Thermal and Environmental Barrier Coating Concepts for Silicon-based Ceramic Matrix Composites

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Abstract

Silicon carbide composites are increasingly used in gas turbine engines to increase the engine efficiency and reduce weight. When used in combustion environments containing residual oxygen and water vapor, they must be protected by an environmental barrier coating (EBC) system to avoid SiC oxidation and volatilization by water vapor. The current EBC system is designed for use at temperatures up to 1316°C, and consists of a silicon bond coat deposited on the composite and a Yb$_2$Si$_2$O$_7$ (YbDS) environmental barrier coating that protects it from the oxidizing environment. Permeation of oxidizing species through the YbDS layer eventually leads to oxidation of the silicon bond coat, and formation of a crystalline $\beta$-cristobalite SiO$_2$ layer at the silicon-YbDS interface. Upon cooling, a $\beta \rightarrow \alpha$-cristobalite phase change results in a 4.9% volume contraction of the SiO$_2$ layer. Thermomechanical analysis has indicated that the associated stored elastic strain energy leads to delamination of the coating system as the SiO$_2$ thickness increases, thereby controlling the life of the coating system. This dissertation proposes, and then systematically explores, several coating design concepts to delay this mode of failure.

The first approach to delamination control sought to convert the SiO$_2$ that is formed on the bond coat to a material that does not create a large stored elastic energy upon cooling from high temperature associated with the phase transformation from $\beta \rightarrow \alpha$-cristobalite. It was based upon a recognition that if SiO$_2$ is in contact with either ZrO$_2$ or HfO$_2$, a solid-state reaction can occur leading to the formation of zirconium or hafnium silicate (zircon or hafnon). Neither silicate undergoes a phase transformation in the temperature range of interest, and their coefficients of thermal expansion (CTE) are well matched to SiC, silicon, and YbDS. Thermomechanical calculations indicated that the stored strain energy developed on cooling would be insufficient to drive delamination. To investigate the concept further, the rate of solid-state formation of hafnon from mixtures of monoclinic HfO$_2$ and $\beta$-cristobalite SiO$_2$ has been investigated by annealing partially consolidated powder composites in air at temperatures between 1250°C-1400°C. Rietveld refinement of X-ray
diffraction (XRD) patterns indicated that at 1250°C the hafnon phase fraction increased linearly with time. At higher reaction temperatures, a region of linear behavior preceded a transition to parabolic reaction kinetics, with the transition occurring at an earlier time as the reaction temperature increased. Arrhenius relations fitted the kinetics of hafnon formation in both the linear and parabolic regimes. Scanning electron microscopy (SEM) indicated that the reaction is consistent with diffusion of SiO₂ as Si⁴⁺ and O²⁻ into HfO₂, similar to the mechanism by which zircon has been proposed to form when vitreous SiO₂ and tetragonal ZrO₂ reacts under similar conditions. The initial linear rate of reaction is consistent with the growth of the contact area between the SiO₂ and HfO₂ particles since the transport of the Si⁴⁺ and O²⁻ through the initial, incompletely formed hafnon phase is rapid. After a thin hafnon layer had formed between the reactants, the rate of hafnon growth slowed, and further growth required diffusion of Si⁴⁺ and O²⁻ through the reaction product, consistent with the observed parabolic dependence of the phase fraction upon time. The overall rate of hafnon formation was found to be rapid compared to the expected rate of SiO₂ formation in an EBC application.

The oxidation of a model system consisting of silicon particles in a highly porous HfO₂ particle matrix was subsequently used to investigate the rate and mechanism by which β-cristobalite SiO₂ was dynamically converted to hafnon when oxidizing silicon was in contact with m-HfO₂. The study compared the net rate of SiO₂ formation in the model silicon + HfO₂ system with that for just silicon particles, and found that the thickness of the SiO₂ layer that formed during high temperature (1250°C-1316°C) oxidation was greatly reduced by the hafnon formation reaction.

