady state analytical solution to the heat equation. T_{TBC-BC} is the temperature at the TBC-bond coat interface, and T_{BC-SUB} is the temperature at the bond coat-substrate interface. Since the coarser mesh run time was on the order of several hours, the finer mesh (at four times the run time) was deemed unnecessary.
Table 3.6 Comparison between finite difference meshes and 1D steady state hand calculation for a simulated TBC

<table>
<thead>
<tr>
<th></th>
<th>ΔX_{TBC} (μm)</th>
<th>Δt (s)</th>
<th>T_{Surface} (°C)</th>
<th>T_{TBC-BC} (°C)</th>
<th>T_{BC-SUB} (°C)</th>
<th>T_{Backface} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse Mesh</td>
<td>10</td>
<td>2x10^{-5}</td>
<td>1225</td>
<td>382</td>
<td>365</td>
<td>20</td>
</tr>
<tr>
<td>Fine Mesh</td>
<td>5</td>
<td>5x10^{-6}</td>
<td>1225</td>
<td>381</td>
<td>367</td>
<td>20</td>
</tr>
<tr>
<td>1D SS (Hand Calculation)</td>
<td>-</td>
<td>-</td>
<td>1225</td>
<td>380</td>
<td>368</td>
<td>20</td>
</tr>
</tbody>
</table>

3.6 Development of Test Rigs and Operational Parameters

As stated in the research goals, much of the effort behind this thesis went into the design, analysis, and re-design of thermal gradient rigs and testing parameters. First, design aspects were investigated, such as torch orientation, fuel-oxygen ratio, pyrometer configuration and placement, and CMAS deposition methodology. Next, test parameters were investigated by cycling samples under different operating conditions. Test outcomes, especially the microstructure of failed TBC coupons, were compared against internal OEM engine experience. Feedback was used in iteration of test design, allowing for improvements to the rig and testing.
4 TEST MATERIALS CHARACTERIZATION AND ISOTHERMAL TESTING RESULTS

4.1 Analysis of As-sprayed TBC Coupons

Micrographs of the four TBC systems used in this work are shown in Figure 4.1. The microstructures of the three OEM coating systems – EBPVD YSZ, APS YSZ, and Solar APS YSZ – are typical for the coating types. Individual columnar grains compose the EBPVD YSZ TBC; the inter-columnar spacing is on the order of 1 micron, although the spacing is larger at the surface where columns come to a point. The APS YSZ and Solar APS YSZ coupons display the “brick and mortar” splat structure. The APS coatings display both fine porosity and large (on the order of 10-30 micron) voids. As is common, the EBPVD TBC is less rough at both the surface and the TBC-BC interface. As for the bi-layer TBCs, there appears to be good adhesion between the APS YSZ inner layer and the bond coat. The surface of the APS YSZ does indeed have a lower roughness than the bond coat layer, which is desirable for the SPPS layer on top [100]. The SPPS GZO layer also appears to have adhered well to the APS YSZ. The porosity at this interface does not appear to be any greater than throughout the layer (Figure 4.2), and there are no large cracks or voids visible. The SPPS GZO layer also has distinct vertical cracking with spacing of about half the coating thickness. This has been shown to increase the durability of SPPS coatings compared to traditional APS coatings [101].
Figure 4.1 As sprayed microstructure of EBPVD YSZ (a), APS YSZ (b), Solar Turbine APS YSZ (c), and bi-layer SPPS GZO/APS YSZ (d)

Figure 4.2 SPPS GZO/APS YSZ Interface

The XRD patterns for each TBC system are displayed in Figure 4.3. The three YSZ compositions are all identifiably yttria-stabilized zirconia in the metastable tetragonal t’ phase.
The relative intensity of the peaks for the EB sample are shifted compared to a random, polycrystalline sample because the EBPVD columns grow in a <100> direction [102]. The APS YSZ samples appear to be primarily t’-YSZ without texture, although there are some monoclinic zirconia peaks. The XRD pattern for the SPPS GZO indicates that it is fluorite phase, since the superlattice reflections indicative of the pyrochlore structure are absent [103]. EDXS indicates that deposited GZO is lean in gadolinium, which could be due to evaporation of the rare earth element in transit [104].
Figure 4.3 XRD Patterns of as-sprayed EBPVD YSZ (a), APS YSZ (b), Solar Turbine APS YSZ (c), and bi-layer SPPS GZO/APS YSZ (d)
4.2 Characterization and Comparison of CMAS Compositions and Precursors

4.2.1 Microstructure of AFRL-03 Powder

The particle size distribution of AFRL-03, provided by the vendor, is shown in Figure 4.4. About 30% of the material is smaller 10 microns, and about 5% of the particles are larger than 75 microns. The wide size distribution and large fine content make the powder prone to caking and very resistant to flow.

![Figure 4.4 Particle size distribution of AFRL-03 powder](image)

As stated, the powder is produced by pulverizing minerals, and the microstructure of the individual powder particles shown in Figure 4.5 illustrates this fact. Individual particles are rough, faceted, and many have large aspect ratios. Each number on the image indicates the location of a point spectrum taken using EDXS. The identity of each particle based on its spectra is given in Table 4.1, which demonstrates the heterogeneity of the powder. Not only are individual particles chemically distinct, but there is significant size segregation between constituents. For example, all of the largest particles are quartz, while mid-size particles are typically aplite or dolomite. The gypsum takes the form of agglomerations of very fine particles, while halite is found in the small, loosely agglomerated material. Within this finer material, there was often a mixture of phases that could not be individually resolved with EDXS. The composition of the AFRL-03 constituents is
show in Table 4.2. PTI provided a chemical breakdown of the aplite that they used in the manufacture of AFRL-03, which allowed for the precursor solution to be made with the same cation ratios.
Figure 4.5 Micrograph of loose AFRL-03 powder

Table 4.1 Phases of individual particles

<table>
<thead>
<tr>
<th>Location</th>
<th>Phase(s)</th>
<th>Location</th>
<th>Phase(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Q</td>
<td>11</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>Q</td>
<td>12</td>
<td>A</td>
</tr>
<tr>
<td>3</td>
<td>Q</td>
<td>13</td>
<td>Q,G,H</td>
</tr>
<tr>
<td>4</td>
<td>Q</td>
<td>14</td>
<td>Q,G,H</td>
</tr>
<tr>
<td>5</td>
<td>D</td>
<td>15</td>
<td>Q,G,H</td>
</tr>
<tr>
<td>6</td>
<td>D</td>
<td>16</td>
<td>G</td>
</tr>
<tr>
<td>7</td>
<td>D</td>
<td>17</td>
<td>Q</td>
</tr>
<tr>
<td>8</td>
<td>G</td>
<td>18</td>
<td>G</td>
</tr>
<tr>
<td>9</td>
<td>G</td>
<td>19</td>
<td>Q,G,H</td>
</tr>
<tr>
<td>10</td>
<td>D</td>
<td>20</td>
<td>Q</td>
</tr>
</tbody>
</table>

Phases include Quartz (Q), Dolomite (D), Gypsum (G), Aplite (A), and Halite (H)
Table 4.2 Nominal Chemistry of AFRL-03 Constituents

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Nominal Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
</tr>
<tr>
<td>Aplite</td>
<td>SiO₂, KAlSi₃O₈ – NaAlSi₅O₈ – CaAl₂Si₂O₈*</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
</tr>
</tbody>
</table>

*Exact chemistry provided by PTI

While AFRL-03 powder is similar to real sand in that it is chemically heterogeneous and has a wide particle distribution, it is quite unattractive as a feedstock for thermal spray or other deposition process. The chemistry of the deposited material could easily be quite different from the initial powder. For example, the fine particles may have insufficient momentum to impact the substrate (Stokes number effect) [105], which would result in the loss of some of the gypsum and salt. On the other end of the size distribution, the large silica grains may not sufficiently melt or soften to adhere to a substrate.

4.2.2 Calorimetry Results, CMAS-1 and AFRL-03

The melt onset temperatures measured from DSC are given in Table 4.3. The melting onset is within 10 °C between each powder and its precursor analog. Thus, at least from the first order perspective of melt onset and penetration into the coating, the precursor solutions should behave similarly to the relevant composition.

Table 4.3 Melt onset temperature of CMAS compositions and chemical precursor solutions

<table>
<thead>
<tr>
<th>CMAS Type</th>
<th>Melt Onset (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMAS-1 Powder</td>
<td>1167</td>
</tr>
<tr>
<td>CMAS-1 Precursor</td>
<td>1176</td>
</tr>
<tr>
<td>AFRL-03 Powder</td>
<td>1196</td>
</tr>
<tr>
<td>AFRL-03 Precursor</td>
<td>1188</td>
</tr>
</tbody>
</table>
4.2.3 Evolution of Phases, CMAS-1 and AFRL-03

Figure 4.6 shows the evolution of phases for the CMAS-1 powder received from the engine manufacturer. The as-received powder pattern indicates a completely amorphous material (a). After heating to 900 °C and cooling (b), the powder appears to have largely crystallized. The amorphous hump almost completely disappeared: the peak-to-noise ratio between the largest peak and the background was over 10 to 1. The pattern was tentatively identified as two silicate compositions, anorthite and akermanite. When the powder was melted and cooled (c), the CMAS again crystallized; this time, only the anorthite pattern remained. The peak-to-noise ratio was over 100 to 1, so the CMAS seems to have almost entirely crystallized.
Figure 4.6 XRD patterns of as-received CMAS-1 powder (a), after calcination at 900 °C (b), and after melting at 1300 °C (c)
Figure 4.7 shows the evolution of phases for the CMAS-1 precursor. Upon drying (a), the CMAS precursor has some amorphous or nano-scale material: background subtraction (b) allows for the identification of calcium sulfate hemihydrate and anhydrous calcium sulfate. The nano-crystalline silica does not appear to have agglomerated sufficiently to introduce silica peaks to the pattern. Calcination removes the waters of hydration, leaving only anhydrite (c). The melted and cooled precursor had very few reflections, but the extant peaks are consistent with anorthite (d).
Figure 4.7 XRD patterns of the CMAS-1 precursor solution as-dried (a), and with the background removed for phase identification (b), calcined at 900 °C (c), and melted at 1300 °C (d)
Figure 4.8 shows the evolution of phases for the AFRL-03 powder. The as-received powder pattern (a) has peaks for each of the advertised constituents, and the relative intensity of the peaks correlate with relative concentrations, i.e. the gypsum and silica peaks are strongest while halite is the weakest. After calcination at 900 °C (b), the gypsum has dehydrated, and, as expected, the dolomite appears to have thermally decomposed, although there is not a strong signal for calcium or magnesium oxide, the typical decomposition products of dolomite [105]. Between the decomposition of the dolomite and the likely melting of the halite, it would appear that there has been some modification within the aplite, possibly from a high albite to a low one. Refined phase analysis would be necessary to make this determination, which was beyond the scope of this project. The pattern after the 1300 °C heat treatment indicates that the material has remained amorphous on cooling (c).
Figure 4.8 XRD patterns of as-received AFRL-03 powder (a), after calcination at 900 °C (b), and after melting at 1300 °C (c)
Figure 4.9 shows the evolution of phases for the AFRL-03 precursor. When the solution is dried (a), there is a large amorphous or nano-crystalline component, but background subtraction allows for the identification of both hydrated and anhydrous calcium sulfate (gypsum and anhydrite) (b). The peak at 21.5° is likely a combination of gypsum and silica. Upon calcination at 900 °C (c), the AFRL-03 precursor residue loses the gypsum peaks, most notably the peak at 11.6°; as such, the peak at 21.5° is now likely predominantly from the silica. Notable is the formation of a diopside phase, which would be a sink for the minor cation elements (Mg, Al, K, Na, Fe) in the solution [106]. Upon melting, the precursor solution remains amorphous, similar to the powder (d).
Figure 4.9 XRD patterns of the AFRL-03 precursor solution as-dried (a), and with the background removed for phase identification (b), calcined at 900 °C (c), and melted at 1300 °C (d)
4.2.4 Summary of comparison between CMAS powder and precursor

In the case of each CMAS composition, precursor and powder had similar (within 10 °C) melt onset points. Once the CMAS constituents are largely melted, it should not matter that the precursor oxides were simple, while the powder oxides were complex. As long as the melt has the same composition, the key material properties of viscosity and reactivity with TBC materials should be similar. However, this is dependent on what actually sticks to the coating for both precursor and powder to be the same. Studying what exactly sticks to the TBC, and how it might evolve over thermal cycling and CMAS accumulation, is an important avenue of study that was beyond the scope of this work.

