Abstract

Thermal barrier coatings (TBCs) are ceramic coatings used on component in the hottest sections of gas turbine engines, used for power generation and aviation. These coatings insulate the underlying metal components and allow for much higher engine operating temperatures, improving the engine efficiency.

These increase temperatures engender a new set of materials problems for TBCs. Operating temperatures in engines are now high enough for silicate impurities, either present in the fuel or ingested into the engines, to melt and adhere to the surface of the TBCs. The effects of four such impurities, two coal fly ashes, a petroleum coke-fly ash blend, and volcanic ash from the Eyjafjallajökull volcano were tested with conventional yttria-stabilized zirconia (YSZ) coatings, and found to penetrate through the entire thickness of the coating. This penetration reduces the strain tolerance of the coatings, and can result in premature failure. Testing on a newly built thermal gradient burner rig with simultaneous injection of ash impurities has shown a reduction of life up to 99.6% in these coatings when ash is present.

Coatings of an alternative ceramic, gadolinium zirconate (Gd$_2$Zr$_2$O$_7$), were found to form a dense reaction layer with each of these impurities, preventing further penetration of the molten ash. This dense layer also reduces the strain tolerance, but these coatings were found to have a significantly higher life than the YSZ coatings.
Testing with a small amount of ash baked onto the samples showed thirteen times the life of YSZ coatings. When the ash is continuously sprayed onto the hot sample, the life of the Gd$_2$Zr$_2$O$_7$ coatings was nearly twice that of the YSZ.

Finally, a delamination model was employed to explain the degradation of both types of coatings. This elastic model that takes into account the degree of penetration, differential cooling in thermal gradient testing, and thermal expansion mismatch with the underlying substrate, predicted the failure of YSZ coatings with the observed degree of penetration. The model shows that deposition optimization can be employed to further enhance the life of Gd$_2$Zr$_2$O$_7$ coatings.
Dedicated to my wife Laura
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Chapter 1. Introduction

1.1 Introduction

Gas turbine engines serve two major functions in society. Firstly, they are used in the generation of electricity, and account for a substantial portion of the US and world’s power supply [1]. Secondly, engines are used in aerospace application, namely, to fly jet aircraft [2]. While the size and normal operating conditions of these two classes of engines vary greatly, one commonality is that increasing the gas inlet temperatures improves efficiency, thereby reducing operating costs [3-5]. This increased temperature leads to a host of new materials challenges [6-10].

To achieve these increased temperatures without premature engine failure, thin ceramic coatings are applied to the hot sections of the engines [11-14]. These thermal barrier coatings (TBCs) allow as much as a 300° C increase in surface temperature [11]. However, with these increased temperatures, a new problem has been enabled, namely that of ingested silicate particulates [6-10, 15-17]. These particulates can melt and adhere to the surface of the TBCs, and eventually lead to premature spallation of the coatings [18].
This document is intended to serve as a case study on the effects and interactions of several such particulates with thermal barrier coatings, with the goal of mitigating the damage caused by these impurities. In this chapter, a brief outline of gas turbine engines will be presented, highlighting the differences and similarities between power-generating and aircraft engines. In the second chapter, an introduction to thermal barrier coatings will be presented. In this context, a broad level overview of the current status of thermal barrier coatings will be included, so as to frame this work. The third chapter will focus on the typical impurities ingested by these types of engines as well as the impurities used in this study. Chapter 4 will spell out the specific objectives of this work. The following chapter will provide the general procedures used in the experimental work presented here. Chapters 6 and 7 will outline the findings of this work in the context of thermo-chemical and thermo-mechanical interactions. In Chapter 8, the combined thermo-chemical-mechanical effects of impurities on TBCs will be explored. Chapter 9 will then present the results of mechanical modeling, in an attempt to better understand spallation avoidance strategies. Finally, the last chapter will conclude and provide insight into the future of TBCs.

1.2 Gas Turbine Engines

As previously stated, there are two major uses for gas turbine engines; power generation and as a means of propulsion for aircraft. Both of these classes of engines rely on the same operating principals [19], and many of the operational concerns are shared between them.
One of the major concerns for the end users of both types of these turbine engines is cost. Operating at higher temperatures increases the efficiency of the burn, and thereby results in lower operating costs [20-21]. To this end, three major developments have enabled the use of higher operating temperatures. Firstly, the steady progression of better structural alloys has allowed an increase of about 4° C per year improvement [20]. The implementation of film cooling has allowed a significant jump in the allowable temperatures. Blades and other complex components are actively cooled from the inside, and have cooling holes, which eject cooling gases onto the surface of the materials. It should be of note that while film cooling allows for greater temperatures, it also decreases the overall efficiency of the engines [21]. The final advancement allowing greater use temperatures is the implementation of thermal barrier coatings [11-13]. This is illustrated in Figure 1.1

From Figure 1.1, it is clear that the use of TBC systems allows a large jump in both maximum surface temperature and gas inlet temperature. This results in increased efficiency, and ultimately reduced operating costs.
Figure 1.1. Historical maximum surface and gas inlet temperature in gas turbine engines with and without thermal barrier coatings. Adapted from [20].

Figure 1.2 shows photographs of both types of engines. In Figure 1.2A, a Siemens SG5-8000h power-generating engine is shown. This engine, when coupled to the appropriate generator, produces 340MW of electricity and is fired with natural gas. Figure 1.2B shows a GE 90 engine attached to an aircraft, which produces 128k-lbs of thrust. Since the use of the engines is different, the power of each type of engine is measured in different units [19]. Also of note is the overall size difference between power and aero engines. In power generating engines, weight is not a concern, and thus the housing and support structure are typically much more substantial than in aero engines [19].
While the overall design of these two classes of engines is similar, there are important differences, which lead to different operating conditions. The following section outlines several of the key differences, which have an effect on the materials used, with attention paid primarily to the issues affecting TBCs.
1.3 Differences Affecting Materials

Both types of engines operate on the same principle and have largely the same types of components. However, there are several key differences which effect how key materials behave in these engines. These differences include the fuel used to power the engine, typical operating temperature ranges, and environmental differences.

Jet fuel is the primary energy source for aerospace engines. Power generating engines however, can run on a variety of fuels depending on availability and cost [22-26]. Natural gas has been the fuel source of choice for many years because it is clean and readily available. In recent years, the integrated gasification combined cycle (IGCC) concept has allowed for the development and use of alternative fuels, such as synthesis gas, or syngas [23-26]. This is primarily made by extracting the energy from coal or other hydrocarbon sources and using that energy to produce a gas that is very high in hydrogen content. As will be pointed out in later chapters, this as-produced syngas can be much higher in impurities that can have detrimental effects on engine components.

The operating temperatures of the two types of engines are also significantly different. In aero engines, maximum temperature is used during take off and landing, and lower power is consumed during cruising [27].

In power generating engines, the typical engine cycle is much longer, and stays at a relatively constant temperature. Of course, this depends on the demand for electricity and redundancy built into the power grid [28]. These differing thermal cycles will result in different thermal expansion mismatch stresses and different lifetimes for coatings.
The final key difference between aero and power engines is the environment of the engine. Power generating engines are at a stationary location, and the ingestion of stray materials can be controlled to a great extent, typically through filtration of the inlet air. Aero engines however are vulnerable to ingestion of impurities depending on their location. This can include airborne sand particulates, volcanic ash, or even birds and other wildlife. For this reason, engines must be designed with high safety factors and monitoring of air quality conditions is important. Several of these impurities will be discussed in greater detail in later chapters.

With a very broad level understanding of these two types of engines and an understanding of several key differences between the two types, a closer examination of one critical component in the gas turbine engine, the thermal barrier coating, follows.
Chapter 2. Thermal Barrier Coatings

2.1 Introduction to Thermal Barrier Coatings

Thermal barrier coatings are a complex system of coatings that have stringent materials properties requirements on each layer. The typical coating contains at least three layers atop of the underlying substrate, each of which has a critical function to the overall system [11]. This chapter will outline the structure of the conventional system and the materials properties desirable for each layer with emphasis on the ceramic topcoat of the system, as well as the standard methods of producing such systems. Additionally, this chapter will outline the causes of failure in these systems, and the outline of complexity in failure prediction and “lifeing” of these coatings.

2.2 TBC Systems

As previously mentioned, thermal barrier coatings are a complex system of coatings with many different functions to serve. Figure 2.1 shows a schematic view of a conventional coating system [11]. The various layers of the system, starting from the left of the figure, are the superalloy substrate, the bond coat, and thermally grown oxide, and
finally the ceramic top coat. The substrate is the main structural component of the part in question, and is typically made of a “single” crystal gamma-gamma prime Ni-based superalloy for the most demanding parts. This is the material of choice because it maintains strength, creep resistance, and fatigue resistances at high temperatures. Also, the alloys used are oxidation resistant up to very high temperatures. In older turbine engines where the operating temperatures were lower, and in cooler sections of current engines, the super alloy is uncoated. It is important to note that the superalloys used in turbine engines all have relatively high coefficients of thermal expansion, \( \sim 15 \times 10^{-6} \, ^\circ\text{C} \) [29]. All subsequent layers are made to mimic this thermal expansion as closely as possible to lessen the stress induced by rapid heating and cooling of the system.

Figure 2.1 Schematic showing the structure of a typical thermal barrier coating. The blue line represents the temperature profile across the system [11].
The bond coat was originally developed as an oxidation resistant layer to overlay the structural components with. Bond coat compositions vary greatly depending on the intended use of the component, as well as the underlying metal composition [11, 30-31]. In power engines and many aero engines, bond coats can have a composition of the MCrAlY type, where M can be Co, Ni or other atoms. Typically, bond coats range in thickness from 50-300µm in thickness [11].

One overarching theme in bond coat development is that the bond coat serves as a reservoir of aluminum. The aluminum serves the function of forming a coherent Al₂O₃ scale, which slows the rate of oxidation drastically [32]. Additional considerations in bond coat choice include the interaction of the bond coat with the underlying substrate alloy. Primary and secondary reaction zones are typically observed, which can alter the properties of the structural metal components.

The next layer for consideration is the thermally grown oxide layer (TGO), which is typically Al₂O₃, formed from oxidation of the outer surface of the bondcoat material. This thin layer grows with high temperature exposure to the combusting gases in the turbine. Depending of the bond coat composition, other phases can form, such as a NiAl₂O₄ or FeAl₂O₄ spinel, which can be detrimental to the life of the system [31]. The exact chemistry of spinel formation depends on the chemistry of the bond coat in use. The thermal expansion coefficient of Al₂O₃ is 8.1x10⁻⁶/°C, much lower than that of the substrate or bond coat. Also, the TGO is constrained, and as a result, growth stresses can be rather large and contribute to the spallation of the system.

The final layer in a conventional TBC system is the ceramic top coat. The function of the top coat is the reduction of the temperature of the underlying materials.
Typical coatings range in thickness from 100µm to 1mm and can provide as much as a 300° C drop in temperature of the underlying layers [11].

The material of choice for the last 40+ years has been 7-8wt% yttria stabilized zirconia (7YSZ) [30]. This material was chosen because it has an extremely low thermal conductivity, high toughness, and a high thermal expansion coefficient (~11 x10^-6 /C) for a ceramic [30].

While 7YSZ has been the industrial standard, constant work on developing alternative materials with further optimized properties has been undertaken both from an academic and industrial point of view. One such alternative material, gadolinium zirconate (Gd₂Zr₂O₇), was originally developed for it’s extremely low thermal conductivity [12-13, 33-35]. Figure 2.2 shows the measured thermal conductivity of fully dense pellets of 7YSZ and Gd₂Zr₂O₇ over a wide range of temperatures. Clearly, with a lower conductivity, a thinner coating could be used to achieve the same temperature reduction or, an increase temperature reduction could be achieved with the same coating thickness. A more detailed look at the properties and requirements for these materials will be explored in subsequent sections.
2.3 Top Coat Processing

The majority of top coats are applied by one of two methods, electron-beam physical vapor deposition (EB-PVD), and air plasma spray (APS). The resulting microstructures of these two very different processes can be seen in Figure 2.3. A closer look at each of these deposition processes follows, but the overarching goal is to produce coatings which are strain tolerant and of low conductivity. In both cases, porosity and discontinuity in the microstructure allows for this. The strain tolerance is needed to
accommodate the thermal expansion mismatch between the underlying metals and the top coat material.

![Figure 2.3. Typical microstructures of ceramic top coats for TBCs made by the (A) EB-PVD process, and (B) APS process.](image)

In addition to the EB-PVD and APS processes, there are several other processing routes that have not yet been used on a wide, industrial scale. These other methods include solution precursor plasma spray (SPPS), direct vapor injection (DVI), as well as a host of other techniques aimed at very specific niche markets.

2.3.1 EB-PVD

Electron beam physical vapor deposition is typically the preferred deposition method for rotating parts in aircraft engines [13]. This is primarily due to the extreme
strain tolerance imparted by the resulting microstructure. The vertical cracks present allow the coating to open and close with heating and cooling cycles. Additionally, since air has a low thermal conductivity, the vertical cracks allow for a reduction in the overall thermal conductivity of the sample, though not as low as APS.

The deposition process uses several high-energy electron beams, which strikes an ingot of the desired top coat material. As material is volatized away, the vapor then deposits on the first surface that it comes in contact with. As a result, the process is deemed line of sight, in that deposition can only occur on the surface of the sample facing the target. Figure 2.4 schematically illustrates the EB-PVD chamber [36].

Figure 2.4. Schematic of the deposition chamber used to produce EB-PVD coatings [36].
There are several drawbacks to the EB-PVD process. Firstly, the overall cost of producing such coatings on a large scale can be prohibitive. Secondly, the microstructure is very susceptible to molten impurities, which can flow rapidly down the vertical cracks effectively infiltrating the top coat. As will be discussed in later chapters, this infiltration can play a significant role in the overall life of the component.

2.3.2 APS

The air plasma spray process is typically used on non-rotating parts in aircraft engines, and almost exclusively in power generating turbines. Since the cost is significantly lower than that of EB-PVD coatings, thicker coatings are typically produced by this method. The microstructure is characterized by high porosity and a series of cracks and splat boundaries typically running parallel to the surface of the coating. These parallel cracks are excellent at reducing the thermal conductivity of the coating by phonon scattering, resulting in coatings with a lower thermal conductivity than EB-PVD. This is illustrated in Figure 2.3. Typically, the overall level of porosity is targeted between 15-20%.

In the APS process, powder feedstock is fed through a hopper into a plasma jet, which propels the powder toward the surface of the substrate. The temperature in the plasma is high enough to melt the particulates, so that on impact, a splat is formed. Through successive layering of individual splats, the coating is built up. A schematic showing the APS process is shown in Figure 2.5 [37].
The lack of vertical cracks in the resulting microstructure results in a less strain tolerant coating when compared to EB-PVD coatings, but have a lower thermal conductivity [13]. Also, the complex nature of parameters involved in the plasma spray process can result in coatings with an increased variability in microstructure and life [38].