The insight from these kinetic studies were coupled with thermomechanical calculations to propose the design of a duplex silicon-HfO₂ bond coat EBC system that could delay coating delamination, and increase the lifetime of the coating system, by at least a factor of two by the incorporation of a 3-5 µm thick HfO₂ layer at the silicon-YbDS interface. A combination of at-
mospheric plasma spray and electron beam directed vapor deposition methods were developed to deposit duplex silicon-HfO$_2$ bond coats with YbDS EBC layers on SiC substrates. Thermal cycling between 110°C and 1316°C in a steam environment for up to 1000 1-hour cycles confirmed that the growth of a $\beta$-cristobalite SiO$_2$ layer on the silicon outer surface was accompanied by reaction with m-HfO$_2$ to simultaneously form hafnon. This reduced the average SiO$_2$ thickness by about a half compared to that seen in an otherwise identical silicon-YbDS system. A secondary reaction between the YbDS and the m-HfO$_2$ layer resulted in the formation of a cubic fluorite Yb$_2$O$_3$-stabilized HfO$_2$ phase at the hafnon-YbDS interface. Thermomechanical modeling indicated the energy release rate at any of the interfaces in the evolving coating system would be insufficient to cause delamination before all HfO$_2$ had been converted to hafnon.

The rate at which SiO$_2$ forms during the oxidation of silicon is exponentially dependent upon temperature. The time for the onset of delamination can therefore be increased by decreasing the reaction temperature. The dissertation therefore investigated the challenges that may be encountered for reducing the bond coat temperature via the use of a thermal barrier coating (TBC) applied to the YbDS surface. To investigate the feasibility of such an approach, a model HfO$_2$ TBC deposited on a silicon-YbDS EBC system was investigated. Thermomechanical calculations indicated that a highly porous TBC layer was necessary to reduce the considerable risk of TBC delamination upon cooling from its deposition temperature. Furnace annealing and thermal cycling experiments in steam environments were used to investigate the mechanisms by which coating failure occurred. The experiments identified the formation of a cubic fluorite Yb$_2$O$_3$-stabilized HfO$_2$ phase at the YbDS-HfO$_2$ interface, consistent with recent thermochemical assessments of the SiO$_2$-HfO$_2$-Yb$_2$O$_3$ ternary system. The coefficient of thermal expansion of this phase was measured, and its CTE of $12.3 \times 10^{-6} \, ^\circ\text{C}^{-1}$ was found to be two to three times that of the layers to which it was bonded, leading to channel cracking and delamination upon cooling.
The dissertation then went on to explore an alternative approach for reducing the bond coat temperature by investigating the feasibility of modifying the composition of the YbDS layer to reduce its thermal conductivity toward the amorphous material limit (\(\sim 1 \text{ W m}^{-1} \text{ K}^{-1}\)), while retaining a CTE that remained well matched to the bond coat. A systematic series of experiments investigated the phase stability of multiple rare-earth disilicate mixtures and discovered two Yb-Gd-based disilicate systems that met these requirements: a four-component \((\text{Yb}_{0.25}\text{Y}_{0.25}\text{Lu}_{0.25}\text{Gd}_{0.25})_2\text{Si}_2\text{O}_7\) system with a CTE of \(5.1 \times 10^{-6} \degree\text{C}^{-1}\) and a thermal conductivity of \(1.18 \text{ W m}^{-1} \text{ K}^{-1}\), and a five-component \((\text{Yb}_{0.2}\text{Y}_{0.2}\text{Lu}_{0.2}\text{Er}_{0.2}\text{Gd}_{0.2})_2\text{Si}_2\text{O}_7\) system with a CTE of \(3.9 \times 10^{-6} \degree\text{C}^{-1}\) and a thermal conductivity of \(1.71 \text{ W m}^{-1} \text{ K}^{-1}\). These single-phase systems had a melting temperature well above that needed for EBC applications, and were phase stable throughout the range of temperatures experienced in an EBC application, thereby providing a promising route for the future development of a combined thermal and environmental barrier coating (T-EBC) system.
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A PhD dissertation is certainly a culmination of long days in the lab, late nights behind the computer analyzing data, and many weekends writing that could otherwise be spent relaxing. The resulting work is something I am proud of, and it has raised my determination as a scientist to find the truths behind data, and the reasoning behind experimentation, to a much higher level than it was when I started some 6.5 years ago.