One notable success in the development of the chemical precursor solutions was that the XRD patterns show a very strong calcium sulfate signal. This means that the calcium nitrate and L-cysteine reacted to form a significant amount of calcium sulfate. Sulfates have been shown to behave differently than oxides as a TBC contaminant [107], so their presence in the CMAS precursor is important for realistically mimicking the real CMAS compositions. The fact that both the CMAS-1 powder and precursor crystallize on cooling from the melt, while the AFRL-03 powder and precursor do not, is also promising. Again, this is indicative of the fact that, given the same cations in the melt, the melt from these two different sources should behave the same. This result also suggests that optical basicity cannot tell the whole story when it comes to predicting the severity of CMAS attack. When it comes to non-reactive coatings like YSZ, a CMAS that naturally crystallizes is not going to be able to do as much damage in a cyclic heating and cooling environment. Residual CMAS on the surface that crystallizes will not be as available for melting and penetration on subsequent heating cycles.
The CMAS materials and their precursor solutions do form different oxides during heating, which is likely to have implications on any solid state reactions that occur between TBC and CMAS. While such solid state reactions have been identified on ex-service engine hardware [108], they have not been so far identified as a significant contributor to TBC degradation. The effects of melting and penetration into TBC porosity are much more catastrophic. Thus, when running experiments well above the CMAS melt point, where all the CMAS constituents should be in the melt, the precursor solutions appear to be good analogs for the CMAS compositions.

4.3 Isothermal Furnace Testing Results

The life results from the isothermal furnace tests, normalized to the baseline life of the Solar APS YSZ specimen, are given in Table 4.1. Both the Solar APS YSZ and bi-layer GZO/YSZ TBC baseline life samples lasted more than 100 cycles, so the samples contaminated with CMAS did have cyclic lives greater than one. However, the minor increase in relative CMAS durability of the bi-layer TBC is not indicative of GZO’s superior performance in other trials [93].

The samples cycled with deionized water showed a roughly 60% reduction in cyclic life compared to the baseline samples, suggesting that moisture damage [109] and thermal shock were likely contributors to the failure of the CMAS-contaminated samples. However, the fact that the CMAS lives were about 25% that of the deionized water lives indicates that the CMAS is doing some portion of the damage. Applying this result to the thermal gradient rig design, a liquid precursor should not be sprayed on the sample when it would thermally shock the sample, nor should the solution be allowed to wick into the coating.
Table 4.4 Results of cyclic furnace testing with CMAS (normalized to baseline APS YSZ sample)

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>APS YSZ</th>
<th>SPPS GZO/APS YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>No CMAS Baseline</td>
<td>100%</td>
<td>58%</td>
</tr>
<tr>
<td>DI Water Spritzed</td>
<td>34%</td>
<td>31%</td>
</tr>
<tr>
<td>CMAS Spritzed</td>
<td>10%</td>
<td>9%</td>
</tr>
<tr>
<td><strong>CMAS Life Reduction</strong> (= 1 – CMAS Life/Baseline Life)</td>
<td><strong>90%</strong></td>
<td><strong>85%</strong></td>
</tr>
</tbody>
</table>

Examining the failure morphology and microstructure of the baseline and CMAS contaminated coupons reveals several key pieces of information. Macro photos of the coupons, shown in Figure 4.10, show that the baseline failure in the APS YSZ coupons occurred near the top coat – bond coat interface. The ceramic remained a fairly monolithic layer. Failure of the CMAS-contaminated sample was also near the interface, but the ceramic fractured in a more piecemeal fashion. In the case of the bi-layer GZO/YSZ coupons, primary failure occurred within the ceramic top coat in both cases.
Cross sections of the samples, Figure 4.11, elaborate on this failure mode. Both Solar YSZ coupons failed within the top coat, just above the interface, which is a common failure mechanism for APS YSZ TBCs [110]. The bi-layer GZO/YSZ coupons delaminate between the GZO and YSZ coating layers, suggesting that the adhesion between the two layers was not as strong as initially assumed.
However, the most clear result from this testing is to prove the necessity of the thermal gradient rig. The test temperature, necessary to ensure complete melting of the CMAS, is well above the typical operating temperature for metallic bond coat compositions. As such, failure due to the bond coat oxidation is aggressively accelerated, which means that there was little time to accumulate much CMAS. That is why there is little sign of CMAS accumulation or penetration of the ceramic. The concentration of CMAS was insufficient to identify penetration using the common technique of elemental mapping using EDXS. Furthermore, there was minimal chemical interaction between the TBC and CMAS, likely due to the fact that the test temperature is just at the approximate melt point of the CMAS. A thermal gradient across the coupon, as is experienced

Figure 4.11 Micrographs of failed TBC cross sections: Solar APS YSZ baseline without CMAS (a) and with CMAS (b); SPPS GZO/APS YSZ baseline without CMAS (c) and with CMAS (d)
in engine service, allows for high enough surface temperatures for the CMAS-TBC chemical interaction to be kinetically favorable, while the bond coat temperature is low enough so as to allow for enough hot time and cycles to incrementally accumulate a detectible amount of CMAS.
5 FIRST GENERATION THERMAL GRADIENT RIG

5.1 Construction

5.1.1 Initial Configuration

After exploring multiple design options, the basic configuration of the rig that was initially developed can be seen in Figure 5.1. This design was based on the test rigs developed at Jülich and Ohio State [92], [95]. The source of heat flux was a surface-mix fuel-oxygen glass-working torch (Red Max, Nortel Manufacturing). In an engine, the pressure in the hot section can be more than 30 atmospheres [86], resulting in high Reynold’s numbers and high heat transfer coefficients between the hot gas path and engine components. Using an oxygen flame in the lab increases the flame temperature compared to the engine, which partially compensates for the lower heat transfer coefficient resulting from the pressure being roughly one atmosphere. The figure shows the rig during the heating phase of a thermal cycle, when the flame is impinging on the sample holder, which contains the TBC coupon. A jet of compressed air on the back side of the coupon actively cooled the sample; varying the jet flow allowed for control of the temperature gradient across the test coupon. The torch was mounted on a translation stage. During the cooling cycle, the torch was moved off the sample, and a front-side cooling jet of compressed air rapidly quenched the front surface of the sample.
Figure 5.1 Layout of first generation thermal gradient rig

The fuel selected for this rig was propane; since it is inexpensively stored as a liquid, a supply large enough to run for long durations could be acquired. Sourcing sufficient compressed oxygen, however, was a challenge. The standard K cylinder holds 300 cubic feet of gas, which would be consumed in less than a day of rig operation. Manifolding and replacing gas bottles would be cumbersome and expensive, and EH&S and the Fire Marshal were opposed to having a liquid oxygen cylinder in a lab with an open flame. A solution was found in the form of oxygen concentrators. These devices, which have both medical and industrial applications, feed pressurized air into a zeolite bed, which traps nitrogen. The remaining gas, which is 90-95% oxygen, then flows out of the concentrator. For the first generation rig, three refurbished portable medical concentrators (Figure 5.2) (M15, Unlimited Oxygen) were utilized to prove out the concept.
The sample holder design is shown in Figure 5.3. The three layer sandwich configuration allowed the TBC coupon to be loosely constrained in all directions. The back plate, made from Haynes 230 alloy, had a hole larger than the sample and four small tabs to prevent the sample from falling out the back. The two front half-plates, only one of which is shown, were made from Haynes 214 and prevent the sample from falling down. The diameter of the hole formed by the two front plates was 0.063” smaller than the diameter of the sample, which prevented the flame or CMAS spray from wrapping around the sample. The slots cut radially from the hole reduced thermal stresses due to thermal cycling, increasing the life of sample holder plates. The middle piece, also made from Haynes 214, prevented the sample from moving laterally; the hole was 0.063” larger than the sample, allowing it to expand and contract without constraint. One drawback of this sample holder design was that it buried the sample within the sample holder: the front surface of the sample sits in a stagnation zone with respect to the flame, and the large thermal mass draws heat out of the sample from the edges. However, this design compared favorably to other options explored with respect to cost, ease of manufacture and durability. Front half-plates endured up to 800 hours of testing, middle plates up to 2000 hours, and the back plates did not, to date, show any degradation from thermal cycling.
The front and back surface temperatures of the TBC coupon were measured using infrared pyrometers (OS550a series, Omega Engineering), which were sensitive in the 8-14 micron range. YSZ has a high transmission coefficient in the mid IR, and its emissivity in the short and mid IR is highly temperature dependent. However, in the 9-14 micron range, the emissivity of YSZ is both close to 1.00 and only slightly temperature dependent, making a long wavelength pyrometer essential for accurate surface temperature measurement [111]. Several other gradient rigs in the literature measure the surface temperature with a pyrometer but use a thermocouple installed in a hole drilled into the side of the coupon to measure the TBC-bond coat interface temperature. This was not practical for this work, since the majority of test coupons were received from OEMs already sprayed; drilling a hole for a thermocouple post-deposition risked damage to the coating. Measuring the back face temperature proved a challenge, because the metallic substrate has an initially low emissivity that progressively rises with increasing oxidation. Therefore, the back faces of coupons were painted with a high temperature engine header paint (Flameproof™, VHT Paint), whose emissivity was measured to be approximately 0.95.

The CMAS deposition scheme for the gradient rig used the same precursor solution as the isothermal furnace tests in Section 4.3. Here, the liquid was placed in a pressurized bottle on top
of a heating/stirring plate to promote long-term stability: at room temperature, the L-cysteine tended to precipitate out of solution. The precursor liquid was fed through an air atomizing nozzle (BETE Fog Nozzle) to spray onto the TBC surface. The atomizing nozzle had a pneumatic shut-off valve, which allowed for a controlled dose of solution to be sprayed during a specific part of each thermal cycle. The fact that nitrates were used as the precursor chemicals for most of the metal oxides was advantageous because they are inherently sticky when partially dried. This helped the CMAS adhere to the coating, even as the same was blown on by a flame and held upside down.

All rig operations and data collection were automated with a custom interface and control system using LabView software and hardware. The torch output power (propane and oxygen flow) was controlled using a closed-loop PID algorithm implemented in LabView. The process variable for the control loop was the surface temperature of the TBC. The rig was installed in a fume hood to vent the waste gases, draw the generated heat out of the room, and contain testing debris. The valves for air, propane, oxygen, and CMAS precursor, mass flow controllers, pyrometer control boxes, LabView acquisition modules, and all associated electronics were built into a separate module from the rig frame (Figure 5.4), which allowed these components to be outside of the fume hood.
5.1.2 Subsequent Improvements

As rig operation progressed, several other innovative improvements were added to increase safety, testing throughput, and convenience. The rig was expanded to include a second sample position; instead of shuttling between a heating position and a cooling position, the torch moved from heating one sample position to heating the other sample position. Compared to adding a second torch to the rig, this eliminates torch down time and wasted fuel to keep the torch burning during cooling cycles. One consequence of having one torch and two sample positions is that the thermal cycle now required symmetric hot and cold times, marginally reducing the gains in testing throughput.