2.4 Top Coat Materials

As previously stated, the top coat materials need to have a set of material parameters to be a useful top coat. Firstly, the coating must be composed of a low thermal conductivity material to provide the thermal protection for the underlying components. Also, the material must be phase stable through the use temperature, preventing any phase transformation which can damage the coating. Mechanically, the material must adhere well to the bond coat and TGO, and provide a robust interfacial
toughness to prevent premature failure [18, 39-41]. In terms of materials properties, this corresponds to high fracture toughness, an appropriate thermal expansion coefficient, and optimized in-plane elastic modulus. While many materials have been evaluated for use as top coats, two top coat materials are the focus for this work, namely 7YSZ and Gd$_2$Zr$_2$O$_7$, which will be explored in more depth.

2.4.1 Yttria Stabilized Zirconia

Yttrium stabilized zirconia has been the standard material for TBC top coat for over forty years due to its attractive combination of properties [30]. As shown in Figure 2.2, the thermal conductivity of 7YSZ is lower than most conventional ceramics due to the unique oxygen defect structure present. This defect structure allows oxygen to diffuse through the coatings very rapidly, which is why an oxidation resistant bond coat is used in TBCs.

The structure of 7YSZ coatings is a meta-stable tetragonal phase, often referred to as t’. The equilibrium phase diagram is shown in Figure 2.6 [42]. Since the t’ phase is metastable, at high temperature and after long-term exposure, phase transformations can occur and can limit the useful life of coatings. However, the kinetics are such that only a very small amount of the monoclinic phase is observable at the end of a parts life with current operating temperatures.

One of the main reasons that 7YSZ has been the material of choice is the high toughness value. Typical toughness values for porous APS coatings range from 30-45 J m$^{-2}$ [18].
Figure 2.6. A portion of the equilibrium phase diagram for the ZrO$_2$-YO$_{1.5}$ system with the metastable, non-transformable tetragonal phase marked [42].

The mechanical properties of YSZ are also very well established. The thermal expansion coefficient is high for a ceramic, typically measured around 11 ppm C$^{-1}$ [18]. This allows for a good match with the underlying substrate material, and will minimize the stresses induced during thermal cycling.
2.4.2 Gadolinium Zirconate

Gadolinium zirconate is a much newer material than 7YSZ. It was originally developed for its ultra-low thermal conductivity, about 1/3 lower than 7YSZ [33-35], as shown in Figure 2.2.

The pyrochlore phase of Gd$_2$Zr$_2$O$_7$ is phase stable to above 1500° C, and above 1700° C the fluorite phase is stable. Figure 2.7 shows the equilibrium phase diagram in the Gd$_2$O$_3$-ZrO$_2$ system [43]. The difference between these two phases is an ordering of the oxygen defect sites, so transition between these phases is volume conserving and does not contribute to the failure of the coatings. However, the disordered defect structure of the pyrochlore results in increased phonon scattering, leading to a reduced thermal conductivity.
Figure 2.7. Equilibrium phase diagram of the ZrO$_2$-Gd$_2$O$_3$ system. Gd$_2$Zr$_2$O$_7$ is marked, with the pyrochlore structure stable at lower temperatures, and the fluorite structure stable at higher temperatures [43].

Mechanically, the Gd$_2$Zr$_2$O$_7$ does not fair as well as YSZ. While the thermal expansion coefficient has been estimated as nearly the same as YSZ [66], the fracture toughness is significantly lower than that of YSZ [44]. Because of this lower interfacial toughness and the possibility of forming unwanted interfacial phases with the TGO, most Gd$_2$Zr$_2$O$_7$ coatings are applied on top of the thin YSZ layer to maximize coating life [13,45-46]. As will be illustrated later, the interfacial toughness is critical to preventing spallation.
2.5 Failure of TBCs

Thermal barrier coatings can fail in a number of ways depending on the materials and testing procedure used to induce the failure. Several dominate failure mechanisms are presented here, though this list is not meant to cover all systems or mechanisms. Then, several recent attempts at empirically and mechanistically modeling the life of coatings are presented.

2.5.1 Failure Mechanisms

There are many ways that TBCs can fail in engines. Gradual cracking and/or stress accumulation is expected due to the thermal expansion mismatch between the underlying substrate and the TBC. Damage can also come from the underlying bond coat and TGO layers. Geometric effects can lead directly to failure as well. Finally, damage from foreign objects is also a threat to the ceramic top coats.

In any layered system with differing thermal expansion coefficients, upon thermal cycling, stresses will be generated [18]. In the ceramic top coat, these stresses coupled with the plentiful defects and stress concentrators build into the microstructure can lead to eventual spallation of the coatings [47]. This intentionally defective microstructure allows for some level of strain tolerance, but cracks grow over thermal cycling. For this reason, an optimized selection of materials allowing for the lowest thermal expansion
mismatch is desirable, as well as optimization of the microstructure to maximize the strain tolerance.

The effects of sintering can also lead to the degradation of coatings. Sintering eliminates the pores, cracks, and splat boundaries needed for the strain tolerance. In TBCs in use, sintering occurs more rapidly at the outer surface of coatings due to the thermal gradient in which they are used.

Effects from the underlying layers can also lead to the failure of TBCs. As shown in Figure 2.3, the optimized interface for EB-PVD coatings is extremely flat, and for APS coatings, the optimized interface is undulated. This surface preparation has proven to be extremely important in preventing early failure of coatings.

In the case of EB-PVD coatings, after thermal cycling, rumpling can occur. This rumpling is the roughening of the interface, as shown in Figure 2.8, and drastically shortens the life of the coatings [48-50]. Research to prevent rumpling has dominantly focused on bond coat development.
Figure 2.8. Rumpling, or roughening of the originally flat interface between the top coat and bond coat shown in (A) can lead to the formation of voids, which can lead to failure in TBC systems. (B) A schematic diagram showing this effect [48].

In APS coatings, the optimized interface is rough, which maximizes adhesion. However, thermal cycling results in regions of tension and regions of compression around these undulations. Finite element modeling reveals the exact locations of these regions as well as the level of stress generated in a given thermal cycle [51-52]. Figure 2.9 shows the results of one such finite element study. This study also includes the effects of the TGO growth stresses, which are highly dependant on the thermal history of the sample.
Figure 2.9 FEM simulations showing the effects of undulations in the bondcoat on stresses during thermal cycling [51].

Care must be taken when attempting to model air plasma sprayed coatings using finite element or other modeling methods. The properties of coatings have a viscoplastic nature at elevated temperatures, as well as yield anisotropy [53]. Incorporating the correct property relationships has been undertaken, and the results are very different from modeling assuming linear elastic properties [54].

Geometrical effects can also lead to failure in coatings. In actual engines, this typically is due to the pressure and temperature differences around different sections of rotating parts [55]. In laboratory testing, these geometric effects typically take the form of edge, or sharp corner effects [55]. Sharp corners act as additional stress concentrators, and have been shown accelerate the failure of coatings.
Foreign objects, whither in the form of impurity gaseous species, fine particulates, or large particles can also lead to the failure of TBCs by either erosion or impact damage [56-57]. This subject is covered in detail in the following chapter.

2.5.2 Prediction of Failure/Lifeing

Many attempts at determining the life of thermal barrier coatings have been made in an effort to maximize the usefulness of coatings in engines. However, with the variety and complexity of the materials involved, no one model or approach has emerged as dominate for all situations and systems.

The majority of life models rely on empirical data sets [48, 58-59]. Parameters in these empirical models are often very involved, and include materials properties, geometric considerations, thermal conditions, and adjustable fitting parameters to allow a given data set to “fit” the model. The results of these models are charts that attempt to predict the time to failure for a given set of conditions/materials, such as the chart in Figure 2.10. In this chart, the one major factor controlling life is the temperature of the bond coat interface. This implies a failure that is very dependent on the TGO growth.
Figure 2.10 Time to failure chart created semi-empirically to predict the failure of coatings [58].

A delamination model, which does not rely on fitting parameters, has been gaining popularity in the TBC field. This model relies on the linear elastic stress generated in a multilayer system from the differential elastic properties and differential cooling [18]. This model also takes into account the effects of penetration from molten impurities, which is becoming an increasingly concerning problem. The mechanics of this model will be outlined in Chapter 9 of this work.
Chapter 3. Impurities in Gas Turbine Engines

3.1 Introduction to Gas Turbine Impurities

A variety of different impurities can be ingested into gas turbine engines either by ingestion with inlet air flow, or as an impurity present in the fuel. These impurities can be broadly broken down into three categories; large foreign objects debris, gaseous impurities, and fine particulates. Foreign object damage, or FOD as it is often referred to, is a constant difficulty facing aircraft engines and typically leads to large impact damage on the TBCs, and frequently even spallation [56-57]. Gaseous impurities are more likely to be found as a fuel contaminant, and thus are present in both aero and power turbines [60-63]. The third classification of impurities, fine particulates, can be present in fuel or ingested from the inlet air [7-10, 50, 63-71].

The effects of several of these impurities have been studied, and their effects of coatings have been characterized. FOD, which is more closely related to an erosion issue than a chemical attack, has been found to lead to large-scale spallation localized to the area of impact [56-57]. An example of erosion and FOD damage can be seen in Figure 3.1 on an EB-PVD coating.
Figure 3.1 Damage from impurity species on EB-PVD coatings ranging from (A) erosion to (B) and (C) FOD of different types [56].

Gaseous species can also have detrimental effects on TBC materials. Numerous studies have shown the hot corrosion behavior of coatings in the presence of common fuel impurities, such as \( V_2O_5 \), and reaction between these species and TBC materials can degrade the outer surface of the coatings. For example, \( V_2O_5 \) reacts with \( Gd_2Zr_2O_7 \) to form \( GdVO_4 \) and monoclinic zirconia [60].

One proposed solution to help with gaseous impurities is laser glazing the surface of the material [74]. The laser glazing process modifies the surface of the coating and produces segmentation cracks, which allow the coating to be more compliant. This added strain tolerance allows coating to survive longer in the presence of gaseous impurities such as \( V_2O_5 \).

The study of fine particulates has, prior to this work, almost entirely focused on calcium magnesium alumino-silicate (CMAS) particulates, typically ingested in sandy, desert environments [7]. Chemically, CMAS has been found to penetrate through the open porosity and crack structure of TBCs, as well as exfoliate the grains. Also, dissolution of the metastable tetragonal t’ zirconia occurs until the melt reaches the solubility limit for zirconia. Grains of the thermodynamically stable, lower yttria content,
tetragonal zirconia. This partially stabilized zirconia can then transform into the monoclinic structure on cooling [7]. This penetration results in a loss of strain tolerance in the coating, and eventually premature spallation can occur [18].

Several strategies have been proposed to mitigate the effects of molten CMAS on TBCs. Early mitigation strategies attempted to use a noble metal layer or dense alumina layer, deposited on the outermost surface of the coating, to act as a dewetting agent or sealant, and thus not allow molten particulates to stick to the hot surfaces and penetrate [63, 72-73]. Two major problems with these methods were the thermal expansion mismatch between the noble metal and the coating led to the rapid formation of mud-flat cracking, and that the metal layers were rapidly removed by erosion.

More recent attempts to mitigate the effects of CMAS focus on altering the chemical composition of the top coat material to interact with the CMAS in such a way as to crystallize the glassy phase into a stable, non-reactive layer. During the reaction process, some degree of penetration into the coating is expected, at which point the arrest occurs. The result is a dense outer layer with uninfiltrated TBC underlay.

One successful approach is the incorporation of aluminum and titanium oxides into the YSZ in solid solution [8-9, 69]. As the CMAS interacts with the coating, aluminum oxide accumulates in the molten glass, effectively shifting the composition from the pseudowollatintite to anorthite, which crystallizes easily and rapidly. This is shown schematically in Figure 3.2 with an arrow showing the accumulation of alumina from the starting CMAS composition. The result is an anorthite crystalline reaction product that prevents further penetration of the CMAS into the coating.
Figure 3.2 Isothermal sections at 1200° C from the CaO-SiO₂-AlO₁.₅ phase diagram showing the composition of CMAS sand. An arrow has been drawn to show that the additional of alumina shift the composition to the CaAl₂Si₂O₈ phase, which crystallizes easily.

One other top coat material that has been found to mitigate the damage from molten CMAS is gadolinium zirconate [66]. This coating, as previously mentioned, was developed because it has a very low thermal conductivity. Chemically, the arresting behavior is similar to the YSZ with alumina/titania additions, in that the Gd ions accumulate in the molten CMAS, and lead to the crystallization of the molten front, preventing further penetration.
This work focuses on two sources of impurities other than CMAS. Firstly, three types of coal fly ash are considered. This ash is a byproduct of the gasification of coal, and can be found in the IGCC engines described later in this chapter. Typically, large, complicated filtration systems remove all but the finest of these ashes when they are functioning properly but degradation of these filtration systems can occur [15,70].

The other impurity studied in this work is volcanic ash. Ash from the March 2010 eruption of the Icelandic volcano, Eyjafjallajökull was used in this study. A closer look at the origins, chemistry, and thermal properties of these ashes is explored in the following sections.

3.2 Sources of Impurities

The contaminants studied in this work include three fly ashes and volcanic ash from the Eyjafjallajökull volcano. The source of each of these contaminants varies, as well as the method of ingestion into gas turbine engines.

As mentioned in Chapter 1, power generating turbines rely on fuel flexibility, and plants can use gasified coal or other petroleum products as the primary fuel source, in the form of syngas. Figure 3.3 shows the schematic diagram outlining an integrated gasification combined cycle (IGCC) power plan.
The result of the IGCC power system is a huge improvement in efficiency, achieved by capturing heat from the gas turbine and using that heat to run a steam turbine. This improvement has been estimated at a fifteen percent efficiency improvement [75], which more than accounts for the amount of electricity generated in the US in 2009 by wind, solar, geothermal, and biomass power generation combined [1].

The gas purification steps required to produce burnable syngas are complex and rather involved. Gas scrubbers are typically used to remove large solids such as slag, and
some of the gaseous impurities like ammonia and sulfur. Other purification techniques are used to remove heavy metals and other contaminants, but at the cost of efficiency of the overall system [77]. Also, the proposed IGCC plant includes the removal of CO₂ prior to burning the syngas.

Volcanic ash is a naturally occurring problem, and with the increase temperatures of modern jet engines, this ash can melt and adhere to hot sections of the turbine. This can lead to infiltration and spallation of the coatings. Historically, around 100 jet aircraft have flown through volcanic ash clouds [78-79]. As a safety measure, no fly and limited-fly ash concentrations have been established. It is greatly beneficial to build in additional safety mechanisms into engines, such as ash resistant TBCs [69].

3.3 Chemical Components

Prior to this study, the majority of published TBC work focuses on the effects of CMAS glass. The composition of CMAS varies greatly depending on the location of the sand used to model it. Table 3.1 shows two typical compositions of CMAS that have been used to studies with TBCs.

Table 3.1 Chemical composition of CMAS glass from literature and four ashes used in this study.
The chemical makeup of the four ashes used in this study was determined by XRF, PIXE, and ICP. Table 3.1 also shows the tabulated values of the ash components for all four ashes used in this study. From these results, clearly all of the ashes and CMAS are silicate based, but with a wide range of silica content. The relative amount of the various chemical components controls the ashes behavior, such as viscosity, reactivity, and crystallization behavior.