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1 Introduction

Silicon carbide composites based on fibers such as Hi-Nicalon Type S\textsuperscript{1-2}, and silicon carbide matrices made from pre-ceramic polymers, densified by silicon melt infiltration\textsuperscript{3}, are beginning to be used for non-stressed applications in the hottest sections of gas turbine engines, such as the combustor and high-pressure turbine\textsuperscript{4-11}. Chemical reactions between residual oxygen and water vapor species in the hot combustion gas stream and the surface of these SiC-based components initially results in formation of SiO\textsubscript{2} (s) and CO (g). The rate at which this happens is dependent on the combustion gas temperature, pressure, and composition\textsuperscript{12}. The SiO\textsubscript{2} thermally grown oxide (TGO) that forms subsequently reacts with water vapor from the high temperature combustion gas stream to form volatile silicon hydroxide gas species (e.g. Si(OH)\textsubscript{4}), at a rate that increases with the combustion gas temperature, pressure, composition, and gas flow speed over the SiO\textsubscript{2} surface\textsuperscript{13,14}. Requirements for the combustion gas temperature in a modern gas turbine engine now exceed $\geq$1300$^\circ$C, and the rate of loss of the composite has been reported to reach $\geq$1 $\mu$m/hour\textsuperscript{14,15}. To extend the life of SiC components in this engine environment, component surfaces exposed to the reactive gas stream must be protected with an environmental barrier coating (EBC) system whose function is to reduce SiC recession and reduce the flux of oxidizing species reaching the composite surface, and thereby decrease the rate of oxidation and volatilization\textsuperscript{16-20}.

Over the past two decades, numerous different combinations of material layers have been investigated in an attempt to reduce the influx of oxidizing species to the SiC component surface, although the search for a protective system is challenging\textsuperscript{16,21-26}. Materials for EBC systems need to not only reduce the permeation of oxidizing species, but also withstand stresses generated during thermal cycling (thermomechanical compatibility), and must exhibit thermochemical compatibility so the material will not adversely react with the SiC composite. However, candidate materials that meet these two types of design constraints must also not be susceptible to steam volatility such
as the SiC component itself, otherwise this coating would need replacement too frequently.

![Diagram](image)

**Figure 1.1:** Schematic representation of a conventional EBC system for silicon-based CMCs

The steam volatility (i.e. loss of material) rate of candidate EBC materials containing silicon has been shown to scale with their silica activity, so in order to minimize the EBC system thickness it is necessary to utilize a material with a silica volatility substantially less than that of SiC\textsuperscript{12,16,17,19,27}. Furthermore, in order to reduce permeation of oxidizing species through the EBC layer it should be pore and crack free, and have diffusion coefficients for the oxidizing species that are as low as possible at the temperatures of interest\textsuperscript{14–17,26}. Single layer systems, where only an environmental barrier layer is applied to the SiC component, reduce the influx of oxidizing species to the component surface, although these oxidizing species will eventually reach the composite surface and react with the SiC composite to form SiO\textsubscript{2} and CO (g). Subsequently, reaction with the fibers and the interfacial layers on these fibers used to provide crack resistance (e.g. BN) is possible, leading to the formation of glassy silicate phases such as borosilicates, with ensuing loss
of composite strength and fracture resistance. Consequently, bi-layer EBC systems consisting of a bond coat and an environmental barrier are able to protect the underlying SiC-based component and avoid formation of undesired gaseous reaction products. The bond coat must adhere well to SiC and be both thermomechanically and thermochemically compatible with SiC and the environmental barrier above. Figure 1.1 shows an example of such a bi-layer EBC system deposited on a SiC composite, comprising of a bond coat with a thermally grown oxide (TGO) and an environmental barrier layer.