The largest enabler of increased testing throughput, however, was the development of a safety system to allow the rig to operate continuously without supervision. One key design feature of the rig was that all gases passed through normally-closed electromechanical valves. That way, the flow of gases could be instantly shut off, no matter the current rig state, simply by cutting power to the rig. The gas valves would close, and the rig safely shut down, in the event of a building power failure as well. The automation software for the rig also checked multiple parameters for potentially dangerous failure conditions, including sample over temperature,
sample under temperature (possibly indicating a sample fell out), and failure of the closed-loop control to follow the set point function within a user-specified accuracy.

Independent interlocks were added to the system, most importantly a flame-out detector. The most hazardous fault in the system would be if the flame went out, because the control algorithm would maximize torch output to try to follow the set point function, potentially filling the room with propane and oxygen. This could, if left unchecked, lead to an explosion. Since torch control and many of the safety features were controlled by the LabView software, it became critical to detect if any kind of computer failure had occurred. A digital heartbeat signal was continuously calculated by the software, generated, and sent to a timing circuit. If this signal froze “high” or “low” due to computer trouble, the interlock system would cut power to the test rig, causing the gas valves to close.

With the rig running unattended, it became important to have an automatic way to inspect sample failures after the fact, as well as to monitor rig operation remotely. To these ends, a security DVR, normally designed for a building CCTV system, and several consumer video cameras were attached to the rig. With one camera focused on each sample, the system stored several days’ worth of cyclic testing video, which could then be reviewed during the day. In this way, the exact cycle number when a failure event occurred could be documented. The size, time of failure (i.e. during heating, cooling, or rig downtime), and the energetics (slow crack or fast spallation) were also recorded, which could not be done with a still camera taking a picture every cycle. Knowing when during a cycle that failure occurred proved critical to improving the test outcomes of the rig. Between the paired samples and continuous, unattended operation, the testing throughput of the rig nearly tripled compared to the original configuration.
5.2 Initial Operating Conditions

5.2.1 Temperature Profile

In initial testing, the temperature profile used was based on the work of researchers at Jülich (Figure 5.5) and Ohio State. Similar to these previous efforts, the command function was a step input to the target surface temperature, and the PID was tuned to heat the sample to temperature as quickly as possible with an overshoot value of 1% or less of the set point. The propane to oxygen ratio for both the most rapid heating and highest temperature capability was found to be 1:4 by volume; this was set as the fixed ratio throughout thermal cycling. Heating usually took on the order of 45-60 seconds, depending on temperature set point and coating type. The hot cycle was a total of 5 minutes (heating and dwell portions), and the cooling cycle was 2 minutes in duration.

![Figure 5.5 Thermal cycle used for testing on Jülich rig [96]](image)

5.2.2 CMAS Deposition

The Jülich thermal gradient rig utilized a custom flame nozzle with coaxial liquid CMAS precursor feeding, and the CMAS feed ran continuously during their heating cycle [96]. However, they found that they no longer had stable temperature control when the liquid was injected into the flame. We were able to circumvent this problem by spritzing a small dose of solution during the
heating cycle. Spritzing during the dwell portion of the thermal cycle was attempted, but interference between the flame and liquid spray led to little to no deposition of CMAS. Therefore, spritzing occurred during the initial sample heating portion of the cycle. At the beginning of the heating cycle, the torch remained at minimum power under the sample for several seconds to bring the sample up to a temperature between 300 to 500 °C, depending on the sample type. Then the solution was spritzed onto the hot sample and flash boiled. It was previously shown in furnace testing (Section 4.3) that spritzing DI water on the sample does damage the coating, but the continuous heating from the torch on the rig minimized the thermal shock from the water spray.

Figure 5.6 shows a typical thermal cycle for a TBC coupon run on the rig and the first minute of heating enlarged. The temperature axis is normalized to the set point temperature at steady state (%SP). The feature of interest in the first minute of heating is the gradient across the coupon. The maximum gradient across the sample occurred early in the heating cycle, when the torch was at maximum power to heat the sample as rapidly as possible to the set point temperature.
5.3 Rig Validation

Because the optimal design and operation of these thermal gradient rigs are not defined in the community, it was of critical importance to validate our design and investigate how some of the design decisions affected rig performance.

5.3.1 Effect of Rig Orientation on Temperature Stability

Based on the Jülich and Ohio State designs, the rig was first configured with the torch horizontal. However, as Figure 5.7 shows, buoyancy forces bent the flame, diverting it away from
the center of the TBC coupon. Furthermore, the extent of diversion was dependent on the torch output power, leading to temperature instability (~5% of set point) and strong oscillation in the PID output. As shown in Figure 5.1, the rig was reoriented with the torch vertical early on in the design process. This allowed buoyancy forces to assist in temperature stability, dropping the variability by roughly an order of magnitude (~0.5% set point).

![Image](Figure 5.7 A horizontal flame is perturbed by buoyancy forces (a), while the vertical flame has much better temperature stability (b))

5.3.2 Effect of Pyrometer Angle

When utilizing any measurement device, it is important to have a physical understanding of exactly how the device operates to collect a measurement. Otherwise, one might unwittingly introduce sources of error into the measurement.

The pyrometers used on the rig are bolometer-type, which optically collect infrared radiation to heat a sensing element. In reality, the pyrometer is physically responding to the incident radiative power on the sensing element. For a perfectly Lambertian surface with uniform temperature, the intensity of radiation measured from a surface decreases with the cosine of the angle, as shown in Figure 5.8a. However, the apparent area over which an observer or measurement device collects radiation increases by the cosine of the angle (Figure 5.8b). These two effects cancel each other out, and the luminance (intensity per unit area) on the sensor remains
constant. So, if the TBC is a perfectly Lambertian surface, then the temperature reading should be insensitive to pyrometer viewing angle, assuming no in-plane temperature gradient.

To measure the effect of viewing angle, the following experiment was carried out, shown in Figure 5.9. An APS YSZ coupon was placed on a hot plate set to its maximum temperature output, 540 °C. To detect any variation in the hot plate temperature output, a K-type thermocouple was attached to the side of the coupon and measured throughout the experiment. The surface temperature of the TBC was measured using a rig pyrometer at six angles between 0° (normal to surface) and 45°. The radial distance between the TBC coupon and the pyrometer was kept constant.
The measurements shown in Figure 5.10 indicate little variation in the thermocouple reading over the course of the experiment, with only a 0.6% dip during the measurement at 20°. The pyrometer reading was similarly invariant, up until the shift from 40° to 45°. The dip at 45° was confirmed by repeating the experiment at 350°C. Based on these results, the pyrometers on the rig were placed such that the viewing angles were 40° from normal or less.

![Figure 5.10 Variation of pyrometer temperature measurement with angle](image)

5.3.3 Comparison between Pyrometers and LWIR Thermal Camera with Thermocouples

A second consequence of the pyrometer angle can be observed in Figure 5.8b. As the viewing angle increases, the area over which the pyrometer is collecting radiation distorts from a circle to an increasingly elongated oval. This would not matter if the TBC surface were at uniform temperature, but there is expected to be a negative temperature gradient from the center to the edges of the test coupon. Since the pyrometer reports one temperature value for the whole viewing area, it was initially unclear what this value physically represented.

In order to gain a better understanding of the temperature reported by the pyrometers, measure the in-plane gradient across the TBC coupons run on the rig, and confirm that we could estimate the interface temperature of a TBC coupon from the front and back temperature measurements, the following experiment was carried out. Two holes were drilled in the back of a
TBC coupon by EDM to a depth that would approach, but not break through, the substrate-bond coat interface. Both holes were \(\frac{1}{16}\)” from the coupon center, 180° apart (see Figure 5.11). Two 30-gauge S-type thermocouples were installed in the holes, and then cemented in place with water glass.

![Figure 5.11 TBC coupon with thermocouples installed near interface](image)

This sample was placed in the gradient rig, and the surface temperature was measured both with the pyrometer and with a long wavelength infrared (LWIR) thermal camera (T650sc, FLIR). This camera has a spectral range very similar to the pyrometers, 7.5 – 13.0 µm (compared to 8 – 14 µm for the pyrometers), and a resolution of 640 x 480 pixels. Because the insulation sheaths of the thermocouples interfere with the pyrometer measurement of the back temperature, the thermal camera was used to estimate the average temperature across the back surface as well. Using the front and back surface measurements, the TBC-BC interface temperature was estimated using the one-dimensional steady state heat conduction equation and representative TBC properties. This was compared to the thermocouple readings.

The findings from this experiment were the following. First, Figure 5.12 shows the temperature distribution from the LWIR camera in an isothermal false color scheme. The white oval on the image shows the approximate region of best agreement between the LWIR camera and the pyrometer reading at steady state, which correlated with the hottest part of the sample: this
makes a certain amount of physical sense, given that the intensity of radiation is proportional to the fourth power of temperature. Nevertheless, confirming that the pyrometer is biased towards the hottest part of the collection area is important information for understanding what the gradient rig is actually reporting.

![Isothermal contour map of TBC coupon at temperature Table 5.1 shows the normalized temperature measurements at steady state, including the estimated interface temperature using the front and back temperatures and assumed material and layer thickness parameters. Comparing the estimated interface temperature with the thermocouple data showed very good agreement, indicating that, at least at the center of the TBC coupon, we can estimate the steady state interface temperature based on the boundary conditions. This analysis assumes that the thermocouples were reading temperature values at or very near the interface. The actual size of the thermocouple bead and the thermal gradient within the substrate portion of the coupon (up to 100 °C, based on 1D steady state calculations) do not allow for a more precise measurement.](image-url)
Table 5.1 Measurements and estimate of 1D temperature distribution

<table>
<thead>
<tr>
<th>Location of Temperature Value (Measurement Device)</th>
<th>Normalized Temperature (% of Front Pyrometer Reading)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Front Surface (Pyrometer)</td>
<td>100%</td>
</tr>
<tr>
<td>Front Surface (LWIR Camera)</td>
<td>101%</td>
</tr>
<tr>
<td>Backside (LWIR Camera)</td>
<td>67%</td>
</tr>
<tr>
<td>Interface (Thermocouple 1)</td>
<td>76%</td>
</tr>
<tr>
<td>Interface (Thermocouple 2)</td>
<td>74%</td>
</tr>
<tr>
<td>Interface (Calculated from Measurements)</td>
<td>75%</td>
</tr>
</tbody>
</table>

Finally, Figure 5.13 shows the temperature distribution across two orthogonal line scans of LWIR camera data from the TBC surface. The hottest reading was again about 1% above the pyrometer reading, and the variance across the middle 50% of the coating is less than 5%. However, there was a significant temperature drop towards the edge of the TBC coupon, up to 20% of the front surface setpoint temperature. The in-plane temperature gradient would complicate any effort to model the stresses within the TBC during testing. Reducing the in-plane gradient, possibly with a sample holder re-design, became a future design goal.

![Heat map with line profiles across TBC surface (a) and temperature distribution (b)](image)
5.3.4 Validation of Spritzing Strategy

One critical concern for the spritzing of the liquid precursor solution was that it not wick into the coating during cycling. Such wicking would allow for CMAS contaminants to essentially be deposited below the surface of the sample, leading to unrealistic penetration. It would also evade the formation of CMAS-blocking and sealing layers in reactive TBCs, reducing their apparent CMAS durability. To prevent wicking, the solution was sprayed onto the TBC when the surface temperature was at least 300 °C to promote flash boiling. To check that the solution flash boiled without wicking in, an APS YSZ test coupon was cycled in the rig in the following way. During the heating cycle, the torch was moved under the sample and left at a minimum power output for the whole heating cycle, six minutes. CMAS spritzing occurred in the normal fashion (see Section 5.2.2), and the cooling cycle was unaltered. The surface temperature history during one minimum power heating cycle can be seen in Figure 5.14. The sample was cycled 120 times in this fashion, then mounted in epoxy and sectioned for analysis.