### 3.4 Viscosity and Melting
Testing the reaction between glasses and ceramics at elevated temperatures requires knowledge of the melting temperature and viscosity of the glasses. For this reason, differential thermal analysis (DTA) was used to detect the onset of melting, and any possible crystallization in the ashes used in this study. The viscosities of CMAS as well as the ashes used in this study were then estimated using existing chemical models.

Figure 3.4 shows the DTA data for the lignite fly ash and volcanic ash. The onset of melting occurs near 1150° C for the lignite ash, and around 1100° C for the volcanic ash. All testing performed with these ashes were done at temperatures at or above 1200° C, well above the measured melting temperatures.
Figure 3.4. Differential thermal analysis of lignite fly ash and volcanic ash showing the onset of melting to be near 1150° and 1100° C respectively. Testing was done with constant heating at the rate of 600° C/hour.

The viscosity of these two ashes, as well as the other two fly ashes used in this study was calculated based on chemical composition [80]. Figure 3.5 shows the viscosities of the four ashes and the viscosity of a typical CMAS glass used in TBC studies. Since the composition of fly ashes can vary greatly depending on the source of the ash, these viscosity calculations were check against literature values of measured ash viscosities [81] of similar composition, and good agreement was found.
Figure 3.5 Calculated viscosities of two compositions of CMAS, three coal fly ashes, and volcanic ash.

From Figure 3.5, it is expected that the volcanic ash, which is the most viscous, will penetrate into TBC samples slower than the other ashes. The PRB ash, being the least viscous, should penetrate into the open pores and cracks the quickest. The lignite ash, having a moderate viscosity will be the focus of much of the testing in subsequent chapters. The chemical interactions between these coatings and TBCs are highlighted in Chapter 6.
Chapter 4. Objectives of this Work

4.1 Objectives of This Work

The primary objective of this work is to understand the interactions between silicate impurities other than CMAS and ceramic thermal barrier coatings, and to develop thermal barrier coatings that resist damage in the presence of these silicates.

Due to the complexity in the interactions between silicate impurities and thermal barrier coatings, the first objective of this work was to understand the mechanisms of degradation to conventional 7YSZ TBCs in the presence of molten silicates. This understanding was focused firstly on a chemical understanding of the degradation mechanisms. Next, understanding how these impurities affect the mechanical robustness of the coatings.

With this chemical and mechanical understanding of the effects of ash on 7YSZ, an alternate TBC top coat material, Gd$_2$Zr$_2$O$_7$ was selected and demonstrated to mitigate the effects of molten silicate impurities. Again, following the broad headings of firstly understanding the chemical, then the mechanical, and finally the combined chemical/mechanical effects.
Lastly, a better understanding of the mechanics of delamination was developed. Starting with a previously published delamination model [18], an understanding of the modes of failure in the different coatings, with and without silicate impurities is undertaken. Modifications of this model are employed to provide insight into the prediction of failure, as well as to highlight several methods to lengthen the useable life of TBCs.
Chapter 5. Experimental Procedure

5.1 Introduction to Procedures

This chapter provides the general set of experimental procedures used in this work, and is broken down into sections concerning materials preparation, the various types of testing performed, and finally characterization of the resulting tests.

5.2 TBC Preparations

All TBC samples used in this work were air-plasma sprayed TBC on Haynes Alloy 214 substrates. The substrates were water jet cut from large sheets into 25.4 mm diameter circles, 3.175 mm in thickness. Samples used for chemical analysis had the TBC top coat material applied directly to the substrate. Samples used for mechanical testing were grit blasted, then had a proprietary NiCrAlY bond coat applied by vacuum plasma spraying at GE Aviation in Cincinnati, Ohio prior to the APS top coat application.

Top coats were applied at Stony Brook University in the Center for Thermal Spray Technology using an atmospheric direct-current plasma torch with an 8-mm diameter nozzle and a swirl flow gas distribution ring, Model f4-MB by Sulzer Metco
Inc. The powder feed stocks for these coatings were obtained commercially. The 7YSZ powder used in all of these studies was Saint-Gobain Grade 9204, and the Gd₂Zr₂O₇ powders were TransTech custom manufactured powder. The thickness target for the coatings used in this work was 200 microns, though some batch to batch variation does occur. Additionally, parameters were optimized such that the volume fraction of porosity in both sets of materials would be near 18% [82].

5.3 Impurity Preparations

Four separate impurities will be discussed in this work. Two coal fly ash samples, a blend of petroleum coke and coal ash from an IGCC gassifier, and finally volcanic ash from the Eyjafjallajökull volcano in Iceland. The diverse origin of each of these impurities is warrant to a closer examination.

Two coal fly ashes were obtained through collaboration with the Department of Mechanical and Aerospace Engineering, The Ohio State University. A lignite fly ash, referred to simply as lignite, is the impurity used for the majority of this work due to the large amounts obtained. A second fly ash was received from the Phoenix River Basin power plant, and is so named PRB. This is from a subbituminous coal, so it is chemically quite different from the lignite ash.

Prior to testing, these coal ashes were ball milled on a roller mill in Nalgene bottles containing yttria tetragonalized zirconia milling media (1cm diameter, Union Process) for three days in ethanol. This was done to ensure that the particulates were fine and had a narrow size distribution [70]. After milling, the ethanol was evaporated from
the ash and the resulting powder was crushed by hand to obtain a very fine, fluffy particulate.

Ash was obtained from Tampa Electric’s IGCC plant as well. This ash is primarily the result of a failure in the filtration system, which allowed ash to travel much further in the power generating process than it normally would. This ash is the result of the gasification of a petroleum coke and subbituminous coal blend, and will be referred to as the ash pet coke/ash blend.

The pet coke/ash blend, as received, had a very wide size distribution, ranging from particles under 50 microns to chunks larger than several centimeters. This ash was sieved to remove all particulates larger than 106 µm, then ball milled in the same fashion as the other coal ashes prior to any testing or analysis.

The chemical composition of these ashes was measured using wavelength dispersive x-ray florescence (WD-XRF) after dissolution into a lithium borate flux and fusion into glass beads with a flux to ash weight ratio of 10:1. The pet coke/ash blend would not dissolve in the flux, and was sent out for proton induced x-ray emission spectroscopy (PIXE) at Elemental Analysis Incorporated. The thermal properties were measured by differential thermal analysis (DTA) using an inert alumina reference at the Orton Ceramic Foundation. The DTA was performed with a temperature ramp of 10° C/min up to 1500° C in an air atmosphere.

Finally, ash from the Eyjafjallajökull volcanic eruption in March 2010 was obtained and studied on TBCs. This ash was provided through collaboration with the Institute of Geosciences at the University of Iceland. Chemical analysis of this ash
accompanied the obtained sample [83]. DTA was performed on a sample of this ash as well, as described above.

The viscosity of each of these silicate impurities was calculated using with a model proposed by Senior et al [80] based on the obtained chemical compositions of the various ashes. This viscosity was compared to the measured viscosity of multiple fly ash samples and found to be in general agreement with reported literature values [81].

Testing with the various ashes was performed by two methods. The first method, denoted here as the “baked on” method, was done for all of the isothermal testing and some of the thermal gradient testing. For this application method, ash was mixed with a small amount of ethanol to form a thin paste, which was dropped onto the surface of the TBC to be tested. The viscosity of the paste was adjusted to allow for a uniform and smooth layer of paste to be applied. The ethanol was then allowed to evaporate, and the mass was measured to determine the solids loading from the drop cast. This process was repeated until the desired loading was obtained.

The second method of applying ash, denoted as the “spray on” method was used exclusively in thermal gradient testing. Ash was mixed in the appropriate concentration in deionized water, sonicated and mixed for at least 15 minutes on a stir plate. This mixing allowed for a relatively good dispersion of the ash, though some of the ash settled to the bottom of the beaker after one hour if left in a non-mixing state. The mixed ash solution was then loaded into the thermal gradient burner rig, described below, and sprayed onto the surface of the TBCs during the hot portion of thermal cycling.
5.4 Isothermal Testing

Isothermal testing was performed primarily to determine the chemical interaction between the various ashes and the TBC top coat. Button samples of diameter 25.4 mm were quartered using a diamond wafering saw, and ash was applied using the bake on method described above. The ash loading was maintained at 35mg/cm$^2$ for the majority of samples with the coal fly ashes. On occasion, samples were loaded with a thinner ash layer of 8mg/cm$^2$ to allow for characterization of the reaction layers that formed. The samples loaded with volcanic ash were loaded with 15mg/cm$^2$ to conserve the limited quantity of ash available.

Once loaded with ash, the samples were placed in alumina crucibles with alumina lids and heat treated at various times and temperatures. The majority of the work presented here was heat treated at 1200° C for 24 h. This temperature was chosen based on engine operating conditions, and was sufficiently high to ensure melting of the impurity ashes. The time of 24 h was chosen because it was sufficiently long to see the full effects of the ash interaction with the top coat materials. Some additional testing was performed at longer times to ensure long-term stability. The specific time and temperature for each test will be presented with the results in the following chapters.

After heat treatment, the samples were typically sectioned and mounted in epoxy for characterization in cross section. Several samples were also observed from a top-down perspective to better understand the nature and location of the delamination.
5.5 Isothermal Cycling

Isothermal cycling tests were performed to measure the number of cycles to failure on coatings without ash. As will be highlighted in Chapter 9, isothermal cycling with ash present is not a representative test and is therefore only mentioned briefly.

The testing of samples without ash was performed to get an understanding of the lifetime of the coatings, and indirectly understand the toughness of the ceramic top coats. This testing was performed by using a bottom loading thermal cycling furnace, with a one hour cycle time. The samples are raised into the hot section where it ramps the temperature rapidly to the set point, typically taking about 5-10 minutes to reach temperature. The samples dwell at this temperature until a total time of 50 minutes have elapsed, including the ramp time, then the stage is lowered and a fan forces cooling air over the sample for 10 minutes, bringing the temperature back to near room temperature. A typical temperature profile of this type of test is shown in Figure 5.1.
One important note in performing this test is the arrangement and configuration of the samples. Samples should be placed on an angled piece of refractory, such as firebrick, so that the surface of the coating is angled towards the fan, giving more rapid cooling. This angled fixturing also allows for easy determination of spallation, since the spalled coating will then simply slide off the sample.

In these tests, failure is determined to be the number of cycles required for one half of the coating to be removed from the underlying metal. The one half spalled rule was judged by visual inspection, and not a quantitative measurement, however, in the majority of isothermal cycling, the entire coating would fail at the same cycle, leading to total spallation.
5.6 Thermal Gradient Testing

To better understand the effects of ash on the lifetime of TBCs, testing was performed in a custom built thermal gradient burner rig. This section first outlines the principals and use of the rig, then explains the experimental procedures used to obtain the results presented in Chapters 7 and 8.

5.6.1. Thermal Gradient Burner Rig

As previously mentioned, the protection afforded by TBC systems in use relies on a thermal gradient across the coating [11]. Active cooling channels achieve this with forced air cooling inside of the Ni superalloy components. This thermal gradient can lead to complex stress states due to thermal expansion mismatch between the underlying metal and the coating, and between the coating and the infiltrated by ash region of the coating [18]. To more accurately test coatings, a thermal gradient is needed. Additionally, as will be shown in Chapter 9, testing ash infiltrated coatings in isothermal testing is not a valid indicator of coating lifetime.

The thermal gradient burner rig presented here is based on the design of Vassen et.al [84] and the design of a similar piece of equipment at GE Aviation. A schematic drawing and photograph of the rig is shown in Figure 5.2. Samples are heated from one side with an oxygen-propane torch and actively cooled from the rear with compressed air during the hot portion of the cycle. During the cold portion of the cycle, the torch adjusts to a very small flame of only propane, and compressed air is sprayed at the front surface.
of the sample. Pyrometers are used to measure the temperature of the front and rear surface of the sample. Simultaneous injection of water and or ash is achieved with an auxiliary nozzle adjacent to the torch nozzle. The system is computer interfaced which records the temperature profiles and controls the flow of gases to the torch and thus control the temperature. A more detailed look at some of the critical components of the rig follows.

Figure 5.2. Schematic of the thermal gradient burner rig during (A) the heating cycle and (B) cooling cycle, and (C) photograph of the burner rig during the heating cycle.
For thermal gradient burner rig testing, samples are mounted between two Haynes Alloy 214 plates, which have been water jet cut from a larger sheet. Figure 5.3 shows a photograph of one of these plates from the inside. The beveled lip on both the front and rear plate allows the sample to sit between the plates loosely and not make damaging contact with the sample holder. The face plates distort in shape as a result of thermal cycling, and samples are periodically checked to ensure a loose fit, and not allow clamping of the sample between the metal. If needed, stainless steel washers were added between the plates to ensure adequate separation.

Figure 5.3 Photograph of the sample holder used in the thermal gradient burner rig. Samples are sandwiched between two of these plates with the inner lip allowing a loose hold on the sample.
The oxygen-propane torch used was originally intended to be used as a glass-working torch, primarily for high SiO$_2$ or “hard” glass. This torch was selected due to the flame size and because it is has two flame ports. The small pilot port premixes the combustion gases, while the larger main port uses surface mixing of the burning gases.

The flame velocity has not been measured, but with the ratio of propane and oxygen used, the velocity can be estimated to be near 4.5m/s, which is the maximum velocity for the combustion of these gases [85]. This slightly propane rich gas mixture was chosen to maximize flame velocity. This high flame velocity, while not directly studied in this work, can be useful in the testing on other types of coatings, such as environmental barrier coatings [86-88]. The fuel/oxidant ratio can be set to adjust the flame speed as needed for future testing.

Pyrometers are used to measure the temperature of the front and rear surface of the sample. The rear pyrometer measures emission at the spectral wavelength of 5µm. The emissivity of the Haynes Alloy 214 samples was calibrated to ensure accurate rear temperature measurements. This was achieved by first welding a thermocouple to the bare metal backside of a sample. This thermocoupled sample was placed in a box furnace and the temperature was measured and recorded against the furnace temperature over the range of 23-1100° C. Then, this sample was placed in the burner rig, and heated at constant gas flows until a steady state was reached. The emissivity value on the pyrometer was then set to minimize the error between the pyrometer and the thermocouple measurement. Over the entire temperature range, an emissivity value of 0.74 was chosen to provide the least error.
The front side pyrometer measures the spectral radiation emitted from the sample in the wavelength range of 8-11 microns. This spectral range was chosen so that the pyrometer would not measure emission from the burning of oxygen or propane. Additionally, at this wavelength, zirconia based materials have a known emissivity of near 1, eliminating the need for emissivity calibration or adjustment as a function of temperature [67].

Cooling air is supplied to the rear surface of the samples continuously during testing. During the cold portion of the cycle, a solenoid is opened to allow cooling air to flow to the front surface of the coating, while simultaneously, the flame is depleted of oxygen and the propane is turned down to a very low level. The compressed air inlet to the system is maintained at a constant pressure of 50 psi. The propane remains at this low level so reignition of the torch is not necessary between each cycle.

The rig is interface to a computer by a Labview data collection and control system. An automated program was written to control all parameters and collect the relevant data, such as temperatures and gas flows. The user interface of the program is shown in Figure 5.4. This program allows the burner rig to be used in a variety of modes, such as fully automated mode, or user controlled mode. In automated mode, the user defines a front temperature set point, and a simple PID loop controls the flow of gases to achieve the desired temperature. Additionally, the user can control some of the PID settings from the front interface to decrease the initial overshoot and allow for a smoother hold at temperature. A maximum back side temperature input is used to automatically stop the system if the coating has failed. Without the insulating coating, the backside temperature reaches a higher temperature, so this can be used as a program stop.
Figure 5.4 Front panel of the Labview program written to control thermal gradient burner rig.

The addition of fluid spray into the burner rig makes it a very versatile system for thermal gradient testing. The fluid is injected next to the primary flame nozzle using a commercial fluid sprayer. The fluid spray nozzle selected provides a fine conical spray of mist, which is primarily directed at the flame. This allows for injection of water, salts, or fine suspended particulates into the flame. The water vapor content experienced by the samples is estimated to around 25mL/minute of spray.
For the purposes of mechanical modeling, the temperatures at the front surface and at the interface between the top coat and bond coat are of primary concern. Since this latter temperature is not measured directly, and extreme transients are experienced during cooling, a simple finite element program was created to determine this interface temperature. Figure 5.5 shows the simplified geometry used in this model. Temperature dependant thermal conductivity as well as the density and heat capacity were input into the model with the measured temperature profile from the front and rear surfaces. The output was the interfacial temperature during the transient quenching of the sample.

![Figure 5.5. FEM model geometry used to calculate the temperature of the top coat/bond coat interface in thermal gradient cycling.](image-url)
5.6.2 Thermal Gradient Parameters

For the gradient work presented in this thesis, the thermal cycle consisted of 5 minutes of heating, followed by two minutes of cooling. A typical temperature profile is shown in Figure 5.6. This cycling was repeated either with or without the injection of water and ash until one half of the original TBC surface spalled. The one half threshold was determined by visual inspection.

![Figure 5.6 Typical temperature profiles from the thermal gradient burner rig showing the front side and backside temperatures for one thermal cycle.](image)

The procedure for testing of samples with spraying ash is nearly the same as without ash spray. For the ash-spraying sample in this work, ash loading of 1g/L of
deionized water was mixed as previously mentioned, and loaded into the fluid reservoir. The program was set to start the spray of ash three seconds into the hot cycle and stop at the end of the hot portion of the cycle. This three seconds without spray allows the flame to stabilize prior to the injection of fluid.

5.7 Characterization

An assortment of characterization techniques were used in this work to further the understanding of the various chemical and mechanical effects. As previously mentioned, many samples were sectioned, mounted in epoxy and polished in cross section using standard metallographic processing. These samples were examined in the scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) to determine chemical species present. The EDS was also used to generate elemental maps showing the extent of interaction between ash and top coat.

Image analysis was used to determine porosity of the materials based on the contrast of the resulting micrographs. In this analysis, at least 10 micrographs were used and the average was taken to ensure accurate measurements. The porosity of specific regions was also measured using image analysis. Here, micrographs were cropped to the region of interest, and the porosity was measured over multiple micrographs.

When called for, the focused ion beam (FIB) was used to extract and thin foils of material for examination in the transmission electron microscope (TEM). Samples examined in the TEM were examined in bright field and dark field modes, as well as high
angular annular dark field (HAADF) mode. Selected area electron diffraction (SAEDP) was used to identify phases in the reactions zones.

X-ray diffraction was used primarily for phase identification. Samples for XRD typically had a lower ash loading so that the signal could identify phases through the thickness of the interaction zone between the ash and top coat.
Chapter 6. Thermochemical Effects

6.1 Introduction

In this chapter, the chemical effects of the four ashes under study were determined first for 7YSZ, and then for the newer coatings of Gd$_2$Zr$_2$O$_7$. As mentioned in Chapter 5, these studies were performed on APS coatings of comparable thickness and porosity, typically consisting of one quarter of a 25.4mm diameter button samples. The TBC top coat was applied directly to the Ni superalloy substrate, which was Haynes Alloy 214. Care was taken to apply the ash evenly across the entire surface of the sample so as to produce uniform reactions.

The effects of ash will first be explored on 7YSZ samples. The reactions between the ashes will be shown for each ash followed by a generalized mechanism that can be applied to all of these contaminants. Next, the same procedure is followed for coatings of Gd$_2$Zr$_2$O$_7$. 

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6.2 Effects of Ash on 7YSZ

The chemical interaction of the four ashes with 7YSZ has been determined and is illustrated for each ash below, followed by a general mechanism by which silicate impurities interact with 7YSZ. Each of the chemical interaction tests were performed at 1200°C with a 24 hour hold time unless otherwise noted.

6.2.1 Lignite Fly Ash on 7YSZ

The first ash impurity studied was Lignite fly ash. The chemical and physical properties of this ash can be found in Chapter 3. A coating of 35 mg/cm² of ash was applied evenly to the top surface of 7YSZ coatings and the system was heat-treated. Figure 6.1 shows a cross section SEM image of the after interaction with the Lignite fly ash. The red dashed line shows the original thickness of the ceramic top coat. Large voids are clearly observable, and the microstructure has undergone many changes. Figure 6.1 also shows EDS maps of the sample showing the location of various chemical components. A higher magnification image of this sample is shown in Figure 6.2. Here, rounded grains of a lighter phase appear embedded in a dark matrix.
Figure 6.1. (A) Cross-sectional SEM micrograph after reaction between lignite fly ash and 7YSZ at 1200° C for 24 hours. Chemical EDS maps of (B) Si, (C) Ca, and (D) Zr show that the ash penetrated through the thickness of the coating. The dashed red line shows the original thickness of the coating.
Figure 6.2. Higher magnification SEM micrograph showing the interaction of lignite fly ash and 7YSZ after reaction at 1200° C for 24h.

A TEM foil was removed from the sample using the FIB in an area similar to that shown in the red box of Figure 6.1. The resulting foil is shown in Figure 6.3 with selected area electron diffraction patterns for several of the grains present. Additionally, EDS was performed and is shown in Figure 6.3 to show the chemical composition of some of the various regions.
Figure 6.3. (A) TEM bright field image of the resulting microstructure of an area similar to that in the red box in Figure 6.1. (B) SAEPD of tetragonal zirconia grain separated by glassy phase, as confirmed by (C) chemical analysis via EDS.

From the resulting microstructure and Figures 6.1-6.3, it is clear that the ash has penetrated through the entire thickness of the coating and has changed the microstructure drastically. The presence of yttrium in the glassy phase cannot be ruled out in by the EDS data presented in Figure 6.3C. The molten ash did manage to penetrate through the entire thickness of the coating, distorting the optimized microstructure in the as received sample.

The damage caused by lignite fly ash is similar to the observed damage from molten CMAS glass. Though chemically very different, the full penetration of the silicate impurities occurs in both systems at 1200°C in a timeframe of less than 24 hours.
Additional experiments were done at higher temperatures. Figure 6.4 shows the microstructure and EDS mapping of 7YSZ with Lignite 1250° C with a 24h dwell time. Again, full penetration is observed and large voids have formed throughout the thickness of the coating, effectively changing the microstructure of the coating.

Figure 6.4. (A) Cross sectional SEM micrograph of the reaction between lignite and 7YSZ at 1250° C for 24 hours. Elemental maps show the penetration of (B) Zr and (C) Si.

These changes in microstructure away from the optimized “as sprayed” condition are expected to drastically shorten the lifetime of the coatings, as well as affect the
coatings ability to insulate underlying metal components. The majority of fine porosity and splat boundaries that allow the coating to be strain tolerant are no longer present, and are instead replaced with large voids. The effects of ash on the lifetime of TBC coatings will be explored in Chapters 8 and 9.

6.2.2 PRB Ash on 7YSZ

While the origin of the PRB ash is different from that of the lignite ash, the overall chemical effects of the interaction are quite similar. Figure 6.5 shows cross sectional SEM as well as EDS mapping of the ash interacted TBC after 24h at 1200° C. The microstructure after reaction appears to be much more dense than in the as-received state.
Figure 6.5 Interaction between YSZ and PRB ash at 1200° C for 24 hours, showing (A) cross sectional SEM as well as EDS mapping of (B) Zr and (C) Si.

Figure 6.6 shows the cross sectional SEM and EDS mapping for testing at 1250° C for 24 hours. Again, full penetration has occurred, drastically altering the microstructure of the coating.
Figure 6.6 Interaction between 7YSZ and PRB ash at 1250° C for 24 hours showing (A) cross sectional SEM and EDS maps of (B) Zr and (C) Si.

The estimated viscosity of this ash is significantly lower than that of the lignite, so penetration of the open porosity and cracks would occur more rapidly at testing temperatures. Detailed TEM characterization was not performed of this sample since the interaction between 7YSZ and lignite fly ash had already been undertaken. One notable difference between the PRB ash and the lignite ash is the presence of large voids when reacting 7YSZ with lignite, which are not present in the reaction with the PRB ash. With the lower viscosity of the PRB ash, trapped gaseous species could escape the molten glass much easier, allowing for an overall densification without large void formation.
6.2.3 Pet coke Fly Ash Blend on 7YSZ

The effects of the pet coke/fly ash blend on the 7YSZ coatings were also considered. As previously stated, this ash came from an IGCC system which was experiencing filtration issues, so this may be the most relevant ash to study for land-based turbine applications. Testing was done for 24 hours at 1200° C, which is hotter than the turbine from which these samples came from typically runs [89]. The increased temperature was chosen to accomplish two things: firstly, to accelerate the testing, and secondly as operation temperatures increase with each generation of turbine, the elevated temperature was used to help understand problems before they arise in actual engines.

Figure 6.7 shows the cross sectional SEM and EDS chemical maps of the interaction between the pet coke/fly ash and a 7YSZ TBC. The formation of large voids was not as dominant in this reaction as it was in the interaction between 7YSZ and lignite with the same heat treatment.
Figure 6.7. (A) Cross-sectional SEM of the reaction between pet coke/fly ash blend and 7YSZ at 1200° C for 24h. EDS maps show that both (B) Si and (C) Zr run throughout the thickness of the sample.

The mechanism of this large void formation has not been studied extensively, as it is unlikely that an engine in use will see conditions where ash is applied at low temperatures in large amounts before interacting with the coating. However, it is believed that the volatilization of chemical species may be responsible for the formation of these voids. These gas pockets get trapped in the glass, and can escape if the viscosity is low enough, as is the case for the PRB ash. The lignite ash has a higher viscosity and therefore does not allow the bubbles to escape. In the case of the pet coke/ash blend, a
large concentration of SO$_3$ is present, which can volatilize at a temperature below the onset of melting in this ash, allowing the gaseous species to escape easily.

Regardless of the lack of large voids, full penetration of the molten ash was observed in this testing. This filling of the open porosity will limit the strain tolerance in the coating, and thermal expansion stresses will likely lead to premature failure of the coating during thermal cycling.

6.2.4 Volcanic Ash on 7YSZ

The chemical effects of volcanic ash from the Eyjafjallajökull volcano on conventional 7YSZ coatings were also investigated. Testing was performed at a lower solids loading of 15mg/cm$^2$ due to availability of materials. However, this ash loading has proven to be sufficient to fully penetrate coatings of 7YSZ. Again, testing was performed at 1200°C for 24 hours. Figure 6.8 shows the cross sectional SEM and silicon EDS map of this interaction. Full penetration is again observed, as are large voids near the surface of the sample.
Figure 6.8 Interaction of volcanic ash with 7YSZ, showing (A) cross-sectional SEM micrograph and EDS map of (B) Si.

Figure 6.9 is a TEM bright field image and selected area electron diffraction patterns from the areas indicated the glassy phase and monoclinic zirconia. EDS spectra of the glassy phase is also included in Figure 6.9. This foil was removed from an area similar to that of the red box in Figure 6.8.
Figure 6.9. Bright field TEM micrograph from a region similar to the red box in Figure 6.8, showing monoclinic zirconia separated by glass. SAEDP and EDS confirm that this phase is amorphous and composed of Si and Al, the major cations of the volcanic ash.

6.2.5 General 7YSZ Mechanism

The reaction mechanism between 7YSZ APS coatings and all four ash used in this study appear to be very similar. Degradation of the original coating microstructure
occurs by the following mechanisms, happening concurrently. The molten ash penetrates the open porosity and cracks present in the microstructure to accommodate the thermal expansion mismatch. Secondly, the molten ash penetrates the ceramic grain boundaries exfoliating the zirconia grains. Finally, reaction between the ash and ceramic leads to transformation of the t’ yttria stabilized zirconia grains into other zirconia phases with a lower concentration of yttria. This yttria is accumulated in the glassy phase, but does not appear to significantly alter the crystallization kinetics of the glass.

These three phenomena are remarkably similar in the cases of all four ash samples as well as in studies done with CMAS glass. This mechanism is depicted schematically in Figure 6.10. Here, the advancing molten glass front is shown to penetrate through the entire coating, as was observed with all four ashes.
6.3 Effects of Ash on Gd$_2$Zr$_2$O$_7$

Gadolinium zirconate, as previously discussed in Chapter 2, is an alternate top coat material, which has several desirable properties, such as a lower thermal conductivity. Previous studies have shown that EB-PVD coatings of Gd$_2$Zr$_2$O$_7$ were resistant to molten CMAS [66], but studies on coal derived ashes and volcanic ash has not been previously undertaken. The effects of each of the four ashes used in this study
on Gd$_2$Zr$_2$O$_7$ will be discussed in detail, with special attention paid to the arrest of the molten ash well short of full penetration.

6.3.1 Lignite Fly Ash on Gd$_2$Zr$_2$O$_7$

The reaction between lignite fly ash and gadolinium zirconate is quite different than the reaction between lignite and YSZ. Figure 6.11 shows the cross section SEM of a sample of Gd$_2$Zr$_2$O$_7$ and the sample after the reaction at 1200° C for 24 hours with corresponding EDS maps. A large amount of the original 35mg/cm$^2$ of ash remains on top of the sample, and a clear reaction zone is formed, under which the coating appears to be relatively unchanged. Again, the red line indicates the original thickness of the coating. Approximately 150 microns of un-infiltrated coating remain under this reaction zone of the original thickness of 200 µm.
Figure 6.11. Examination of the reaction between Gd$_2$Zr$_2$O$_7$ and lignite fly ash after isothermal heat treatment at 1200° C for 24h. (A) SEM micrograph and corresponding EDS maps of (B) Zr, (C) Si, and (D) Al.