![Figure 5.14 Temperature history of sample cycled at minimum torch power](image)

The micrographs in Figure 5.15 show that a relatively thick (up to 40 microns), conformal layer of CMAS formed on top of the ceramic; higher magnification reveals that this material did not penetrate into the intersplat cracks of the APS coating. This indicated that, regarding depositing CMAS only on the surface of the sample, spritzing appeared to be a valid deposition
strategy. In the higher magnification image at right, one can also observe distinct strata in the CMAS layer. This is likely due to the incremental dosing, adding thin layer upon thin layer of CMAS, which also suggests that the CMAS did not melt at all during this experiment.

![Images of CMAS layers](image)

*Figure 5.15 CMAS coats the surface of the sample (a) but does not wick into the cracks (b)*

These results allow for an approximation of the deposition efficiency of the CMAS spritzer as well. Assuming the nitrates fully decomposed to oxides (which might not be the case for calcium, potassium, and sodium nitrates [112]), with a density of ~2 g/cm³ and complete coverage of the TBC surface, the CMAS layer would weigh about 40 mg. The total CMAS content of 120 spritzes would be about 550 mg, so the deposition efficiency of the CMAS spritzer is on the order of 7%. This might be different if the CMAS were fully melted and reacted with every cycle, and this might also be different for different coating systems. It is reasonable to expect that the surface roughness of the TBC would have an effect on the adhesion of early CMAS, until a continuous layer of CMAS is developed.

### 5.4 Initial Test Results on the Gradient Rig

Based on these parameters, TBC coupons showed a characteristic failure mode and morphology from thermal cycling with CMAS attack. For a number of cycles, the sample would
accumulate CMAS without any evidence of damage. Then, shallow, localized pitting of the coating would occur, as seen on the APS YSZ coupon in Figure 5.16. Once exfoliation began, a coating was progressively removed with every cycle. Curiously, these small spallation events would always occur during the ramp to temperature, which contradicts the standard understanding of TBC failure explained by the Evans-Hutchinson Model.

The cross-section of the damaged APS YSZ TBC coupon in Figure 5.17 also showed some unexpected features. The dashed line indicates the deepest penetration of CMAS into the TBC coupon, which was not very uniform, even over small areas. Second, the spallation occurred at a very shallow depth, only about 10% coating thickness. Examining the spalled and spalling material revealed some retained CMAS and a little evidence of chemical interaction between the YSZ and CMAS. However, since the residual CMAS was shed along with these thin lamella of TBC, there was little chance for it to further penetrate or interact with the coating. The thin
delamination depth, little accumulation/interaction before failure, and especially the failure on heating were not representative of the expected failure mode, both theoretical and seen in engines.

Figure 5.17 Cross section of failed sample (a) and enlarged view of surface (b)

5.5 Results of Finite Difference Modeling

One possible explanation for the spallation observed would be if a significant, non-linear transient thermal gradient were to develop in the ceramic. The thermal stresses associated with such a thermal gradient can be quite severe. In order to model the transient temperature distribution through the TBC coupon, the explicit finite difference code described in Section 3.5 was implemented. The boundary conditions used were the front and back time-temperature history of a TBC sample run using the cycle shown in Figure 5.6.

Examining the temperature history during heating, the fastest heating occurred at about 14 seconds into the cycle, with a value of approximately 100 °C/s. Figure 5.18 shows the modeled temperature distribution through the TBC coating (x = 0 at the surface) at several time points during this most rapid heating. The thermal gradient appears to remain very linear as the surface temperature increases. Therefore, it appears that, under these conditions, the heating rate is still low enough for the steady state solution to dominate the time-dependent temperature distribution.
Another way to visualize the TBC’s ability to develop a non-linear thermal gradient is to impose a jump in surface temperature in the model, then see how long the gradient takes to become linear. As Figure 5.19 shows, even with an instantaneous jump of 100 °C, the temperature distribution becomes essentially linear within 0.1 seconds and stays linear as the coupon approaches equilibrium. For comparison, the maximum temperature increase between 0.1 second time steps for the actual sample was on the order of 10 °C. Despite the low thermal diffusivity of the coating, the coating is so thin that it cannot sustain non-linearities for any appreciable amount of time. For this reason, it was determined that these non-linearities were not the culprit behind this undesirable failure behavior.

Figure 5.18 FDM temperature distributions through the TBC during the fastest heating rate

Figure 5.19 FDM temperature distributions through the TBC with an artificial temperature jump
5.6 Thermally Sprayed CMAS as Novel Deposition Mechanism

5.6.1 Thermally sprayed CMAS

Another hypothesis behind the observed failure during heating was that the precursor solution was introducing some sort of spurious damage mechanism, either from the thermal shock of spraying described earlier or the thermal decomposition of the nitrates on heating. In order to decouple the precursor evolution from the thermal cycling of the sample, deposition of CMAS using the SPPS process was developed. By injecting the precursor solution into a plasma torch, the solvent evaporation and thermal decomposition processes occurred off of the surface of the TBC. Ideally, the CMAS is also heated to a molten or semi-molten state in the plasma plume, allowing it to impact on the TBC surface in manner much more analogous to the actual engine.

Using the SPPS process, a thin layer of CMAS was deposited onto APS YSZ TBC coupons. The spray parameters used are shown in Table 5.2. During deposition, the TBC overspray on the coupons flaked, making weight measurements of the CMAS coating inaccurate. Thus, the CMAS deposition efficiency of this process was not measured.
Table 5.2 Spray parameters for thermally sprayed CMAS

<table>
<thead>
<tr>
<th>Plasma Gun</th>
<th>Metco 9MB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gun Nozzle</td>
<td>GP</td>
</tr>
<tr>
<td>Plasma Current/Voltage (V)/(A)</td>
<td>650/70</td>
</tr>
<tr>
<td>Feedstock</td>
<td>1 wt% CMAS-1 Precursor Solution</td>
</tr>
<tr>
<td>Delivery System</td>
<td>SPPS Delivery System with BETE Fog Nozzle (FC4/AC1501 Fluid/Air Caps)</td>
</tr>
<tr>
<td>Feed Rate</td>
<td>55 mL/min</td>
</tr>
<tr>
<td>Scan Speed (mm/s)</td>
<td>450</td>
</tr>
<tr>
<td>Scan Width (mm)</td>
<td>400</td>
</tr>
<tr>
<td>Raster Size (mm)</td>
<td>3</td>
</tr>
<tr>
<td>Gun Standoff (mm)</td>
<td>44</td>
</tr>
<tr>
<td>Preheat Passes</td>
<td>5</td>
</tr>
<tr>
<td>Coating Passes</td>
<td>25</td>
</tr>
</tbody>
</table>

The surface view and cross section of the CMAS coating on APS YSZ TBCs are shown in Figure 5.20. The surface view indicates that the CMAS formed a continuous layer over the TBC surface. The cross section shows that the coating was conformal; relatively thin, about 10 microns, and slightly porous with the occasional thick and densified layer over coating asperities. Assuming the layer was fully dense, and with a glass density of about 2.5 g/cm$^3$, the CMAS load would be 12.5 mg, or 2.5 mg/cm$^2$. This loading would be expected to cause observable coating degradation, but not spallation [113].
To determine what phases formed during the SPPS process, CMAS-precursor solution was sprayed onto a large steel plate, then scraped off with a razor blade. The X-ray diffraction pattern, shown in Figure 5.21 indicated that the material was largely amorphous, although there was evidence of calcium sulfate precipitation, similar to the dried precursor solution in Section 4.2.3. The source of the iron peak is most likely flakes from the steel plate removed during scraping.
5.6.2 SPPS CMAS Samples on the Gradient Rig

A TBC coupon with SPPS CMAS was placed in the gradient rig and run with the same thermal cycle as earlier. During the test, there was no damage observed after the first thermal cycle was complete. However, when the torch ramped up for the second heating stage, there was sudden, energetic, and extensive spallation across the coating surface, as shown in Figure 5.22. Visually, the spallation was similar to the gradual exfoliation observed previously; it simply happened all at once and with more velocity.
The cross section of the failed sample (Figure 5.23) revealed results very similar to the previously cycled sample. The spallation was similarly shallow in most places, although there was occasionally a deep delamination to about 40% coating thickness. Most of the CMAS remained on the surface, although there was evidence of some shallow penetration. Given the short hot time allowed by this experiment, the chemical interaction between the CMAS and the TBC were expectedly minimal. Based on these findings, the liquid precursor spray was determined to not be the root cause for failure on heating.

To better understand the state of the coating just before a second heating would cause failure, a second sample with SPPS CMAS was cycled only once. The cross section in Figure 5.24 showed only minimal cracking in the coating. Occasional vertical channel cracks had formed and
filled with CMAS; these are important failure initiation sites for subsequent delamination [37]. Again, due to the very short hot time, there was minimal penetration into the coating and little to no chemical interaction between CMAS and ceramic. But the key finding in this test was to contradict another hypothesis for the observed failure during heating. It had been proposed that the majority of cracking was occurring during cooling, but that the ceramic was still loosely adhered. Then, subsequent heating from the torch simply knocked this loose material off. But the cross-sectional microstructure clearly shows that the coating was still quite intact after cooling. The damage must occur during heating.

Figure 5.24 Cross section of interrupted test shows little damage (a), only the occasional channel crack filled with CMAS (b)

5.7 Rationalization of Results

After multiple hypotheses were rejected, the following hypothesis, illustrated in Figure 5.25, was proposed. Upon initial heating to operating temperatures, the TBC and the substrate relax and become essentially stress free. On cooling, the thermal contraction of the superalloy substrate is imposed on the thin ceramic coating. Because the CTE of the superalloy is higher than the ceramic top coat, the ceramic is put into compression.
When the coupon is subsequently heated, there are several possibilities. If the heating is slow and the transient thermal gradient small, the expansion of the substrate will begin to unload the ceramic. If heating is very rapid, then the temperature of the ceramic will climb rapidly compared to the substrate, which will then impose further compression on the ceramic. If this excess compression is too large, then the coating can experience spallation buckling; the energetic nature of the coating loss observed, especially with the SPPS CMAS samples, did suggest a buckling mode.

![Figure 5.25 Rationalization for spallation on heating](image)

One difference between the test rig and the engine is that, in the engine, the “cooling” air fed through turbine components is siphoned from the compressor. It has been adiabatically compressed, dramatically increasing the temperature. So, as an engine spools up, a room temperature TBC-coated component is going to be heated by the “cooling” air from the compressor, as well as the hot gases coming from the combustor. Comparatively, the cooling air on the test rig is at approximately room temperature. This realization, that the backside cooling air is not actually cool, was a critical insight in enabling forward progress for this test rig and project.
5.8 Rig Modifications

Based on this hypothesis for failure on heating, several modifications to the rig were made. First, the rig and test cycle were altered to minimize the transient thermal gradient during heating. One enabling feature was to vary the propane-oxygen ratio throughout the thermal cycle. The torch requires a minimum propane flow rate to maintain a flame that does not damage the torch face or self-extinguish. But, since the test rig uses a surface-mix torch, it was possible to significantly overblow the oxygen without extinguishing the flame. In this way, the torch could be operated far away from its intended flame profile to create a weak flame that barely impinged on the sample. The two extreme flame shapes are shown in Figure 5.26. Between these, the propane-oxygen ratio was varied in such a way as to allow the control system to follow a 2 minute ramp to temperature with fairly successful fidelity, as can be seen in Figure 5.27. Note that now the maximum gradient occurred just before the surface temperature reached the steady state value. The maximum gradient was also roughly 70% of its previous value (during the ramp), depending on sample type and test condition.

Figure 5.26 Maximum flame output with standard stoichiometry (a) and with oxygen overblown flame (b)
Figure 5.27 Representative thermal cycle with minimized transient gradient

5.9 Modified Results

After the physical and operational modifications, there were significant differences in the failure mode and morphology of TBCs, especially APS YSZ. As Figure 5.28 shows, spallation was much deeper, occurring very near the bond coat in some locations. Looking at the cross section, coating loss was up to 95% of the coating, delaminating just above the bond coat.