A higher magnification look at the interaction zone is shown in Figure 6.12. In this micrograph, the top region is the lignite fly ash, then the interaction zone, and the bottom is the uninfiltrated Gd$_2$Zr$_2$O$_7$. Dashed lines have been drawn to highlight these different regions. A TEM foil was removed from the interaction zone in an area similar to the area shown by the box in Figure 6.12.
Figure 6.12. Higher magnification micrograph of the interaction between Gd$_2$Zr$_2$O$_7$ and lignite fly ash after isothermal heat treatment at 1200° C for 24h.

Figure 6.13 shows the thinned region of the TEM foil taken from this interaction zone along with selected area electron diffraction patterns of several of the observed phases. This region contains three major phases; a calcium-gadolinium-silicate apitite phase, an anorthite phase, and a calcium stabilized zirconia phase. The existence of these phases was confirmed by XRD, shown in Figure 6.14, which was performed on a sample tested with 8mg/cm$^2$ of ash. The lighter ash loading was to prevent the substantial ash deposit on the top of the reaction zone shown in Figure 6.11.
Figure 6.13 Examination of the interaction zone between Gd₂Zr₂O₇ and lignite fly ash. (A) Bright field TEM showing grains of several materials, including Ca₂Gd₈(SiO₄)₆O₂, cubic zirconia, and CaAl₂Si₂O₈. SAEDP shows these phases to be (B) Ca₂Gd₈(SiO₄)₆O₂ or apatite, (C) cubic zirconia, and (D) CaAl₂Si₂O₈ or anorthite. (E) EDS confirms the anorthite phase.
Figure 6.14 X-Ray diffraction pattern after reacting Gd$_2$Zr$_2$O$_7$ with 8mg/cm$^2$ lignite at 1200°C for 24 hours, confirming the phases found in the TEM.

The penetration was arrested around 50 µm into the original thickness of the coating, leaving approximately 150 µm of unaffected coating below the interaction zone. The mechanics of a partially penetrated coating will be presented in Chapters 8 and 9.

In the reaction zone shown in Figure 6.13, the presence of faceted, elongated grains is also observed. These grains are the apitite grains, and are more clearly seen in the high angle annular dark field (HAADF) image shown in Figure 6.15. Also seen in this micrograph are rounded grains. These grains are the transformed zirconia, in this case, calcium stabilized zirconia. This micrograph is oriented such that the top of the foil corresponds to the upper portion of the interaction zone.
Figure 6.15. HAADF micrograph of the interaction zone between Gd$_2$Zr$_2$O$_7$ and lignite fly ash after isothermal testing at 1200° C for 24h showing faceted apatite grains and rounded zirconia grains separated by amorphous glassy phase.

The mechanism for the formation of this dense reaction layer is explained as follows. The molten ash penetrates the surface pores and cracks, and begins to exfoliate grains just as in the case of 7YSZ. Additionally, dissolution of the Gd$_2$Zr$_2$O$_7$ is occurring, resulting in an accumulation of Gd and zirconium in the glassy phase.

Zirconium has a fairly low solubility in silica melts, and once the solubility limit is reached, the thermodynamically stable phase will precipitate out of the melt. In this case, with the large amount of Ca present in the melt, the thermodynamically stable phase is a calcium-stabilized zirconia. This leaves an accumulation of Gd in the molten glass,
which continues to accumulate until a critical amount is reached. This critical level allows for the nucleation and growth of the apatite phase, \( \text{Ca}_2\text{Gd}_8(\text{SiO}_4)_6\text{O}_2 \).

Precipitation of the apatite phase in turn depletes the molten glass of Ca and Si, shifting the remaining composition of the glass towards the alumina and iron oxide rich regions. If plotted on a CaO-SiO\(_2\)-Al\(_2\)O\(_3\) ternary phase diagram, this shift corresponds to a shift towards the anorthite phase. A 1200° C isotherm of this phase diagram is shown in Figure 6.16 with the starting composition of lignite in terms of the CaO, SiO\(_2\), and AlO\(_{1.5}\). The starting composition is very close to the anorthite field, and depletion of the glass of Si and Ca by the formation of apatite would shift the composition further into this area. As mentioned earlier, anorthite crystallizes relatively quickly compared to other phases in this system [90]. The crystallization of anorthite leaves little to no residual glassy phase.
Figure 6.16 Isotherm of the SiO$_2$-CaO-AlO$_{1.5}$ phase diagram at 1200° C with the starting composition of lignite fly ash marked.

The stability of this newly precipitated apatite phase is also a point of concern. Studies have shown that this phase is stable above 1400° C [91], which is higher than current engine operating conditions.

To ensure that this reaction zone truly arrests the molten front, testing was performed at much longer times. Figure 6.17 shows a representative SEM cross-section after 168 hours at 1200° C. The interaction zone does appear slightly thicker and less
uniform across the coating. However, between 100 and 150 microns of the coating appear to be un-infiltrated by the molten glass, which is slightly more penetrated than the 24 hour case. Note that the contrast was adjusted in the SEM to maximize the delineation of the interaction zone, so the residual ash sitting on top of the reaction zone appears black.

Figure 6.17 Cross-sectional SEM showing the interaction between lignite fly ash and Gd$_2$Zr$_2$O$_7$ after 168 hours at 1200º C. The bottom 100-150 microns appear to be un penetrated by the molten ash.
6.3.2 Pet coke/Fly Ash Blend on Gd$_2$Zr$_2$O$_7$

The interaction between the pet coke/fly ash blend and the Gd$_2$Zr$_2$O$_7$ coating was very similar to the interaction observed between the lignite ash and Gd$_2$Zr$_2$O$_7$. Penetration was arrested due to the formation of a dense reaction product layer, but in this case, the ash and reaction product layer spontaneously spalled off of the uninfiltrated coating. Samples of the coating and the spalled overlayer were collected and examined in cross section. Figure 6.18 shows the reaction product and residual ash layer that spalled from the surface. Again, long faceted crystals are observed and presumed to be apatite. Rounded grains of a transformed zirconia are also observed in the reaction layer.
Figure 6.18. (A) Cross-sectional SEM of the spalled region of the interaction between pet coke/fly ash blend and Gd$_2$Zr$_2$O$_7$ at 1200$^\circ$ C for 24h with the corresponding EDS maps of (B) Zr, (C) Gd, (D) Si, and (E) Al.
Figure 6.19 shows the uninfiltrated region of the sample. Note that the sample started at a coating thickness of \( \sim 200\mu m \), and the remaining coating is around 150\( \mu m \) thick. The mechanics of this type of spallation is explored in Chapter 9.

![Figure 6.19](image)

Figure 6.19 (A) Cross-sectional SEM of the interaction between \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) and pet coke/fly ash blend after 24h at 1200° C and corresponding EDS maps for (B) Zr, (C) Si, and (D) Al.

Clear similarities can be drawn between the interactions of the pet coke ash blend and the lignite interactions. The presence of a well defined reaction phase consisting of
faceted grains, shown to be a hexagonal apatite phase, and rounded zirconia grains appear to form an impervious reaction product layer, which prevents further penetration.

6.3.3 Volcanic Ash on Gd₂Zr₂O₇

The final chemical interaction under consideration is between volcanic ash and Gd₂Zr₂O₇ APS coatings. In this interaction, again a dense reaction layer forms, as shown in Figure 6.20. The interaction zone between the volcanic ash and the Gd₂Zr₂O₇ coating is much narrower than observed with any of the fly ashes, as evident by the lack of penetration of the Si seen in the Figure 6.20B. This may be due to the higher viscosity of the volcanic ash.

Figure 6.20. (A) Cross-sectional SEM showing the interaction between volcanic ash and Gd₂Zr₂O₇ coatings at 1200° C for 24h and corresponding EDS map for (B) Si.

A foil was removed from a region similar to the region indicated by a red box in Figure 6.20, and examined in the TEM. In this case, the interaction region was narrow
enough that the residual ash on top of the sample, the interaction zone, and the uninfiltred coating were contained within a single foil. This foil is shown in Figure 6.21 with SAEDPs and EDS of several of the phases present. Similar to the fly ash cases, the reaction zone contains an apitite phase, a transformed zirconia phase, and the residual ash phase. In contrast to the lignite ash, the volcanic ash has a small amount of calcium oxide present. This results in the apatite phase indexing to $\text{Gd}_{0.33}(\text{SiO}_4)_{2}\text{O}_6$ and the transformed zirconia phase indexing to tetragonal zirconia.
Figure 6.21 (A) Bright field TEM of the interaction zone between Gd$_2$Zr$_2$O$_7$ and volcanic ash after reaction at 1200° C for 24h. SAEDP of the phases in the interaction zone show the presence of (B) Gd$_{9.33}$(SiO$_4$)$_6$O$_2$ apatite, (C) tetragonal zirconia and (D) Gd$_2$Zr$_2$O$_7$. (E) EDS confirms that little no silicon is present in the Gd$_2$Zr$_2$O$_7$; the location of the major Si line is marked with red arrow.

Again, the mechanism is similar to the other observed Gd$_2$Zr$_2$O$_7$/ash interactions. The arrest is a result of accumulation of Gd in the molten ash, until a critical amount is
reached at which point precipitation of the apitite phase occurs. This leaves the cubic \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) depleted in Gd, which then transforms into the lowest energy, phase available, which in this case, is tetragonal zirconia. The growth of the apitite phases consumes much of the silica of the ash, which is composed of 90 wt% silica, effectively stopping the advancing front of the ash.

6.3.4 General \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) Mechanism

While minor differences arise due to the diverse chemistry of the impurities applied, the following general chemical mechanism can be attributed with the arrest of the penetrating molten ash. The ash rapidly flows into surface pores and cracks, and begins to penetrate grain boundaries. Additionally, dissolution of \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) grains enriches the glassy phase with Zr and Gd ions until the solubility limit for Zr is reached. At this point, the thermodynamically stable zirconia phase precipitates out of the melt. When a critical level of Gd ions is reached, nucleation and growth of an apatite phase begins, removing a good portion of the silica (and calcium if present) from the system. This shifts the remaining glass composition significantly, and creates a dense reaction product layer, preventing or drastically slowing any further penetration. This mechanism is shown schematically in Figure 6.22.
Figure 6.22 Schematic diagram showing the mechanism by which coatings of Gd$_2$Zr$_2$O$_7$ arrest molten silicates.

One major difference in the interaction of impurity ashes and the two coating types is the depth of penetration. This penetration is to be minimized so as to preserve the strain tolerant microstructure below, which prevents spallation of the coatings. In the subsequent chapters, coating lifetime is considered with and without impurity ash present, and the mechanics of delamination are examined in greater depth.
Chapter 7. Thermomechanical Effects

7.1 Introduction

The lifetime of TBCs is of great importance to engine designers, as it can limit the time and/or temperature of an engine. To that end, several tests have been employed to determine coating lifetime. In this work, isothermal cycling and thermal gradient burner rig testing are used to determine the coating lifetime. This chapter focuses on the lifetime of coatings without impurity ashes, and the following chapter deals with the effects of ash on the lifetime of coatings.

It is of note that the components tested in this work were flat button samples with underlying substrate of Haynes Alloy 214 and a NiCrAlY bond coat. This is a polycrystalline nickel superalloy, and not employed in new materials designs. One major difference relevant to this work between Haynes 214 and second or third generation single crystal superalloys is the thermal expansion coefficient (CTE), which is, on average, \(18.6 \times 10^{-6} \, \text{C}^{-1}\) over the temperature range of 25-1000°C for Haynes 214 [29]. The CTE for several other superalloys and bond coat materials is shown in Figure 7.1 [92-93]. The thermal expansion coefficient for 7YSZ is around \(11 \times 10^{-6} \, \text{C}^{-1}\) over the
same temperature range. This larger difference between CTEs is a major contributing factor when comparing lifetime numbers measured as a result of this work with lifetime numbers in the literature. However, all samples used in this work were of the same material and received the same bond coat, so lifetimes measured for the two top coat materials are truly an effect of the top coats.
Figure 7.1 Coefficient of thermal expansion for various superalloys and bond coats [92,93].
7.2 Isothermal Cycling to Failure

Isothermal furnace cycling is an industrial standard to determine lifetime of coatings, and principally used to compare changes in materials or processing [92]. These tests are typically done in the temperature range of 1000-1121° C, and usually do not exceed 1150° C. Testing at higher temperatures allows for excessive oxidation of underlying metal components such as the bond coat and substrate.

Previous results have shown the lifetime of 7YSZ APS coatings on similar substrates with the same NiCrAlY bond coat were performed at lower temperatures, but with much thicker coatings. At 1121° C, these samples failed after less than 50 cycles [94].

Since all of the chemical analysis testing was performed at 1200° C, and engine temperatures are moving towards ever increasing temperatures, isothermal cycling testing was performed on samples of 7YSZ and Gd$_2$Zr$_2$O$_7$ at 1200° C. The results are summarized in Table 7.1.

Table 7.1 Cycles to failure of 7YSZ and Gd$_2$Zr$_2$O$_7$ in isothermal and thermal gradient testing.

<table>
<thead>
<tr>
<th></th>
<th>Isothermal Cycles to Failure</th>
<th>Thermal Gradient Cycles to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>7YSZ</td>
<td>88</td>
<td>947</td>
</tr>
<tr>
<td>Gd$_2$Zr$_2$O$_7$</td>
<td>4</td>
<td>143 and 256</td>
</tr>
</tbody>
</table>
The large difference between number of cycles to failure in the previously tested samples at 1121°C and the samples tested here at 1200°C can be attributed to the high thickness of the coatings and temperature differences.

The other important difference is the difference between 7YSZ and Gd$_2$Zr$_2$O$_7$. Gd$_2$Zr$_2$O$_7$ has a significantly reduced toughness, and as a result, failure is observed at a much lower lifetime. Also, over long exposures, the chemical compatibility of Gd$_2$Zr$_2$O$_7$ with the forming TGO has been questioned [46]. One method that many in industry as well as in academic research have undertaken to improve the life of Gd$_2$Zr$_2$O$_7$ coatings is to apply a thin layer of 7YSZ onto the bond coat, then apply Gd$_2$Zr$_2$O$_7$ to the desired thickness. This methodology allows for the higher toughness 7YSZ to be at the critical interface where spallation is dominantly observed. However, the creation of a new interface between the 7YSZ and Gd$_2$Zr$_2$O$_7$ may now be the dominant location of spallation. Also, the processing of 7YSZ and Gd$_2$Zr$_2$O$_7$ in an APS system requires separate optimization for each material. Several researchers are currently undertaking work of this nature [95].

Layered coatings of 7YSZ and Gd$_2$Zr$_2$O$_7$ were prepared and used for thermal cycling lifetime prediction. Figure 7.2 shows the as-received cross sectional microstructure of these coatings from an optical microscope. At the time these coatings were produced, optimization of the processing had not been performed and extensive cracking and damaged interface between the two ceramic layers.
Figure 7.2 Optical micrograph of the as-sprayed layered samples, consisting on a Gd$_2$Zr$_2$O$_7$ top layer with 7YSZ as an intermediate layer, between the Gd$_2$Zr$_2$O$_7$ and bond coat.

The isothermal cycling of these layered coatings was not performed due to limited amounts of materials; however, thermal gradient testing was performed, and will be discussed in the following section.