Figure 5.28 Sample failure surface after modifications (a) and cross section (b)

Comparing more intact sections of coating with the initial testing efforts (Figure 5.29a and Figure 5.29b) showed a similar CMAS penetration depth, about 40% of the coating thickness. It is reasonable that the penetration depth should be unchanged: given sufficient CMAS, the
penetration depth should be most strongly a function of the thermal gradient across the sample, which was unchanged. However, the penetration appeared more uniform, i.e. the TBC porosity was more completely filled down to that depth. Also, Figure 5.29c shows that there was greater chemical interaction between the CMAS and TBC in the modified testing compared to the previous work with excessive gradient. Another crucial observation was that failure was no longer occurring during the ramp to temperature. Material was observed to crack during cooling. Other times, material would fall off just as the low power torch moved over the front of the sample. However, this form of spallation appeared very different from the prior damage on heating. First, the spalled material was much thicker than the earlier, shallow delaminations. Second, these pieces were observed to drop down from the surface, whereas the earlier TBCs had material violently eject from the surface. These characteristics suggest that, instead of spallation buckling, these failures were of severely damaged material having their last connections broken by the relatively minor thermal shock of the weak flame. Feedback from the engine manufacturer suggested that these results were more in line with engine experience, a critical project milestone.
5.10 Discussion: Comparison between GTE and Rig Environments

There are several differences between the environment of a gas turbine engine and the rigs that have been developed to test TBCs; however, steps have been taken to minimize the potential problems arising from those differences. The numbers below have been taken from a NASA report on a DC-8 aircraft with four CFM56-2 engines at cruise [86]. First, the pressure ratio of the engine is 28:1 compared to the pressure ratio of approximately 1:1 on the rig. This, paired with the higher
gas velocities in the jet engine, means that the Reynolds number of the combustion gas in the engine is significantly higher than that of the gas on the rig. The higher Reynolds number leads to greatly increased heat transfer to the TBC in the engine. We partly mitigate this by using an oxy-propane flame (adiabatic flame temperature 2526 °C), which greatly increases the flame temperature compared to the engine (~1050 °C).

The other key difference, and what led to the modifications to rig operation and improved test outcomes, was the realization that engine cooling air was not cool. The high pressure compressor discharge air for the CFM56-2, which runs through the cooling channels of the high pressure turbine, is approximately 400 °C. And since the compressor is necessarily running during engine spool-up, the “cooling air” will preheat turbine components and reduce the thermal gradient across them. And so, despite the high heat transfer of the combustion gas leading to rapid heating, the thermal shock experienced by the TBC is minimized. Since it was not feasible to heat the backside cooling air on the test rig, the decision was made to reduce the thermal shock during sample heating. This was accomplished by reducing the thermal gradient during heating. There would be great value in modeling the transient stress distribution in the TBC sample during heating on the rig and comparing it to that of engine components. This would allow for better refinement of the rig operating parameters to more closely match those of the jet engine. Unfortunately, the details necessary to model the engine in such detail are typically proprietary.

5.11 Summary of Findings

From the first generation thermal gradient rig, the following key discoveries were made:

1. Modeling the transient one-dimensional temperature distribution suggests that the temperature gradient remains essentially linear throughout the heating cycle.
2. Pyrometer temperature measurements of TBCs are independent of viewing angle up to about 40°.

3. When utilizing a low velocity torch, the temperature stability is greatly improved by orienting the torch vertically to take advantage of buoyancy forces, rather than fight against them.

4. Attempting to replicate the rapid heating in an engine results in excessive transient thermal gradients, leading to coating spallation during heating. According to the engine manufacturer, this was not like failure modes observed in engine service. The excessive gradient is primarily due to the fact that engine cooling air is several hundred degrees above room temperature.

5. Lowering the heating rate removed the spallation during heating, which was enabled by controlling the fuel and oxygen ratios independently.

6. Greater testing throughput was enabled by cycling two samples on the same torch, but more importantly by designing a robust safety and monitoring system to allow for unattended testing.
6 SECOND GENERATION GRADIENT RIG

6.1 Construction

6.1.1 Improvements from First Generation Rig

Based on the promising results derived from the first generation gradient rig, the engine manufacturer requested the development of a second generation gradient rig with enhanced capabilities and testing throughput. After a second iteration of design and construction, the major components of this rig can be seen in Figure 6.1. The improvements to the original rig design (described in detail below) are:

1. Commercial thermal spray torches engineered to melt and deposit oxide powders
2. Modular construction to facilitate maintenance and repair, and minimize downtime
3. Design and construction of a uniquely low-flow powder feeder
4. Independent control of heating and cooling at each of six sample positions to minimize thermal variations between those positions
5. Utilization of a blackbody calibrator to add custom calibration curves to each pyrometer reading, increasing measurement accuracy
6. Improved sample holder to reduce in-plane thermal gradients on the TBC coupon

Over 100 purchase orders for hardware and a complete renovation of the surrounding lab space were necessary to execute this rig development, speaking to its complexity.
Many of the changes between the first and second generation gradient rig can be seen in Figure 6.1 above. A fundamental difference between the rigs is the replacement of the single glass-working torch with multiple combustion thermal spray torches (6P-II, Oerlikon Metco). These torches are engineered for the coaxial feed and deposition of thermal spray powders. This allows for the deposition of molten and semi-molten CMAS powder onto TBC coupons, replacing the previously used chemical precursor solution. These torches also have about three times the heat flux capacity of the torch on the first generation rig. Metco manufactures hardware to operate these torches on several gases, including propane. In the photograph, two of the three planned torches are installed; each torch shuttles between two sample positions, so the rig can test up to six samples simultaneously.

Similar to the first generation rig, all of the control electronics are separated from the test stand, keeping them well away from the heat, flames, and dust generated during testing. Given the increased number of components and complexity of the multiple torch configuration, the control hardware was constructed in modular boxes, which were then installed on a server rack.
along with the control computer and security DVR (Figure 6.1b). This allows for easier replacement of individual components when they need repair or recalibration.

An increased number of safety interlocks were added to the system as well. With three torches running, an optical flame-out detector could not practically be used to detect when one torch was extinguished. The steel enclosure too effectively reflects ultraviolet radiation (which the optical detector senses). So individual gas-ionization detectors were placed on each torch. A flow sensor was placed in the ventilation duct to ensure that the ventilation system is always on when the rig operates. This rig also incorporated a digital heartbeat signal which was connected to a timing circuit. If the computer or the control software were to freeze or unexpectedly end, the rig would shut down. Finally, similar programmatic safety checks were implemented, including sample temperature overheating or underheating and failure of gas flows to reach set values.

The system required a powder feeder for the flow of CMAS powder through the thermal spray torches. Commercial systems are typically designed for much higher mass flow rates of material than are desirable for this CMAS dosing application. Therefore, a custom powder feeder was developed based on a fluidized bed principle (Figure 6.1c). The feeder is designed for independent flow and metering control for each torch. While conventional powder feeder systems are designed for mass flow rates on the order of pounds per hour, this feeder is designed to operate in the regime of 0.1 pounds per hour or less.

Rig control and data acquisition were once again fully automated using LabView hardware and software. Each torch and cooling nozzle is independently controlled and metered, which means the rig has the capability to perform six different thermal cycles with or without CMAS. This also means that thermal variations between sample positions can be minimized by compensating the torch power and cooling air flows. Possible sources of variation include
differences in convective and ventilation air flow around samples in different positions or in the heat flux between the torches for a given gas flow.

Another improvement was facilitated by the purchase of a blackbody calibrator (M330, Lumasense), which allowed for the independent verification of the accuracy of the LWIR pyrometers (OS550a Series, Omega Engineering). It was discovered that the accuracy of internal calibration on some of the pyrometers was less accurate than the stated ±1% of reading, so correction factors for each pyrometer were added in software to improve the accuracy of the temperature measurements.

Based on the desire to reduce the in-plane gradient across the TBC coupon during testing, a new sample holder design was also implemented, as seen in Figure 6.2. The key feature for reducing the gradient across the sample face was to bring the sample either flush or slightly proud with respect to the surface of the sample holder. This was achieved by resting the sample on the heads of three alumina bolts (Ceramco). As in the first generation rig, the front plates are made from Haynes 214, while the back plate is Haynes 230. To further thermally isolate the sample, the middle layer of the sample holder is a flexible alumina refractory mat (APA-1, Zircar). The sample is slightly pressed into this refractory, ensuring that the back side cooling air does not wrap around the sample and interfere with the flame.
6.1.2 Advanced Infrastructure and Lab Space

The increased capability of the new rig necessitated greatly increased laboratory space and infrastructure; these were not readily available on campus. Therefore, roughly a year of effort went into developing a vacant and distressed laboratory space for the supply and operation of this second generation gradient rig (Figure 6.3). Based on the demonstrated utility of oxygen concentrators on the first generation rig, an industrial-grade oxygen concentrator was purchased and installed (AS-G, AirSep), as well as a high purity air compressor and refrigeration drier (BSD-50T, Kaeser). This compressor supplied air for both the oxygen concentrator and the rig itself for cooling air flow, CMAS powder carrier gas, and pneumatic actuators. A new, 1000 gallon propane tank was installed outside due to the increased consumption from three torches. However, when the ambient air temperature drops below about 20 °F, the vapor pressure of propane drops below the minimum supply pressure necessary for this rig, about 40 psig. To allow the rig to operate regardless of weather, a flameless tank heater was installed (Second Sun, Algas-SDI). To bring the room up to building code, make-up air was also added to replace the air extraction from the test enclosure, which was also a custom construction. The routing for the supply of electricity, propane, oxygen, compressed air, and make-up air in the renovated laboratory space were all designed specifically for operation of this rig.
6.2 Preliminary Performance

6.2.1 In-plane Gradients

The in-plane gradient across the TBC coupon with the new sample holder design was measured in the second generation gradient rig using an LWIR Camera (T650sc, FLIR). The results can be seen in Figure 6.4. Compared to the 20% drop in temperature at the edges of the sample in the first generation rig (Section 5.3.3), the temperature variation in the new sample holder design is no more than 10% of the setpoint value. It should be noted that this image also demonstrates another utility of the thermal camera, namely the detection of misalignment between torch and sample. Some of the brightness at the right edge of the sample can be attributed to geometry, but the hot-spot on this sample is slightly off-center. Based on this observation, the
torch was re-aligned. Also worthy of note is the temperature distribution across the alumina bolt heads. The inner edges reach temperatures on the order of 300 °C above the sample temperature, and there is a considerable temperature gradient across the bolt head. The long term durability of these alumina bolts is one design challenge that remains for the continuous, unattended operation of this rig.

![Figure 6.4 Heat map with line profiles across TBC surface (a) and temperature distribution (b)](image)

**Figure 6.4** Heat map with line profiles across TBC surface (a) and temperature distribution (b)

### 6.2.2 Initial CMAS Deposition Test

Initial validation tests of the CMAS powder feeder were performed by depositing AFRL-03 onto an EBPVD YSZ TBC coupon in the rig. Refer to Section 3.2.2 for composition and Section 4.2 for characterization of the AFRL-03 powder. The TBC coupon was heated to approximately 50 °C above the AFRL-03 melt point. The sample was held at temperature for 3 minutes, the CMAS feeder was run for 1 minute, then the sample was held at temperature for another 4 minutes. After the sample cooled, it was observed that there was some localized TBC spallation, making a weight gain measurement impossible.

The surface microstructure of as-deposited EBPVD YSZ was compared with the sample with CMAS on the surface (Figure 6.5a and Figure 6.5b, respectively). CMAS completely covered the surface of the TBC out to about 50% of the sample radius (Figure 6.5c), then tapered off to
near-zero at about 75% of the sample radius. The coverage appeared fairly uniform in all directions. The CMAS material appeared to be partially melted, although many grains of rough, fractured material were still evident. Where the coverage is less complete, wetting and penetration into the columnar structure was observed, as can be seen in the lower left quadrant of Figure 6.5c (boxed-in area).