7.3 Thermal Gradient Cycling to Failure

Since coatings were designed to be used in a thermal gradient, testing in gradient conditions can yield a much more comprehensive understanding of the forces and
damage mechanisms present in actual engine coatings, as well as a better understanding of coating lifetime. This testing was performed in our custom built thermal gradient burner rig, which is described in detail in Chapter 5. A sample temperature profile of one thermal cycle is shown in Figure 5.6.

The lifetime of several samples is tabulated in Table 7.1. All samples had the front surface temperature maintained at 1200°C for the duration of the hot portion of the cycle, and cooled to under 100°C by the end of the cold portion of the cycle. Since the thermal conductivities of YSZ and Gd$_2$Zr$_2$O$_7$ are significantly different, the temperature at the TBC/bond coat interface differed for the two materials. This interfacial temperature was calculated as 1050°C for 7YSZ samples, and 1038°C for Gd$_2$Zr$_2$O$_7$. This 12°C difference can make a significant difference in the growth of the TGO, and thereby greatly affect the stress behavior. Additionally, if thicker coatings were used, this difference would be much larger.

Again, a lower life was observed for the Gd$_2$Zr$_2$O$_7$ coatings compared to the coatings of 7YSZ. Photographs of the failed samples are shown in Figure 7.3. In this testing, failure was determined as one half of the original coating surface removed. From these macro images, the differences in failure modes can be observed. In the case of 7YSZ, deep delamination occurred across wide areas of the center region of the sample. Both Gd$_2$Zr$_2$O$_7$ samples appeared to fail by edge delaminations, which eventually spalled material around the sides of the samples and worked inwards.
Figure 7.3. Photographs of TBCs after failure in thermal gradient burner-rig testing of (A) 7YSZ after 947 cycles, and (B) Gd$_2$Zr$_2$O$_7$ after 143 cycles.

Figure 7.4 shows cross sectional SEM micrographs of the unspalled region of the two of the failed samples pictured in Figure 7.3. In both samples, cracking in the remaining coating is observed. In the YSZ sample pictured in Figure 7.4A, cracks along the interface between the bond coat and top coat are present. In Gd$_2$Zr$_2$O$_7$, the cracking clearly runs through the top coat and not the interface.

Figure 7.4 SEM micrographs of the unspalled regions of failed samples of (A) 7YSZ after 947 thermal cycles, and (B) Gd$_2$Zr$_2$O$_7$ after 143 thermal cycles.
The layered $\text{Gd}_2\text{Zr}_2\text{O}_7$/YSZ sample was also cycled to failure in the thermal gradient burner rig, and this sample survived 201 cycles. Figure 7.5 shows the sample after failure.

Figure 7.5 Photograph of layered 7YSZ/ $\text{Gd}_2\text{Zr}_2\text{O}_7$ sample after 201 thermal cycles.

The failure of this sample occurred primarily at the interface between 7YSZ and $\text{Gd}_2\text{Zr}_2\text{O}_7$. Figure 7.6 shows a top down SEM micrograph of the failed region of this sample and corresponding EDS maps. From these maps, a large amount of yttrium is observed in Figure 7.6 D, showing that failure occurred leaving much of the 7YSZ in place. This is not surprising considering the observed cracking seen between the layers, as shown in Figure 7.2.
Figure 7.6. (A) Top-down SEM micrograph of failed 7YSZ/ Gd$_2$Zr$_2$O$_7$ layered sample and corresponding EDS maps of (B) Zr, (C) Gd, (D) Y, (E) Al, and (F) Ni. The large amount of yttrium observed shows that the failure occurred between the Gd$_2$Zr$_2$O$_7$ and YSZ layers.

In addition to the lifetime, several other pieces of information can be obtained from these samples. With the temperature in a gradient, sintering rates can be approximated from the near surface region and the near interface region, resulting in the establishment of a sintering law that is time and temperature dependant. Also, the growth rate of the thermally grown oxide can be established from the resulting microstructure. In the following sections, these values will be calculated for use later in the modeling of delamination in Chapter 9.
7.3.1 Sintering Rate

Sintering, as pointed out in Chapter 2, is one microstructural change that occurs in TBCs that can contribute to their failure. This loss/decrease of porosity leads directly to a lower strain tolerance, an increased thermal conductivity, and an increased elastic modulus. To account for the role of sintering in this work, the effects of sintering will be taken into account in terms of the elastic modulus only.

To account for the effects of sintering on the elastic modulus, first a relationship between modulus and porosity must be established. Many such relationships have been numerically determined by use of complex finite element modeling. The result of these models can be very descriptive for a specific case, but lack the general nature to be applied across different coating morphologies.

An alternate approach is the use of semi-empirical models, which directly relate the amount of porosity to the elastic modulus. Figure 7.7 shows the result of one such model [96]. For this work, the relationship between porosity and elastic modulus is taken to be of the form

\[ E = E_0(1 - cp) \]  

Equation 7.1

where \( E \) is elastic modulus of the porous ceramic, \( E_0 \) is the fully dense elastic modulus, \( p \) is volume fraction porosity, and \( c \) is a constant.
Figure 7.7 Relationship between porosity and elastic modulus. In this case, the points are measured values, the solid line assumes spherical porosity, and the dashed line from another model [96].

From image analysis, the porosity before and after testing is tabulated in Table 7.2. This is the result of measuring at least 1mm$^2$ of area in the near surface and near interface regions, measuring only within a 20µm layer thickness. These porosity values are then used to calculate the elastic modulus using Equation 7.1.
Table 7.2 Results from image analysis showing the volume percent porosity in the top and bottom surface of the coatings after failure in thermal gradient cycling.

<table>
<thead>
<tr>
<th></th>
<th>7YSZ</th>
<th>GZO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting porosity, vol%</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>Top Surface Temp, C</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Top Porosity After Sintering, vol%</td>
<td>14</td>
<td>17.4</td>
</tr>
<tr>
<td>Bottom Surface Temp, C</td>
<td>1050</td>
<td>1038</td>
</tr>
<tr>
<td>Bottom Porosity After Sintering, vol%</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>TGO thickness at failure, µm</td>
<td>5.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Sintering laws can then be calculated in the form of [58]

\[
E(t,T) = \frac{\beta E_0 E_f}{\beta E_0 + E_f - E_0}
\]

Equation 7.2

where \(E_0\) is the elastic modulus at \(t=0\), and \(E_f\) is the fully dense elastic modulus. The parameter \(\beta\) is defined as

\[
\beta = 1 + A \exp\left(-\frac{E_A}{k_B T}\right)t^n
\]

Equation 7.3

where \(E_A\) is sintering activation energy, \(k_B\) is the Boltzmann's constant, \(n\) is the sintering coefficient, \(A\) is constant, \(t\) is time, and \(T\) is temperature. Table 7.3 shows the calculated constants for 7YSZ and Gd\(_2\)Zr\(_2\)O\(_7\). The resulting time and temperature dependence on the elastic modulus are plotted in Figure 7.8 for YSZ, with the TBC top surface sintering at 1200° C, and the TBC bottom sintering at 1050° C.
Table 7.3 Values used to obtain sintering and TGO growth laws for 7YSZ and Gd$_2$Zr$_2$O$_7$.

<table>
<thead>
<tr>
<th>Material</th>
<th>7YSZ</th>
<th>Gd$_2$Zr$_2$O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_A$</td>
<td>1.5</td>
<td>2.09</td>
</tr>
<tr>
<td>$E$ dense (GPa)</td>
<td>200</td>
<td>175</td>
</tr>
<tr>
<td>$E_0$ (GPa)</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>$A$</td>
<td>6.6x10$^3$</td>
<td>8.3x10$^5$</td>
</tr>
<tr>
<td>$n$, sintering</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>$k$, TGO growth</td>
<td>5.8x10$^{-9}$</td>
<td>4.9x10$^{-9}$</td>
</tr>
</tbody>
</table>

Figure 7.8 Elastic modulus of 7YSZ sample calculated from Equation 7.3 for the top surface at 1200°C and the bottom of the top coat at 1050°C.

The establishment of sintering kinetics will be incorporated into an existing delamination model in Chapter 9.
7.3.2 Thermally Grown Oxide Growth Rate

The growth rate of the thermally grown oxide is much simpler to calculate. The thickness of the TGO layer was measured at least 25 points for each sample, and the average thicknesses are tabulated in Table 7.2. The growth rates can easily be calculated assuming there is a zero thickness TGO layer in the as received samples, and that TGO growth rates are of the form [58]

\[
d_{\text{TGO}} = A_{\text{TGO}} \exp \left( -\frac{E_{\text{TGO}}}{k_B T} \right) t^n
\]

Equation 7.3

where \( A_{\text{TGO}}, E_{\text{TGO}}, \) and \( n \) are constants for a given material. The value of the TGO growth exponent was taken from literature [98] as 0.5. Since all of testing was done at one temperature, Equation 7.3 can simplify to

\[
d_{\text{TGO}} = k t^n
\]

Equation 7.4

where \( k \) is the reaction rate constant for the temperature of the bond coat for each material. The values of the materials constants for each material are tabulated in Table 7.3.

This growth rate is directly applicable to modeling of the stresses in coatings of this nature. However, the model presented in Chapter 9 does not rely directly on the growth rate of the TGO, but rather assumes that the growth alters the interfacial toughness of the material. Without a governing law relating the growth of the TGO to the interfacial toughness, this is difficult to incorporate in any meaningful way. However, TGO growth rates are presented here for future incorporation into mechanistic models at a later date.
Chapter 8. Combined Thermo-Chemical/Mechanical Effects

8.1 Introduction

With a solid understanding of the chemical interactions between the different types of ash and the top coat materials, and the lifetime of the coatings without impurities, the combined effects were examined. All thermochemical/thermomechanical testing was done with the lignite fly ash due to availability, and because the viscosity of this ash was near the middle of the obtained ashes. As a first approximation, a known concentration of ash was applied, baked on, and then samples were tested to failure. More representative testing was performed where ash was injected into the flame, resulting in a gradual deposition of the glassy phase during cycling. Results from both types of tests are presented.

Testing in isothermal cycling was not performed as the results produce little relevant data. As will be shown in Chapter 9, failure in an isothermal environment is expected in one thermal cycle if penetration into the coating occurs. An example of this from previous work is shown in Figure 8.1. Here, a TBC coating was tested isothermally with CMAS and failed on the first cycle.
8.2 Baked on Ash

As mentioned in Chapter 5, baked on testing was performed to bridge the gap between chemical testing and continuous spray testing. Here, a thin layer of ash was applied to coatings and baked in a box furnace at 800° C for 1 hour to enhance the adhesion of the ash to the coating. Samples were then cycled to failure in the thermal gradient burner rig described in Chapter 5.

The results of the cycling to failure are shown in Table 8.1. Also listed in this table are the measured lifetimes of the coatings with no ash in thermal gradient testing. The reduction in life for the 7YSZ coating is extremely high at 99.6%, while the
Gd$_2$Zr$_2$O$_7$ sample’s life was reduced by only 73.4%. As with the thermomechanical testing, the materials fail by different mechanisms.

Table 8.1 Results of cycling to failure of coatings of 7YSZ and Gd$_2$Zr$_2$O$_7$ with and without baked on lignite fly ash, and the resulting reduction in sample life.

<table>
<thead>
<tr>
<th>Ash Loading (mg/cm$^2$)</th>
<th>Cycles to Failure</th>
<th>Cycles to Failure With No Ash</th>
<th>Percent Reduction in Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>7YSZ</td>
<td>1.5</td>
<td>4</td>
<td>947</td>
</tr>
<tr>
<td>Gd$_2$Zr$_2$O$_7$</td>
<td>2.1</td>
<td>53</td>
<td>199</td>
</tr>
</tbody>
</table>

8.2.1 Baked Ash on 7YSZ

Surviving only 4 cycles, the 7YSZ sample loaded with 1.5mg/cm$^2$ of baked on lignite fly ash performed extremely poorly. Figure 8.2 shows a photograph of the failed sample, as well as cross sectional SEM of the unspalled region. In the SEM micrograph, penetration of the molten ash is observed ~70 micrometers into the coating, resulting in a much denser surface region, as marked by the dashed red line.
Figure 8.2 (A) Photograph and (B) cross-sectional SEM of YSZ sample with 1.5mg/cm$^2$ lignite ash baked on after 4 thermal cycles. The red line shows the depth of penetration of the molten ash.

Failure of this sample primarily occurred by deep delamination at the interface between the coating and the TGO. This layer is commonly thought of as the weakest
interface, and thus the most likely for failure to occur. This failure is similar to the observed failure without ash, though at an extremely accelerated pace.

8.2.2 Baked Ash on Gd$_2$Zr$_2$O$_7$

The sample of Gd$_2$Zr$_2$O$_7$ with baked on lignite faired slightly better than the 7YSZ, surviving 52 cycles before failure. In terms of life retention from non-ash sample, the Gd$_2$Zr$_2$O$_7$ retained 26.6% of the coating lifetime. Additionally, it is of note that the Gd$_2$Zr$_2$O$_7$ sample had a slightly larger ash loading than the 7YSZ at 2.1 mg/cm$^2$. Loading at these very low levels is difficult to control.

Figure 8.3 shows a photograph of the failed sample along with cross-sectional SEM of an unspalled region. A thin reaction zone is observable at the top surface of the coating. The thickness of the reaction zone varies across the sample, as the deposition process appears to be very localized, but the average thickness is 5 microns.
Figure 8.3 Photograph and cross sectional SEM of Gd$_2$Zr$_2$O$_7$ coating with 2.1mg/cm$^2$ of lignite ash baked on after failure from 52 thermal cycles.

The result of this lack of penetration is the retention of the optimized, porous microstructure. This microstructure allows for the strain tolerance needed to prevent spallation of the coating.
The failure mode of this sample appears to be cracking and degradation of the interface between the coating and the TGO. From the photograph in Figure 8.3, edge delamination also played a significant role in the failure of this sample.

8.3 Continuous Spray Ash

The spraying of ash onto samples during thermal gradient burner rig testing is a test that better represents deposition in actual engines. The spraying of ash is achieved by mixing the ash in a carrier fluid, in this case water, and spraying this mixture through an auxiliary nozzle adjacent to the torch.

With an ash spray system, questions arise as to whether ash will stick to the surface of the hot TBCs, or simply act as an erosive impacting the surface before being carried away. The other concern is whether the deposition, if occurring, is uniform. As will be shown in TBC samples after failure, deposition of the ash is occurring and appears to be fairly uniform across the coatings.

Three samples of 7YSZ and Gd$_2$Zr$_2$O$_7$ each were tested with a continuous spray of ash suspended in water at a loading of 1g/L, and the resulting lifetimes are shown in Table 8.2. Note the large disparity in lifetimes in the samples, which could be a result of the variability in the APS coating deposition process.
Table 8.2 Cyclic life of samples of 7YSZ and Gd$_2$Zr$_2$O$_7$ during continuous ash spraying during thermal cycling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cycles to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>7YSZ1</td>
<td>24</td>
</tr>
<tr>
<td>7YSZ2</td>
<td>29</td>
</tr>
<tr>
<td>7YSZ3</td>
<td>46</td>
</tr>
<tr>
<td>Gd$_2$Zr$_2$O$_7$1</td>
<td>31</td>
</tr>
<tr>
<td>Gd$_2$Zr$_2$O$_7$2</td>
<td>93</td>
</tr>
<tr>
<td>Gd$_2$Zr$_2$O$_7$3</td>
<td>57</td>
</tr>
</tbody>
</table>

8.3.1 Continuous Spray on 7YSZ

Samples of 7YSZ survived an average of 33 cycles with a continuous spray of ash. Figure 8.4 shows a photograph of the three failed samples. The dominant failure mode in all of these samples was shallow delamination under the deposited layer. Figure 8.5 shows the SEM cross sectional of sample 7YSZ1 after failure.
Figure 8.4 Photograph of three failed 7YSZ samples after thermal cycling with continuous spray of lignite ash.

Figure 8.5 Cross-sectional SEM of sample YSZ1 after failure at 24 cycles. The lignite fly ash has penetrated to a depth of 60-100µm, as indicated by the red line.
In the unspalled regions of the coating, the lignite fly ash has penetrated to a depth of 60-100 micrometers, as indicated by the red line in Figure 8.6. The depth of penetration, when compared to the baked on ash case, is very similar, however it took 24 cycles for this sample to reach this depth, implying that in the ash spray case, the deposition of the ash is the limiting factor in the penetration. It is also of note that in both cases, a penetrated layer of 60 – 100 microns is observed at failure. This shows that the stresses generated from a dense layer of this thickness surpass the toughness of the material on rapid cooling.

8.3.2 Continuous Spray on Gd$_2$Zr$_2$O$_7$

In the case of Gd$_2$Zr$_2$O$_7$ with a continuous spray of lignite fly ash, samples survived significantly longer than 7YSZ. As shown in Table 8.2, the lifetime of sample Gd$_2$Zr$_2$O$_7$:2 is approaching the values of the non-ash samples presented in Chapter 7, however there is a significant spread in the data. Figure 8.6 shows photographs of the three failed samples. From these images, failure is primarily observed around the outer edges of the samples, suggesting that edge delamination is a factor.
Figure 8.6 Photographs of the three samples of Gd$_2$Zr$_2$O$_7$ after failure.

Figure 8.7 shows a cross section SEM micrograph of sample Gd$_2$Zr$_2$O$_7$1 after failure at low magnification. The edge delamination failure mode is clearly shown in Figure 8.7, which was taken near the edge of the unspalled coating. Figure 8.8 shows a higher magnification image taken near the center of the sample, at the top of the coating. Here, a dense reaction product layer has formed, and further penetration has been arrested. This confirms the results of the thermochemical testing presented in Chapter 6. The formed reaction layer has a thickness of 2µm.

Figure 8.7 Cross-sectional SEM of sample Gd$_2$Zr$_2$O$_7$1 after failure at 31 cycles.
Sample Gd$_2$Zr$_2$O$_7$2 survived the longest at 94 cycles. From the photograph in Figure 8.6, edge delamination again appears to be the dominant cause of failure. Cross sectional SEM is shown in Figure 8.9 after failure. This micrograph confirms that edge delamination is the major cause of spallation in this sample.
Figure 8.9 Cross-sectional SEM of sample Gd$_2$Zr$_2$O$_7$2 after failure at 93 cycles showing edge delamination.

Figure 8.10 shows SEM of Gd$_2$Zr$_2$O$_7$2 near the surface of the unspalled region. Here, a reaction zone of about 10 microns in thickness is observed, with some additional ash deposits remaining on top of this reaction zone. This implies that the reaction zone could be fully developed, and prevent further deposition of ash from penetrating into the coating.
Overall, the effects of the lignite fly ash in thermal gradient testing have shown to greatly reduce the life of TBC top coats. When spraying ash onto the surface during cycling, the average life of Gd$_2$Zr$_2$O$_7$ coatings was found to be nearly twice that of 7YSZ coatings. Further process optimization in the air plasma spray process and or the use of a YSZ underlay could further improve the life of Gd$_2$Zr$_2$O$_7$ coatings.
Chapter 9. Delamination Modeling

9.1 Introduction

The mechanics of delaminations in TBC systems are very complex, and involve transient temperature and stress distributions, and materials properties that change over time. The addition of a penetratating glassy phase further complicates the problem. The majority of research has focused on the use of finite element analysis combined with experimental results to show validity [40, 53-54, 99-100]. In this approach, the results obtained are often very specific to a specific coating or system, or only focus on one aspect of stresses leading to spallation.

The approach taken in this work follows the work of Evans and Hutchinson [18]. They proposed a simplified multilayered model, and used standard linear elastic fracture mechanics to determine if a coating will spall on a single cool down. The mechanics are applicable whether a dense outer layer is present or not, and delamination depth can be adjusted to account for shallow or deep delamination. This model is presented in a convenient, albeit simplified fashion here, followed by examining several cases of interest. Finally, adjustments to this model will be discussed to further the understanding of TBC delamination.
9.2 Delamination Model

Assume a materials system such as the one pictured in Figure 9.1. A dense outer layer, if present, of thickness \( h \) sits atop a porous TBC. The total thickness of these layers is then \( H \). At depth \( d \), a crack sits, and if the forces are right, will result in delamination. Since APS coatings are highly porous and have splat boundaries and other defects present, this \( d \) could range from near surface cracking to deep delamination where \( d=H \).

Figure 9.1 Schematic of the system used for delamination modeling. A delamination crack at depth \( d \), exerts a force \( P \) and moment \( M \) on a coating of thickness \( H \), which is penetrated by molten deposits to a depth \( h \).
Experimentally, all delaminations occur during cooling. If we assume a stress free state at high temperature, then the relevant stresses are those from the cool down. At \( t_0 \), the initial temperature profile can vary significantly depending on if the sample is being tested isothermally or in thermal gradient. The addition of a dense, glass-penetrated layer again adds to the complexity, having a higher thermal conductivity than the un-infiltrated top coat [71].

On cooling, the change in temperature at the surface and at the TBC/TGO interface are defined as \( \Delta T_{\text{sur}} \) and \( \Delta T_{\text{sub}} \), and the difference between these two is defined as \( \Delta T_{\text{sur-sub}} \).

Stresses arising from the rapid quenching of the system are going to be a result of thermal expansion mismatch between the coating and substrate, \( \Delta \alpha \), and a result of differential quenching if applicable. The stress generated in the dense layer is then

\[
\sigma(\eta) = \frac{E_1 \alpha_{\text{coating}} \Delta T_{\text{sur-sub}}}{(1 - \nu_1)} (1 + c_1 \eta - \phi) \tag{9.1}
\]

and the stress generated in the coating is

\[
\sigma(\eta) = \frac{E_2 \alpha_{\text{coating}} \Delta T_{\text{sur-sub}}}{(1 - \nu_2)} (c_2 (1 + \eta) - \phi) \tag{9.2}
\]

where \( E \) is the elastic modulus, \( \alpha \) is the thermal expansion coefficient, \( \nu \) is Poisson’s ration and \( \eta = y/H \), describing the position. The parameter \( c \) is defined by

\[
c_1 = \frac{k_2 / k_1}{1 - h/H (1 - k_2 / k_1)} \tag{9.3}
\]

\[
c_2 = \frac{1}{1 - h/H (1 - k_2 / k_1)}
\]
where \( k \) is the thermal diffusivity, and the subscripts 1 and 2 denote the dense layer and the uninfiltrated TBC, respectively. The final parameter needed to determine the stress distributions is the dimensionless ratio of mismatch strains, defined as

\[
\phi = \frac{\Delta \alpha \Delta T_{sub}}{\alpha_{coating} \Delta T_{sur-sub}}. \tag{9.4}
\]

With these stress distribution, a force and moment per unit length of the uncracked region above the delamination crack can be defined as

\[
P = \int_{-d}^{0} \sigma(y) dy, \tag{9.5}
\]
\[
M = \int_{-d}^{0} \sigma(y)(D + y) dy
\]

where \( D \) is the location of the neutral bending axes, which can be determined by \( D = d - Rh \). In this equation in which the notation from the literature deviates for clarity, \( R \) is defined as

\[
R = \frac{\mu^2 + 2\Sigma \mu + \Sigma}{2(\mu + \Sigma)} \tag{9.6}
\]

where \( \mu = (d/h)-1 \) and \( \Sigma = (1+\alpha_0)/(1-\alpha_0) \). \( \alpha_0 \) is the Dunders elastic mismatch parameter [101], defined as

\[
\alpha_D = \frac{E_1 - E_2}{E_1 + E_2} \tag{9.7}
\]

where the bar indicates that these are the plane strain modulus, defined as

\[
\bar{E} = \frac{E}{1 - v^2} \tag{9.8}
\]

When considering the case of a dense layer atop of an uninfiltrated layer, the energy release rate can be determined from
\[ G = \frac{1}{2E_2} \left( \frac{P^2}{Ah} + \frac{M^2}{lh^3} \right) \]  
Equation 9.9

where \( A = \mu + \Sigma \), and the moment of inertia, \( I \), is defined as

\[ I = \frac{\Sigma(3(\Delta - \mu)^2 - 3(\Delta - \mu) + 1) + 3\Delta \mu(\Delta - \mu) + \mu^3}{3} \]  
Equation 9.10

where all terms have been previously defined.

If this calculated energy release rate from Equation 9.9 exceeds a critical value determined by the fracture toughness, failure will occur. This critical energy release rate takes the form

\[ \Gamma_c = \Gamma_{ic}(1 + \tan^2((1 - \lambda)\psi)) \]  
Equation 9.11

where \( \Gamma_{ic} \) is the mode I fracture toughness of the material, \( \lambda \) is the mode mixity, and \( \Psi \) is the phase angle, given in terms of the stress intensity factors as \( \Psi = \tan^{-1}(K_{II}/K_I) \). \( K_I \) and \( K_{II} \) are defined as

\[ K_I = \frac{P}{\sqrt{2Ah}} \cos \omega + \frac{M}{\sqrt{2lh^3}} \sin \omega \]  
Equation 9.12

\[ K_{II} = \frac{P}{\sqrt{2Ah}} \sin \omega + \frac{M}{\sqrt{2lh^3}} \cos \omega \]

where \( \omega = 52.1^\circ \) [103].

One note is the importance on the mode mixity parameter, \( \lambda \). A \( \lambda \) value of 1 represents an extremely mode dependant failure, while a value of 0 illustrates a failure which is mode independent. Since toughness anisotropy is extremely difficult to measure in coatings of this nature, the resulting mode mixity of failure is best estimated at a conservative value around 0.25.
With these mechanics established, delamination maps can be produced by setting Equation 9.9 and 9.12 equal, and solving for the temperature parameter $\Delta T_{\text{sur-sub}}$ as a function of $\Delta T_{\text{sub}}$. A sample map taken from [18] is shown in Figure 9.2. The maps are arranged in this fashion to highlight the effects of cooling on the delamination of coatings. Cooling trajectories can be superimposed onto these maps to determine if failure is expected or not. Included in Figure 9.2 are three cooling trajectories. Cooling trajectory 1 shows a very uniform cooling, resulting in a small $\Delta T_{\text{sur-sub}}$. Notice that it crosses from the no delamination zone into the delamination zone during cooling. Trajectory 3 shows an extremely rapid surface cooling, yet still crosses into the delamination zone. In this scenario, only cooling trajectory 2 is expected to not spall.

Figure 9.2 Delamination map with three cooling trajectories superimposed to show the utility of this model [18].
Figure 9.2 also shows the effect of $\lambda$ with values ranging from 0 to 1. Notice that the top portion of the delamination map does not change significantly with $\lambda$. In this region, failure is dominantly due to mode I loading conditions, where a rapid surface cooling (rapid compared to the cooling at the interface) puts the interface in tension. The right side of the delamination contour is loaded in mixed modes, and thus depends greatly on $\lambda$.

Full details and development of this delamination model as presented can be found in the literature [18].

9.3 Isothermal Infiltration

It was mentioned previous in this work that testing TBC samples isothermally in the presence of a penetrating impurity provides very little useful data. Figure 9.3 shows a delamination map generated for 7YSZ coatings on Haynesalloy 214 substrates, the samples used in this work. The values used for all materials properties are tabulated in Table 9.1. Several maps are superimposed with different $h/H$ ratios, showing the effects of differing amounts of penetration of the molten ashes. The cooling trajectory plotted represent that of isothermal testing, where all parts of the sample are expected to cool at the same rate, resulting in no $\Delta T_{\text{sur-sub}}$. 
Figure 9.3. Delamination map for 7YSZ with various amounts of penetration. The red arrow shows the cooling trajectory for isothermal testing, and the blue line shows the cooling trajectory for testing in a thermal gradient. Note that the red line crosses the delamination contours if the penetration is greater than 10% of the coating thickness.

Table 9.1 Materials properties used to generate delamination maps [18].

<table>
<thead>
<tr>
<th>Material</th>
<th>In-Plane Elastic Modulus (GPa)</th>
<th>Thermal Expansion Coefficient (ppm/C)</th>
<th>Poisson Ratio</th>
<th>Mode I Delamination Toughness (J m$^2$)</th>
<th>Thermal Diffusivity (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBC as Deposited</td>
<td>20</td>
<td>11</td>
<td>0.2</td>
<td>45</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>Ash infiltrated</td>
<td>172</td>
<td>11</td>
<td>0.2</td>
<td>-</td>
<td>$2 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
Notice that with very small amounts of penetration, the cooling trajectory crosses
the boundary into the delamination zone on the map. The same is true for Gd$_2$Zr$_2$O$_7$
coatings. The result is that any dense layer atop the TBC will result in spallation in
isothermal testing above ~900°C. Testing below this temperature is unrealistic in terms of
engine temperatures as well as below the melting range of the impurity glasses.

Isothermal testing with impurity ashes was not performed in this work for this
reason. In previous work [97], this testing did show spallation on the first cycle with any
amount of impurities for a variety of coatings and conditions, as shown in Figure 8.1.

The materials properties used to form the delamination maps, tabulated in Table
9.1 are warrant of further discussion. The values used are the values used by the models
authors [18]. An elastic modulus of 20 GPa for an APS coating is within the realm of
achievable moduli. Also, since 7YSZ has been shown for decades to be the toughest
TBC material, the value of 45 J/m$^2$ seems appropriate. For coatings of Gd$_2$Zr$_2$O$_7$, this
value of toughness is probably overestimated.