![Figure 6.5 Surface micrographs of as-deposited EBPVD YSZ (a), EBPVD YSZ coupon with complete CMAS coverage near the center (b), and incomplete coverage at 50% radius (c)](image)

Analysis of the cross section of the sample (Figure 6.6) elaborated on these observations. The CMAS layer was composed of large agglomerates of CMAS material only partially adhered to the surface. These “feet” wetted the TBC surface and allowed for much larger amounts of less
molten CMAS material to stick to the coating. This wetted material was able to penetrate about 100 microns into the coating, as observed by EDXS (Figure 6.7).

Figure 6.6 Cross section of TBC sample with CMAS on surface

Figure 6.7 Elemental maps of zirconium, calcium, and silicon near TBC surface
One important observation is that the agglomerates on the surface were quite heterogeneous, again illustrated with EDXS of one agglomerate in Figure 6.8. The silica-rich regions had sharp, linear edges, and thus presumably are mostly un-melted silica. The middle of the particle, rich in calcium and magnesium, exhibit a lamellar structure, which may indicate decomposition into calcium and magnesium carbonates or oxides. The outer edges of the particle were smooth and rounded, suggesting a greater degree of melting. These were also the locations with the highest sodium content, suggesting that the alkaline elements acted as fluxing agents. This early-melting material would help explain the degree of agglomeration of the CMAS particles, as well as how large, un-melted particles adhere to the TBC surface.
The deposition of a chemically heterogeneous and partially molten CMAS is significant because, in the real world, jet engines do not deposit a pre-homogenized, uniform layer of CMAS onto components with TBCs. With the exception of volcanic ash [114], CMAS-forming contaminants are mostly composed of a mix of minerals, not glass [115]. When ingested into the engine, the low-temperature melting material is going to assist in the adhesion of other particles, which will take more time to melt. Therefore, chemical interactions between the TBC material and CMAS are going to have some time component. That is, the chemistry of the CMAS melt is going to evolve with time. This has direct implications for designing reactive TBC materials and
for understanding the kinetic race between CMAS penetration and reactive formation of blocking phases.

6.3 Discussion: Challenges of Accurate Temperature Measurement

Since a ~25 °C temperature decrease or increase at the bond coat roughly doubles or halves baseline (no CMAS) TBC life, even small errors in temperature measurement could have profound effects on measured TBC performance. This is even more of a concern when comparing the performance of different coatings: a coating tested at an erroneously low temperature will survive longer than expected. This could even invert ranking results, a costly mistake for engine manufacturers. Therefore, is important to understand potential sources of error in the measured temperature of the TBC.

As discussed in Section 5.3.2, the pyrometers on the rig are physically sensing the intensity of the incident radiation on the sensing element, which is converted to temperature using the basic Stefan-Boltzmann equation (6.1).

\[ I = \sigma \varepsilon \left( T_{surf}^4 - T_{surr}^4 \right) \]  

(6.1)

One source of error in this measurement is the fact that the pyrometers view the TBC surface through the flame. Assuming complete combustion, the two species in the flame are water vapor and carbon dioxide. The infrared absorption spectra of these two compounds can be seen in Figure 6.9 [116], with the vertical dashed lines corresponding to the spectral response band (8-14 \( \mu \text{m} \)) of the pyrometers used on both rigs. While both CO\(_2\) and H\(_2\)O spectra are minimized within this range, there is significant absorption, especially at the edges of the spectrum band. Of course, because the combustion products are hot, the gas is also emitting infrared radiation in this range. Therefore, the flame is both absorbing some of the signal from the sample and emitting some signal of its own.
This flame contribution was imaged using an LWIR camera (T650sc, FLIR) during the heating cycle on Rig 1 (Figure 6.10). In the left image, ten seconds into the heating cycle, the flame is clearly visible as the purple plume rising from the bottom of the image to engulf the sample holder. The right image, showing the exact same area at the same magnification, comes from two minutes into heating cycle. Once the sample holder has heated up, the flame becomes very difficult to see, even while watching video. This is likely because the flame is a gas at standard pressure, and thus relatively diffuse. The number of gas molecules between the thermal camera and the sample holder, and thus the material available for generating signal noise, is orders of magnitude smaller than the sample holder itself.

Figure 6.10 False color thermal images of rig heating at 10 seconds (a) and 2 minutes (b)
However, in the interest of minimizing the temperature error wherever possible, the flame contribution to temperature measurement can be removed by means of a blackbody calibrator. The pyrometer would be set up to sight into the blackbody cavity, through the flame, as illustrated in Figure 6.11. By first establishing the baseline calibration without the flame, the effect of the flame could be accurately measured as the deviation from the baseline temperature. The flame intensity could be varied through the full operating range of the test rig to create a correction curve based on the current torch setting. This correction would then be applied in software.

![Figure 6.11 Experimental setup to measure flame contribution to temperature measurements](image)

Another source of error in pyrometry comes from uncertainty of the emissivity of the coating. Most pyrometers use a single value for emissivity in converting intensity into temperature. However, the emissivity of the TBC is both a function of wavelength and temperature, and emissivity of an actual coating will, to some degree, be a function of the surface condition (e.g. roughness). Beyond that, the emissivity of the TBC surface will certainly change due to the accumulation of contaminants on the surface, such as CMAS. The emissivity of new coating materials, such as GZO, have not been characterized as well as YSZ in the literature. Markham et al. describe a test rig to measure the emission spectra of a sample at varying temperature [117]. Such a rig could be used to measure the emissivity of new TBC systems, as well as how thermal cycling and CMAS affect the emissivity.
With all of these potential pitfalls, one might despair of any chance for temperature accuracy. However, as equation (6.1) shows, the calculated surface temperature is proportional to the fourth root of the measured intensity (assuming $T_{\text{surr}}$ is small compared to $T_{\text{surf}}$). Therefore, a 5% error in the measured intensity results in only a 1.3% error in temperature. Likewise, a 25% error in intensity is a 7% error in temperature. The same relationship holds for the assumed emissivity. Thus, the physics of radiation somewhat mitigates the difficulties of temperature measurement.
7 **SECTION 7 – EXPERIMENTAL FINDINGS ENABLED BY GRADIENT RIG TESTING**

With the creation and operation of these thermal gradient rigs with simultaneous, incremental CMAS dosing, there are countless practical, engine relevant questions that may be explored through experimentation. Below, we present two avenues of inquiry that were begun as part of this thesis work. While the results are preliminary, important fundamental conclusions can be drawn. These results need to be replicated and expanded, which will be done in ongoing work.

### 7.1 Dose Rate Dependence

#### 7.1.1 Motivation

For engine and TBC manufacturers, a method for modeling the expected loss of coating life due to CMAS attack has become critical, because TBCs are now a prime-reliant component in the engine. The expected life debit is going to have distinct geographical variation, given the difference in chemistry and concentration of contaminating materials around the world. Indeed, these are two critical parameters that would go into such a life-debit model. Regarding the CMAS concentration, researchers identified a critical dose of CMAS to cause significant damage in one TBC system [113], although this was done under isothermal conditions. However, questions remain regarding the effect of the thermal gradient and incremental accumulation of CMAS. The results that will be shown in more engine relevant (i.e. in a thermal gradient) testing, though preliminary, clearly show that there was not a critical dose to cause failure.

In the absence of CMAS, TBC life is typically a function of TGO growth. As the TGO increases thickness, it can lead to cracking in the ceramic and/or an increase in the stored elastic energy, depending on the coating system. Given sufficient cracking or accumulated elastic energy, the coating fails. On the other hand, a sudden, massive dose of CMAS (see Figure 1.3) will
penetrate uniformly to a depth dictated by the thermal gradient and CMAS melt properties, and failure is determined by the cooling trajectory, as described in the Evans-Hutchinson model. Between these two extremes, we seek to explore how these two failure mechanisms interact, which has never been reported. Is failure a race between two independent mechanisms? Or do the two mechanisms work together, i.e. stiffening of the CMAS-penetrated ceramic causes bond coat oxidation failure to occur sooner? No other researchers have performed an experiment like this, as very few have the necessary equipment.

7.1.2 Experiment

As a preliminary foray into this question of dose rate dependence, the following experiment was carried out on the first generation thermal gradient rig using EBPVD YSZ TBC coupons. First, a baseline sample was cycled to failure in the first generation gradient rig at a surface temperature well above the melting point of CMAS. Then, samples were thermally cycled and spritzed with increasingly dilute concentrations of CMAS precursor solution. Because the liquid volume of the precursor solution spritz remained constant, dilution directly lowered the CMAS dose rate. Initial testing had been carried out using 1/2 wt% CMAS solution, which had resulted in full life testing that could be completed in a number of days. This was therefore used as the upper concentration limit. Samples were cycled to failure using solutions of approximately 1/2%, 1/4%, 1/8%, and 1/16% concentrations. Failure was defined as greater than 50% spallation of the top coat down to visible bond coat.

Reduced CMAS dosing per cycle was carried out by dilution, rather than reducing the time the spritzer was activated, for a number of reasons. First, the amount of solution sprayed was not a linear function of spritzing time, and thus attempting to dial in the correct amount of spray for each dose rate would have required time-consuming trial and error. Second, the interaction
between the liquid spray and the hot TBC surface is an incredibly complex phenomenon. Changing the amount of CMAS solution spritzed during each cycle would thus have introduced undesirable variables into the experiment. Given that even the most concentrated solution was ~99% water, it was assumed that each solution had essentially the same physical properties, leading to the same interaction with the TBC surface on impact and vaporization.

7.1.3 Results and Discussion

The TBC life of the sample under each condition can be seen in Figure 7.1a, normalized to the baseline, no CMAS life. The mass of CMAS sprayed on each sample at the time of failure, Figure 7.1b, is normalized to the 0.5% CMAS concentration experiment.

![Figure 7.1](image)

*Figure 7.1 TBC life as a function of CMAS dose rate (a), and the total amount of CMAS sprayed at the TBC sample at the time of failure (b).*

The most salient feature of this data is the fact that reducing the CMAS dose rate in half did not double the life, as one would expect if the predominant driver of failure were reaching a critical dose of CMAS. Indeed, as Figure 7.1b shows, the total amount of CMAS sprayed at the sample before failure decreased by a factor of 5 as the CMAS concentration decreased. If a critical dose mechanism were dominant, then one would expect the trend line in Figure 7.1b to be relatively flat. It is possible that such a regime may exist at significantly higher dose rates, where the cyclic lives are only a few dozen cycles. While tests were not repeated at each dose rate, the fact that the trend was monotonic supports the conclusion that there is not a critical dose rate.
Because all the samples analyzed were cycled to failure, one cannot fully describe the failure mechanisms operating over the life of these samples. Microstructural analysis of the samples post-spallation does not tell the complete story. However, several trends may be observed when examining the TBC cross sections near the failure zones (the baseline, no CMAS sample was not analyzed because no TBC remained on the substrate after cycling). The micrographs in Figure 7.2 show the whole coating thickness and the bond coat for each of the samples cycled with CMAS. In each case, the top coat has spalled from the TGO, and the TGO has separated from the bond coat to some degree as well. The columnar microstructure of the YSZ grains has remained relatively intact; there are few, if any, lateral cracks running through the ceramic. These features suggest that the underlying failure mechanism, stress overload in the TGO, remained the same over this dose rate regime.
Figure 7.2 Cross section of TBC samples at the edge of the spalled region for 1/2% CMAS (a), 1/4% CMAS (b), 1/8% CMAS (c), and 1/16% CMAS (d).

The interaction between CMAS and the ceramic at the column tips, shown in Figure 7.3, shows very different morphology between test specimens. For the 1/2% CMAS sample in Figure 7.3a, much of the CMAS appears to have remained on the surface, separating into two phases. EDXS analysis shows that, away from the column tips, the darker contrast phase is relatively pure silica, while the lighter contrast phase contains the other constituents of AFRL-03. The material on the surface of the column tips contains the CMAS constituents and significant quantities of zirconium, on the order of 30 cation mol%. It appears that this phase built up in the column gaps,
preventing extensive CMAS penetration. The CMAS on top may have acted as an insulating layer, given how little degradation of the column tips is evident. This is in stark contrast to the 1/4% CMAS sample in Figure 7.3b, where the column tips are severely degraded. The small bright contrast particles on the surface are re-precipitated zirconia, confirming that the CMAS actively melted the column tips. The fact that the 1/2% and 1/4% samples had very similar cyclic lives means that this was due to increased hot time. The 1/8% CMAS sample in Figure 7.3c still shows strong column degradation, but the tips are still fairly well defined. It is at this point that the lesser quantity of CMAS over the life of the sample (only ~25% as much CMAS sprayed compared to the 1/2% CMAS sample) is likely beginning to limit the chemical damage that can occur, especially since the overall cyclic life did not change greatly. Finally, the 1/16% CMAS sample shows more tip degradation than the 1/8% sample. It seems likely that, given the ~50% longer cyclic life and roughly 60% less CMAS, this greater damage is due to a combined erosive effect of the CMAS weakening column tips and cycling causing shallow material spallation.
One caveat to this analysis is that, because these micrographs are from the remains of failed specimens, the exact location on the specimen is not the same in each case. The micrographs for the 1/4% and 1/8% samples are located ~2.5 mm from the sample center, while the micrographs for the 1/2% and 1/16% are located ~5 mm from the center. The in-plane gradient across the center of the specimen was shown to be less than 5% across the middle of the coating in Section 5.3.3, but the strong sensitivity of the CMAS viscosity to temperature will influence CMAS-TBC
interactions. Partial life, fully intact, specimens at several life fractions, as well as replicated tests to increase statistical accuracy would greatly increase the understanding of the mechanisms at play here.

To summarize, these results, while preliminary, are very suggestive of a complex mechanism controlling the life of the TBC. The fact that, with decreasing CMAS concentration, the cyclic life increased monotonically while total CMAS dose decreased, shows decisively that there is no fatal dose of CMAS in this concentration regime. Rather, the combination of thermal cyclic damage, TGO growth, and the stiffening effect of CMAS in the column gaps work in concert to cause TBC failure. To relate these results to the Evans-Hutchinson model, the toughness of the ceramic becomes a time- or cycle-dependent variable. As cycling damage and oxide growth increase, the effective fracture toughness of the ceramic decreases, and the stiffness of the CMAS penetrated layer increases. Thus, the CMAS penetration depth that would cause spallation would decrease. Adding this factor into the model is a first-order correction, without which the model would not be predictive for real engine results.

### 7.2 Comparison between Homogeneous Precursor and Heterogeneous Powder

#### 7.2.1 Motivation

As mentioned in Section 6.1.1, one advantage to the design of the second generation gradient rig is that it presents a unique opportunity for the deposition of heterogeneous CMAS during thermal cycling. This is important to understand the interaction between TBCs and real-world contaminants, which do not take the form of model eutectic compositions or pre-melted materials. Since much work in the literature has been carried out with such model CMAS compositions [68], [70], [72], [118], it is of interest to observe how the same CMAS composition
would interact with a TBC as both a homogeneous and a heterogeneous mixture. Of note is the difference in melt point between the CMAS constituents and the melt temperature of the homogeneous CMAS precursor. Table 4.3 shows these values for AFRL-03. The AFRL-03 powder had a similar melt onset temperature because calorimetry is performed in quasi-static conditions. Melting of the heterogeneous powder should require extra time because some interdiffusion between particles and/or dissolution into the melt is necessary to fully melt the CMAS. This could have direct impact on the understanding and design behind CMAS-resistant TBCs.

Table 7.1 Melt temperature for AFRL-03 constituents, powder, and dried precursor

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Nominal Chemistry</th>
<th>Melt Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>1705</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>2572 (decomposes to CaO &lt; 1200)</td>
</tr>
<tr>
<td>Aplite</td>
<td>SiO₂, KAlSi₃O₈ – NaAlSi₃O₈ – CaAl₂Si₂O₈</td>
<td>1260</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>2572 (decomposes to CaO and MgO &lt; 900)</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
<td>801</td>
</tr>
<tr>
<td>AFRL-03 Powder (Heterogeneous)</td>
<td>See Table 3.2</td>
<td>1196</td>
</tr>
<tr>
<td>AFRL-03 Precursor (Homogeneous)</td>
<td>See Table 3.2</td>
<td>1188</td>
</tr>
</tbody>
</table>

7.2.2 Experiment

In order to observe qualitative similarities and differences between homogeneous and heterogeneous CMAS attack on a TBC, the following experiments were carried out. First, two full life tests were run on APS YSZ TBC samples with CMAS attack. For the homogeneous CMAS, a sample was cycled on the first generation thermal gradient rig using AFRL-03 precursor. As was seen in Section 5.3.4, the precursor solution deposits a uniform material over the TBC surface. For the heterogeneous CMAS, a sample was cycled on the second generation rig using
AFRL-03 powder. Since the powder feeder shown in Figure 6.1 was not fully operational at the time, a commercial rotary powder feeder was utilized (AT-1200HP, Thermach). A fixed volume of powder is tamped into a hole within the feed wheel, which is then entrained into the carrier gas stream and fed into the thermal spray torch. This allows for a controlled dose of CMAS to be delivered with each thermal cycle. These two samples were run to failure, defined as 50% deep delamination over the coating surface. Because the CMAS dose rates between the two rigs could not be equalized, and due to differences in current sample holder design on the rigs, the cyclic life of the TBC on the two rigs is not directly comparable. But the target front surface temperatures were the same on both rigs, so the differences between CMAS-TBC reactions should not be a function of temperature.

Based on the life of the TBC coupon run to failure on each rig, a second sample was run to 40% coating life on each rig. Surface analysis, both XRD and SEM, of these partial life samples was done using the methods described in Section 3.1.1. Both the partial life and the full life samples were examined in cross section in the SEM.

7.2.3 Results and Discussion

Figure 7.4 shows the damage progression of the two TBC samples cycled to full life. In both cases, spallation occurred deep within the coating, near the TBC-BC interface, which was the expected failure mode. One difference between the two experiments was the size of a given spallation event. In the case of the heterogeneous CMAS, there were numerous, more localized spalls as the coating was effectively chipped away. In the case of the homogeneous CMAS, there were only two large spallation events that removed over 50% of the coating surface. At the time of writing, the precursor spray on the first generation gradient rig deposits CMAS more uniformly
over a TBC surface. For this reason, it is likely that the localization of failure on the heterogeneous sample can be attributed to local regions where more CMAS adhered to the TBC earlier in cycling.

In comparing the microstructure of the cross section of the full life samples cycled with heterogeneous and homogeneous CMAS (Figure 7.5 and Figure 7.6, respectively) several features are apparent. First, the micrographs confirm that both samples failed just above the TBC-BC interface. However, the heterogeneous CMAS sample also failed at an intermediate coating thickness. Closer examination reveals that this failure occurred just below the penetration depth of the CMAS (Figure 7.5b), so-called “level ii” delaminations [37]. Furthermore, there appears to be very little chemical interaction between the CMAS and the YSZ in the enlarged micrograph. Much of the CMAS remains on the surface, and the CMAS penetration is only detectible down to
about 150 microns. The lack of reaction is likely due to a relatively short hot time, on the order of 100 minutes. In contrast, the homogeneous CMAS, where the hot time was on the order of 500 minutes, CMAS penetration was much greater, up to the full thickness of the coating in some regions (Figure 7.6a). There were also more indications of interaction between the CMAS and the TBC throughout the thickness of the coating (Figure 7.6b).

Figure 7.5 Microstructure of full-life heterogeneous CMAS sample, showing full thickness and partial thickness delaminations (a); the intermediate delamination occurs just below the fully-penetrated CMAS depth (b)
Figure 7.6 Microstructure of full-life homogeneous CMAS sample showing through thickness delamination (a); there is distinct evidence of CMAS penetration and reaction (fine-speckled regions) throughout the coating (b)
Before microstructural analysis, the surfaces of the two partial (~40%) life samples were analyzed using XRD. Figure 7.7 shows the XRD patterns for as-received APS YSZ and the partial life samples with both homogeneous and heterogeneous CMAS. While there was some modification of the homogeneous precursor surface, the peaks are too small relative to the t’-YSZ signal to give clear evidence of any specific phase. However, the heterogeneous CMAS pattern shows a quite significant silica signal, as well as several minor peaks indicating the presence of an aplite phase. These two signals suggest that there is some quantity of un-melted CMAS adhered to the surface of the heterogeneous sample. The XRD pattern of the as-received AFRL-03 powder is shown in Figure 4.8a.

![Figure 7.7 XRD patterns for baseline APS YSZ, the partial life TBC coupon cycled with homogeneous CMAS, and the partial life TBC coupon cycled with heterogeneous CMAS](image)

The surface micrographs further corroborate this finding. While the surface of the homogeneous CMAS sample (Figure 7.8a) appears quite uniform, with morphology that is quite similar to the as-sprayed APS YSZ coating, the surface of the heterogeneous CMAS sample (Figure 7.8b) has been greatly modified. The two main features that one can see on this surface are discontinuous melt pools of CMAS (especially in the upper right-hand corner) and faceted
crystals of un-melted CMAS stuck in the melt pools. EDXS analysis suggests that many of these un-melted particles are the silica grains from the powder.

Cross sectional micrographs of the TBC coupons further show how the CMAS on the homogeneous sample develops a uniform surface layer (Figure 7.9). The more uniform accumulation likely yields the more uniform penetration seen in the full life sample. The cross section of the heterogeneous sample, shown in Figure 7.10, displays behavior similar to that seen
in Figure 6.6, where small portions of CMAS melt, adhere to the coating, and allow for much larger pieces of un-melted CMAS to accumulate on the TBC surface. This also results in variability of CMAS concentration across the TBC surface, and likely variability in local CMAS composition, although more systematic study would be necessary to analyze this phenomenon. One may assume, however, that, given sufficient hot time, these large pieces of material would eventually melt, developing the more uniform layer of material observed in Figure 7.5b.
Figure 7.10 Cross section of partial life sample with heterogeneous CMAS (near surface)

One result of this analysis is to show that, while precursor solution and oxide powder were shown to have similar chemical behavior in 4.2.4, there are differences in adhesion and melt behavior that can affect the interaction between CMAS and TBC. Therefore, since real-world CMAS is almost always heterogeneous, performing laboratory tests with heterogeneous CMAS will likely produce more realistic results than a homogeneous CMAS.

Because the largest grains of the AFRL-03 powder are silica (refer to Figure 4.5), much of the silica in this CMAS composition will be unavailable to interact with the TBC until these large particles are fully melted. This suggests that the particle size distribution of CMAS affects more than the flow of the debris in the engine, and thus what particles impact components. Once adhered to a TBC, the size of particles will affect the melt composition until all the material is melted. This is a further complication in the kinetic race for reactive TBC compositions to form a protective blocking layer, since apatite formation necessarily requires silica in the melt. According to the theory of optical basicity [63], this reduction of available silica in the melt will increase the
melt basicity, reducing the driving force for reaction between the TBC and the CMAS. This would suggest that a reactive coating might react more slowly when exposed to a heterogeneous CMAS (with large silica grains) than a homogeneous one. The reduced silica content of the melt would also lower its viscosity [119], which would lead to more rapid infiltration of the TBC. Therefore, a reactive coating has less time to form a blocking phase before penetration reaches critical depth.