Table 9.2 shows the measured values of the surface temperature, interface
temperature, and cooling parameters $\Delta T_{\text{sub}}$ and $\Delta T_{\text{sur-sub}}$ for each sample of 7YSZ,
Gd$_2$Zr$_2$O$_7$, and the layered sample with the number of cycles to failure for each sample.
These cooling parameters can then be plotted on delamination maps as the end point of
the cooling trajectory to determine if spallation is expected.
Table 9.2. Tabulated values of the cooling parameters measured for all samples tested in thermal gradient testing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ash</th>
<th>$T_{\text{surf}}$</th>
<th>$T_{\text{backside}}$</th>
<th>$T_{\text{interface}}$</th>
<th>$\Delta T_{\text{surf}}$</th>
<th>$\Delta T_{\text{sub}}$</th>
<th>$\Delta T_{\text{surf-sub}}$</th>
<th>Life (cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>none</td>
<td>1200</td>
<td>905</td>
<td>1023</td>
<td>1129</td>
<td>947</td>
<td>182</td>
<td>947</td>
</tr>
<tr>
<td>GZO</td>
<td>none</td>
<td>1200</td>
<td>907</td>
<td>1011</td>
<td>1117</td>
<td>964</td>
<td>153</td>
<td>143</td>
</tr>
<tr>
<td>GZO</td>
<td>none</td>
<td>1197</td>
<td>930</td>
<td>1028</td>
<td>1094</td>
<td>904</td>
<td>190</td>
<td>264</td>
</tr>
<tr>
<td>YSZ</td>
<td>baked on</td>
<td>1207</td>
<td>859</td>
<td>992</td>
<td>1154</td>
<td>1039</td>
<td>115</td>
<td>4</td>
</tr>
<tr>
<td>GZO</td>
<td>baked on</td>
<td>1197</td>
<td>961</td>
<td>1048</td>
<td>1122</td>
<td>1006</td>
<td>116</td>
<td>53</td>
</tr>
<tr>
<td>YSZ</td>
<td>spray</td>
<td>1201</td>
<td>1026</td>
<td>1095</td>
<td>1153</td>
<td>1009</td>
<td>144</td>
<td>24</td>
</tr>
<tr>
<td>YSZ</td>
<td>spray</td>
<td>1201</td>
<td>961</td>
<td>1056</td>
<td>1138</td>
<td>983</td>
<td>156</td>
<td>46</td>
</tr>
<tr>
<td>YSZ</td>
<td>spray</td>
<td>1200</td>
<td>1013</td>
<td>1088</td>
<td>1128</td>
<td>981</td>
<td>147</td>
<td>29</td>
</tr>
<tr>
<td>GZO</td>
<td>spray</td>
<td>1200</td>
<td>915</td>
<td>1016</td>
<td>1137</td>
<td>1009</td>
<td>128</td>
<td>57</td>
</tr>
<tr>
<td>GZO</td>
<td>spray</td>
<td>1201</td>
<td>947</td>
<td>1036</td>
<td>1135</td>
<td>990</td>
<td>145</td>
<td>93</td>
</tr>
<tr>
<td>GZO</td>
<td>spray</td>
<td>1201</td>
<td>1027</td>
<td>1088</td>
<td>1148</td>
<td>1000</td>
<td>148</td>
<td>31</td>
</tr>
<tr>
<td>YSZ/GZO</td>
<td>spray</td>
<td>1201</td>
<td>902</td>
<td>1000</td>
<td>1093</td>
<td>883</td>
<td>210</td>
<td>201</td>
</tr>
</tbody>
</table>

9.4 Thermal Gradient Testing of 7YSZ

The chemical and mechanical effects of lignite fly ash on 7YSZ coatings have been outlined in previous chapters. Here, the observed results are interpreted in terms of the delamination model.

Figure 9.4 shows the delamination map for shallow delamination of $h=d$ with $h/H$ ratios of 0.1, 0.2, 0.3 and 0.5. Shallow delamination was observed in all 7YSZ samples with continuous spray of ash. Also included in Figure 9.4 are the points indicating the final points on the cooling trajectories for the three 7YSZ samples tested with continuous
spray of ash. The three cooling parameters from the three samples are closely bunched, illustrating the repeatability of the burner rig. This bunch of points is centered around the h/H contour of 0.3, indicating that the samples should fail when penetrated 60µm of the original 200 micron thickness. In the intact regions after failure, the penetration was observed to be in the range of 60-100 µm. While not a perfect fit to the model, this shows a reasonably good fit to the observed infiltration.

Figure 9.4. Delamination map for 7YSZ assuming shallow delamination just under the penetrated region. Maps generated for h/H ratios of 0.1 (blue), 0.2 (red), 0.3 (yellow), and 0.5 (green). Cooling parameters for three 7YSZ samples tested with continuous spray of ash plotted as red x-marks.
Similar degrees of penetration were observed in the other ash sprayed samples at the time of spallation, though the number of cycles to failure varies. This difference in cycles to failure while having nearly the same amount of penetration highlights the sample to sample variation in the APS deposition process as well as the variation in the spraying of ash during testing.

The key to understanding this type of shallow delamination using the model presented here is that delamination is expected at the instant a delamination contour is crossed. In the above example with shallow delamination of 7YSZ, the stresses and thus total driving force for delamination is greater at the bond coat/TBC interface than it is at the observed delamination. However, as the differential cooling is occurring, the outer surface is the first to drop in temperature, and this temperature drop progresses inward. As shown, the stresses are generated from this differential cooling. This time dependence is not directly taken into account in the model. For a more complete understanding of the mechanics of this type of shallow delamination, additional modeling is needed. Finite element modeling could provide further insight into this type of shallow delamination.

9.5 Thermal Gradient Testing of Gd$_2$Zr$_2$O$_7$

The mechanics modeling of Gd$_2$Zr$_2$O$_7$ was also performed. Figure 9.5 shows the delamination map assuming deep delamination at the TGO interface (H=d) for values of h/H of 0, 0.1, 0.2, 0.3, and 0.5. From Chapter 8, the observed penetration was, on average, 10 microns. The cooling parameters from the three Gd$_2$Zr$_2$O$_7$ samples have
been added to the delamination map as well. Notice that these points are clustered around the h/H=0.3 contour. With an observed dense layer of on 10 microns, or h/H=0.05, delamination of these samples is not expected without further deposition of dense material or a growing of the reaction zone.

Figure 9.5 Delamination maps for deep delamination with h/H ratio of 0 (light blue), 0.1 (red), 0.2 (yellow), 0.3 (green), and 0.5 (purple). Red X’s indicate the cooling parameters of the three samples of Gd$_2$Zr$_2$O$_7$ tested with continuous spray of ash.

One major difference between Figures 9.4 and 9.5 is that for 7YSZ, failure is predicted by the delamination map. For Gd$_2$Zr$_2$O$_7$, failure should not have occurred with the observed degree of penetration. This premature failure could come from a variety of sources, but likely stems from either the lower fracture toughness of Gd$_2$Zr$_2$O$_7$ or the
APS processing conditions, and lack of their optimization. Gd$_2$Zr$_2$O$_7$ is a much newer coating, and there is much less expertise in finding the optimum deposition parameters for this material.

9.6 Insight Gained From Delamination Model

The delamination model presented here has been shown to be in good agreement to predict the failure of 7YSZ coating. Several of the materials and system properties can have a significant effect on the delamination in a given system. This section seeks to explain the effects of a few key parameters, and their effect on delamination.

The first parameter under consideration is the toughness of the ceramic. Figure 9.6 shows a series of delamination maps, calculated for 200micron thick top coat with the properties 7YSZ, but varying the toughness. Contours are plotted for toughness values of 30, 45, and 60 J-m$^{-2}$. Achieving coatings with a toughness of 60 J-m$^{-2}$ may not be possible, but it is included for the sake of discussion. Producing coatings of decreased toughness is all too easy to achieve through the use of non-optimized deposition parameters.
An increased toughness moves the delamination contour out, allowing for an increase in the safe, or no delamination area. The critical energy release rate, from Equation 9.11, scales linearly with the toughness, so it is not surprising that the delamination contours do as well.

Coating thickness is a parameter that is controlled by time of deposition. While thicker coating do afford added thermal insulation, they also typically lead to a decreased life. Figure 9.7 shows delamination contours for 7YSZ with thicknesses of 100, 200, 500µm and 1mm.
The added insulation that thicker coatings provide makes a straightforward analysis of Figure 9.7 difficult. The temperature of the interface under a thick coating will be significantly lower than the interface temperature under a thin coating, assuming the same surface temperature. This translates into a lower value of $\Delta T_{\text{sub}}$ over the cooling cycle. The combined effects of this increased insulation and shrinking of the safe zone is dependant on testing conditions.

The final coating parameter under investigation here is the elastic modulus. The in-place modulus can be controlled through the volume percent porosity present in the coating. Figure 9.8 shows delamination maps for a 200µm thick YSZ coating with modulus of 20, 30, and 50 GPa.
From Figure 9.8, clearly the lower elastic modulus allows for a significantly larger area of safe quenching. Adjusting the elastic modulus by means of adjusting the porosity can have other, significant affect on the overall system. The porosity directly affects the thermal conductivity and fracture toughness. As shown in Figure 9.7, a decrease in fracture toughness shrinks the safe zone, and could result in delamination.

9.7 Modification of Delamination Model

This model, as described takes into account the cooling from a stress free state. However, simple modifications can be performed to account for some aspects of the time
and thermal history dependences of the thermal cycling. The use of simple sintering laws as described in Chapter 7 can allow for the adjustment of the in plane elastic modulus to account for sintering of the ceramic top coat.

Figure 9.9 shows delamination maps for 7YSZ in an as received state, and after 947 thermal cycles, which is the number of cycles to failure observed in 7YSZ with no ash. The only adjustment between these two delamination curves is the elastic modulus. The modulus was taken to vary as a function of time at temperature, but a single value modulus was used for the calculation. Figure 9.9 shows three delamination contours, corresponding to an elastic modulus of as received, the sintered value of the bottom of the coating, and the sintered top of the coating after 947 cycles.

Figure 9.9 Delamination maps with E values of as-sprayed, and after sintering at the top and bottom of the coating. Cooling trajectory does not cross contours.
A typical cooling trajectory as also been added to this curve. Sintering appears to play a role in the decreasing of the non-delamination zone, but cannot explain the delamination solely. Rather, other mechanisms, which are working concurrently, are taking place.

The growth of the TGO is one of these factors that affects the stress states in the interface region. However, no clear approach has been found to include TGO growth into the model other than using this growth stresses as a scalable parameter to adjust the interface toughness. A clear relationship showing the effects of thermal cycling on the interfacial toughness goes into the realm of damage mechanics, and is not considered here.
Chapter 10. Conclusions

10.1 Conclusions

The interaction between four different ashes with two thermal barrier coating top coat materials were studied from a chemical and mechanical point of view. The ash impurities used in this study included two coal fly ashes, a petroleum coke/fly ash blend, and ash from the Eyjafjallajökull volcano in Iceland. These impurities were tested on APS thermal barrier coatings of conventional 7YSZ, and $\text{Gd}_2\text{Zr}_2\text{O}_7$, a low conductivity alternative material.

At temperatures similar to gas turbine operating temperatures, each of the impurity ashes was found to penetrate through the entire thickness of 7YSZ coatings. This occurs by three mechanisms, occurring concurrently. These are (i) flowing into open pores and crack, (ii) wetting zirconia grain boundaries and exfoliating grains, and (iii) dissolution of metastable t’ zirconia and precipitation of yttria-depleted zirconia.

In contrast to 7YSZ, the reaction between $\text{Gd}_2\text{Zr}_2\text{O}_7$ coatings and each of the molten ashes at high temperatures formed a reaction layer, which arrested the molten ash and prevented further penetration of the molten ash. This occurs by dissolution of the $\text{Gd}_2\text{Zr}_2\text{O}_7$ grains, which enriches the glass with Gd and Zr ions. The solubility limit of Zr
is quickly reached, and precipitation of the thermodynamically stable phase occurs. When enough gadolinium has accumulated in the glass, precipitation of a stable apatite phase occurs. This precipitation shifts the remaining composition of the glass towards the anorthite phase, which crystallizes relatively easily.

The lifetime of coatings of 7YSZ and Gd$_2$Zr$_2$O$_7$ were tested isothermally and in thermal gradient without ash impurities. The results showed a significantly longer life for 7YSZ.

Coatings of each material were tested in thermal gradient with impurity ashes as well. Under a continuous spray of ash, the life of Gd$_2$Zr$_2$O$_7$ coatings was found to be nearly twice that of 7YSZ. When small amounts of ash were baked onto the surface of the coatings, the Gd$_2$Zr$_2$O$_7$ coatings lasted thirteen times longer than 7YSZ.

Finally, the mechanics of delamination were explored to reveal several interesting features. Firstly, the failed coatings of 7YSZ can be explained in terms of thermal expansion and elastic mismatch between the underlying substrate, ceramic coating, and ash-penetrated layer. The failure of Gd$_2$Zr$_2$O$_7$ coatings did not fit the model well, implying that further process optimization could significantly improve the life of these coatings.

10.2 Future Work

While the work presented here tells a fairly comprehensive story, several follow up experiments could be done to further this research.
Chemically, the similarities between the various ashes tested and TBC top coat materials have been shown to be very similar to each other as well as to CMAS glass on a broad level. Full penetration was observed by all impurities in 7YSZ coatings and a dense reaction layer was formed with all Gd₂Zr₂O₇ coatings. Experiments aimed at isolating the specific effects of several important chemical components of these ashes could provide further insight into degradation and reaction mechanisms.

Testing in thermal gradient is essential to obtaining valid results when measuring the life of TBCs with molten impurities. The optimization of the plasma spray conditions for the Gd₂Zr₂O₇ coatings could significantly enhance the measured lifetimes. Additionally, the use of an optimized 7YSZ/ Gd₂Zr₂O₇ layered coating could afford further enhancement. This approach is necessary since industry is already moving in this direction.

The thermal gradient burner rig built for the work performed here was built with versatility in mind. To that end, testing of TBCs with simultaneous injection of other impurities is easy to perform. These other impurities can include salt spray, sulfur impurities, or testing with CMAS glass. Also, some evidence suggests that water vapor can alter the spallation behavior of TBCs [102].

The burner rig also has uses outside of TBC systems. One use in particular, environmental barrier coatings (EBCs), could benefit from this testing. EBCs are coatings used for SiC and or Si₃N₄ composites that are used dominantly to prevent oxidation of the underlying components at extremely high temperatures. EBCs are typically silicon-containing coatings, and the silicon tends to volatilize in the presence of water vapor, leading to recession of the coating. The velocity of the water has been
shown to be an important factor in this recession testing [86-87], making the thermal gradient burner rig the ideal testing setup for these materials.

The delamination modeling has been shown to predict the failure of 7YSZ coatings reasonably well. Follow up with finite element to illustrate the exact mechanisms of shallow delaminations could be insightful.

The optimization of $\text{Gd}_2\text{Zr}_2\text{O}_7$ coatings could potentially allow the model to predict failure in these coatings as well. The model, however, is limited to an isolated picture of a single quenching event. The incorporation of a simple sintering model was undertaken in this work, which is the beginning of allowing the model to predict cyclic life. The key component missing, however, is the ability to determine the change in interface toughness with thermal cycling. With this damage-mechanics model incorporated into the delamination model, it could prove to be a powerful tool in the prediction of coating failures across a broad range of coatings with different top coats, bond coats, and substrates.
Bibliography