Conversely, a heterogeneous material may take a significant time to develop any quantity of melt. If material is deposited sporadically across the TBC surface, the necessary constituents to form a lower temperature melt may not even be locally present. It could also take time for the constituents to accumulate or migrate to form any appreciable melt pool. This would give a reactive TBC more time to mitigate the CMAS attack locally and a little at a time, even if the overall CMAS accumulation is significant. Comparatively, a non-reactive TBC would be subject to CMAS melt penetration each and every time local conditions become favorable to melt formation. Further study into the melting behavior and the combined kinetics of melting/reaction are necessary to better understand these phenomena.

7.3 Summary

As previously stated, both of these experiments were initial explorations into the capabilities of the two thermal gradients rigs that were constructed. The CMAS dose rate experiment contradicts the notion of a unique critical dose for CMAS failure, since there was a factor of 5 difference between the CMAS sprayed before failure in these experiments. The heterogeneous vs. homogeneous CMAS experiments performed cannot identify one or the other as being more damaging, but the melting and reaction behavior appeared to be quite different on the partial life samples. These results highlight an area of study that has not been previously
considered. If the homogeneous CMAS produces different cyclic life results, then the many homogeneous CMAS tests done to date may not be strictly engine relevant. These findings were only possible with the testing capabilities that were developed.
8 CONCLUSIONS AND FUTURE WORK

8.1 Summary of Effort

Thermal barrier coatings have developed to the point where modern gas turbine engines rely on them for safe and efficient engine operation. They have enabled engines to operate at temperatures that, unfortunately, induce the melting of CMAS-type materials, thereby greatly reducing the expected life of these same coatings. Unlike volcanic ash clouds, CMAS materials are unavoidable: they are geographically widespread, encountered especially at take-off and landing (so they cannot be maneuvered around), and do not disperse with time. Therefore, CMAS attack must be addressed, both in terms of understanding their effect on current thermal barrier coating systems, and of including CMAS-resistance as a key feature of next generation TBCs.

The contribution of this research effort has been to improving the understanding of how to manufacture and operate a thermal gradient rig to test the thermochemical and thermomechanical degradation of TBCs under CMAS attack.

Material characterization of the CMAS powders and their precursor solutions suggested that the precursor solutions successfully resembled their powder form compositions, in terms of melt onset temperature and phases formed during cooling. A method to perform isothermal furnace testing with incremental CMAS dosing was developed, which resulted in cyclic lives greater than one, a problem that had not been previously solved. However, the isothermal testing did not show a strong performance difference between baseline YSZ samples and SPPS GZO samples. The high dwell temperature necessary for melting CMAS, well above bond coat design temperatures, was also an undesirable feature. These results further emphasized the necessity of a thermal gradient rig.
Our first generation thermal gradient rig was developed based on previous work in the literature. Then, improvements were made to improve the safety, stability, and sample throughput of the rig. In particular, given a relatively low velocity flame, the temperature stability of the rig was increased by roughly an order of magnitude by using the torch in a vertical orientation. The video monitoring system allowed for detailed analysis of sample failure progression without continuous on-site monitoring. Initial CMAS testing revealed undesirable failure modes (spall during heating) and morphologies (shallow exfoliation). These were investigated by developing a finite difference model of the transient temperature distribution through the TBC sample and by the innovative process of thermally spraying CMAS onto TBC coupons. We concluded that failure was indeed occurring during heating and was not an effect of precursor decomposition on the TBC surface. Further consideration produced the key insight that attempting to better match the transient thermal gradient during engine operation was more important than trying to match the fast engine heating. After modifying the rig and the cyclic thermal profile during cycling, results that were more engine-representative were produced.

Based on the experience of constructing and operating the first generation gradient rig, a second, more advanced rig was developed. This second generation gradient rig required significantly more lab space and infrastructure, all of which was designed and constructed as part of this effort. Improvements to this rig included greater sample throughput, higher heat flux, and the capability to coaxially inject CMAS powders into the flame, which removes the drawbacks of using CMAS precursor solution. A modified sample holder design reduced the in-plane gradient across sample coupons by one half. Using a heterogeneous CMAS powder, which had not been previously reported in the literature, revealed differences in adhesion and melting behavior.
compared to homogeneous powders. This has direct implications in how reactive TBC compositions will interact with the attacking CMAS.

With the creation of these gradient rigs, countless material and engineering questions can be investigated. Two preliminary experiments were described. First, the effect of CMAS dose rate on YSZ TBC degradation was explored. Results suggested that, over the range of values explored, CMAS dose rate does not act independently of thermal cycling and bond coat oxidation. The CMAS dose at the time of failure varied with dose rate by a factor of 5 in a systematic way. Accordingly, there is no “critical CMAS dose” within the dosing regime examined. These damage mechanisms interact synergistically to control TBC life. These results should be factored into Evans-Hutchinson-type modeling to accurately predict when a coating on a real engine might fail. Hot time and thermal cycling factors should be included to modify the effective stress on the coating due to CMAS penetration.

Second, a qualitative comparison was made between thermal cycling with homogeneous and heterogeneous CMAS. While the failure mode in both cases was similar, there were differences in the chemical reactions between the TBC and CMAS, as well as the melting kinetics of the CMAS during testing. The differences were likely driven by the fact that the homogeneous material needs more time to form low melting eutectics and dissolve further constituent elements into the melt. Thus, the melt chemistry has some evolution over time. This reinforces the observation that there could be fundamental differences between how a TBC will interact with sand ingested by a GTE and with a lab-created homogenous CMAS material.
8.2 Future Avenues of Inquiry

8.2.1 Refinements to the thermal gradient rigs

There are a number of refinements that could be made to the thermal gradient rig design to further improve its capability and accuracy. One critical factor is to increase the accuracy of temperature measurements. As discussed in Section 6.3, even small errors in temperature measurement can have profound effects on the results of life experiments. Currently, there is some flame contribution to the surface measurements in the rig, which should be removed. Based on the blackbody calibrator experiment described in Section 6.3, it should be possible to do so. Another factor influencing temperature is the emissivity of the coating, which evolves with thermal cycling and contamination. Since emissivity directly affects temperature as measured by a pyrometer, this could be a significant source of error. Studies of the evolution of the emissivity of coating materials with cycling and surface contamination, are, therefore, essential for the nascent field of thermal gradient cycling.

Another refinement to the understanding of thermal gradient rig cycling would be a better characterization of the in-plane gradients across samples during cycling. The in-plane gradient complicates the effort of modeling rig results for application to actual GTE components. Any efforts to reduce the gradient would be desirable. Absent that, a better understanding of the in-plane gradient during testing would help remove its effects during modeling.

Finally, there are improvements to be made to the CMAS delivery mechanisms on both generations of gradient rig. For the second generation rig, the operational parameters of the CMAS powder feeder are being investigated to determine how to operate it to deposit CMAS in the most realistic and controllable manner possible. This will also be crucial for any dose-rate dependence testing on the rig. One challenge for a material like the AFRL-03 powder is that it is chemically
size-segregated: the largest particles are all quartz, and the halite is very small. A fluidized bed may perform some size-sorting of the particle flow, which would change the composition of the CMAS impinging on the TBC surface.

Regarding the first generation rig, with its CMAS precursor “spritzer,” it would be desirable to transition away from the use of precursor solution. One potential path forward for the design would be develop a CMAS oxide suspension capable of being fed through the existing system. Challenges would include the development of a stable suspension, as well as ensuring that the carrier liquid successfully adhered the CMAS material to the sample. Adhesion of the precursor solution was promoted by the use of nitrates, which are inherently sticky when dried.

8.2.2 Improving agreement between rig results and engine experience

While one of the key successes of this program was getting the CMAS failure results to look more like what occurs on the engine, there is more work to be done. First, a better understanding of CMAS attack in the engine must be developed. For example, there is no public documentation of the damage progression of CMAS on actual GTE components. While engine manufacturers may have this information, it has not been shared with the research community, mostly for proprietary reasons. Thus, more collaboration between researchers and engine manufacturers is necessary to guide researchers in the right direction as to how CMAS damage progression should look in the lab. And it is likely that CMAS attack is not one singular sequence of events, but a collection of related damage mechanisms that vary between engine types and geographies (as it affects CMAS composition and morphology). Thus, the full potential operational space of thermal gradient testing must be explored to determine what CMAS attack looks like under different conditions. This will allow for testing to be tailored to the specific environment being investigated.
8.2.3 Using thermal gradient rig testing to conduct fundamental investigations

The main goal of designing a new method of testing is to answer questions that could not be previously investigated. Thermal gradient rigs allow for many fundamental questions about TBC-CMAS interactions to be explored, which will be fodder for many future graduate students. But one application-oriented goal is again worth emphasizing: that of developing a so-called “life debit model” for TBCs subject to CMAS attack. That is, to predict how CMAS will reduce the life of specific engine hardware below what would be expected from normal thermal cycling damage.

At a very basic level, the inputs to the model are the engine type and where the engine is flying. These can be broken down to coating material, engine temperatures (i.e. the expected surface and substrate temperatures for the TBC), contaminant chemistry and morphology, and contamination rate (concentration of contaminant and efficiency of contaminant capture). Each one of these factors needs to be fully explored in thermal gradient testing to feed into an accurate life debit model.

- Coating material: it is known that some TBC materials are more CMAS-resistant than others. But this superior performance needs to be quantified to allow for accurate trade studies to be made. Samples of many different coating types need to be tested under similar conditions to determine the relative performance of each under many CMAS attack conditions. One TBC property which requires more study is crack/porosity geometry: the size of the openings into which the CMAS tries to penetrate will play a critical role in the kinetic race between infiltration flow and blocking reactions. More complete baseline (no CMAS) testing of TBC systems is required to have an accurate metric of how deleterious the CMAS effect is for a given coating. Researchers have
done little baseline testing historically, given the extremely long run times necessary. Developing rig configurations with high sample throughput, such as the second generation rig, makes such work more feasible.

- **Temperature:** Melt viscosities are highly sensitive to temperature, as are reaction kinetics to form CMAS blocking phases. Therefore, the effect of surface temperature on how successfully reactive TBC compositions arrest CMAS infiltration will be quite significant, and likely non-trivial. The interplay of surface and substrate temperature on CMAS interactions, both at equilibrium and transient conditions, is a whole investigation unto itself. Validating and refining the Evans-Hutchinson model for many coatings under many different CMAS attack conditions is critical for better understanding and modeling the thermomechanical stresses imposed on TBC coatings and predicting their failure.

- **Contaminant chemistry:** While sand and dust the world over have similar chemical components, the composition, including the presence or absence of minor constituents, can have enormous effect on the actual melting, flow, reaction, and crystallization of the CMAS melt. It would be ideal if the infinite variety of contaminant chemistry could be reduced to a few parameters, such as optical basicity and viscosity as a function of temperature, in order to model how “aggressive” a certain CMAS chemistry may be. Detailed studies would be necessary to determine what properties best parameterize CMAS, as well as the fidelity of any parameter set.

- **Contaminant morphology:** Along with chemistry, the shape and size of contaminant particles will dictate how they adhere to and accumulate on GTE components.
• Contaminant homogeneity: the extent to which the CMAS is already a homogeneous composition will affect its melting behavior, as well as the kinetics of penetration and reaction with CMAS-resistant TBC materials.

• Contaminant concentration / accumulation rate: intuitively, operating somewhere with high concentrations of dust (see Figure 1.3) will be worse than operating in a low-dust environment. But a numerical understanding of the interplay between CMAS-free cyclic damage and CMAS accumulation will be critical in determining how CMAS attack will shorten the expected life of a TBC.

Of course, all of these variables are interdependent: a coating with a lower thermal conductivity will have a higher surface temperature for the same engine, the viscosity of different CMAS chemistries will have different temperature sensitivities, different coatings will have different CMAS capture efficiencies, and many other permutations. All of this is to the benefit of the TBC experimentalist: there is no small mountain of investigation that needs to be carried out before the effect of CMAS on thermal barrier coatings in gas turbines engines can be said to be well understood.

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9 REFERENCES