Many materials exist that promise resistance to permeation of oxidizing species, but many have too low a melting temperature for use in the hot combustion gas environment. Figure 1.2 shows a collection of candidate materials, comparing their coefficient of thermal expansion (CTE) and melting temperature for use in such an environment. A comprehensive list of these materials and their properties can be found in Appendix A. Of those materials that remain, many have a CTE too high compared to the SiC-based substrate to which they would be bonded to, and/or undergo a volume reduction associated with phase changes upon cooling. Generation of tensile thermal stresses during cooling of the coating layers would then result in the formation of channel cracks in the coating, providing fast paths for permeation of oxidizing species towards the exposed underlying material when reheated. The use of coating materials whose CTE is less than that of the substrate results in compressive coating stresses on cooling from a high (stress-free) temperature, and leads to coating delamination at its interface with the substrate. This requirement for thermochemical compatibility within the system greatly reduces the available candidates. Furthermore, the coating system should not be vulnerable to rapid chemical attack by sulfur and vanadium salts that are formed when impurities in hydrocarbon fuels react with air, must be able to resist impact from foreign object debris, and reactions with molten silicates derived from dust that is inevitably ingested by an engine.
Richards et al.\textsuperscript{31} investigated the silicon-ytterbium disilicate (Yb$_2$Si$_2$O$_7$, YbDS) EBC system deposited on a SiC substrate, subjecting the coating system to steam cycling between 110°C to 1316°C for up to 2000 1-hour cycles in a 90 vol% H$_2$O/10 vol% O$_2$ environment, representative of a combustion gas stream. They showed that a (crystalline) $\beta$-cristobalite SiO$_2$ TGO formed during oxidation of their silicon bond coat. During cooling to room temperature, the TGO developed small compressive thermal stresses due to the close match in CTE of the $\beta$-cristobalite (3.1x10$^{-6}$ °C$^{-1}$) with the silicon bond coat (4.1x10$^{-6}$ °C$^{-1}$), and SiC substrate (4.67x10$^{-6}$ °C$^{-1}$). Unfortunately, upon cooling below a temperature of $\sim$240°C, a $\beta$$\rightarrow$$\alpha$-cristobalite phase transformation takes place with a 4.9% volume contraction\textsuperscript{31–34}. This contraction develops large tensile stresses in the TGO, resulting in the generation of a large stored elastic strain energy that can drive channel cracking, and delamination of the TGO from the silicon bond coat.
Exposure of the silicon-YbDS system to steam at 1316°C also resulted in reaction of the YbDS EBC layer with the water vapor to form volatile silicon hydroxide gas species\(^{31}\). This loss of SiO\(_2\) from the YbDS EBC layer resulted in the formation of a porous ytterbium monosilicate (Yb\(_2\)SiO\(_5\); YbMS) layer, which channel cracked upon cooling due to the relatively high CTE of YbMS \((7.2 \times 10^{-6} \ ^\circ\text{C}^{-1})^{35}\) compared to the materials to which it was applied. Cracking and localized spallation of the YbMS reduced the effective thickness of the dense EBC layer, increasing the flux of oxidizing species that permeated toward the silicon bond coat. This resulted in rapid thickening of the SiO\(_2\) TGO and eventual loss of the coating system by delamination\(^{29,30}\).

This dissertation reviews the development of the promising silicon-YbDS EBC systems, and explores novel concepts for potentially suppressing the delamination of the EBC system by reducing the rate of SiO\(_2\) TGO thickening. Two concepts are explored. The first developed in Chapters 2, 3, 4, seeks to react the SiO\(_2\) TGO in-situ with a different material resulting in a reaction product whose CTE is well matched with the other coating layers in the EBC system. The second concept, Chapters 5 and 6, explores thermal management approaches to reduce the temperature of the bond coat surface so that the thermally activated rate of bond coat oxidation can be reduced.

A discussion of these concepts is presented in Chapter 7, and the conclusions are presented in Chapter 8.
2 Hafnium silicate formation during the reaction of \( \beta \)-cristobalite \( \text{SiO}_2 \) and monoclinic \( \text{HfO}_2 \) particles

This chapter is published in the Journal of the American Ceramic Society with the title "Hafnium silicate formation during the reaction of \( \beta \)-cristobalite \( \text{SiO}_2 \) and monoclinic \( \text{HfO}_2 \) particles", and can be digitally found at: http://doi.org/10.1111/jace.17274

The emerging use of silicon carbide composites in gas turbine engines has led to an interest in environmental barrier coating (EBC) systems that can protect them from oxidation and volatilization by hot combustion gases containing both oxygen and water vapor\(^{16-20}\). The currently implemented EBC approach applies a silicon bond coat layer to the composite surface to impede oxygen and water vapor transport to the composite surface, and a rare-earth disilicate environmental barrier layer, such as ytterbium disilicate (\( \text{Yb}_2\text{Si}_2\text{O}_7 \), YbDS), to (a) slow the permeation of oxidants from the hot gas stream to the silicon surface, and thus slow the rate of \( \text{SiO}_2 \) formation on the silicon surface, and (b) to reduce its rate of its corrosion by reactions with water vapor\(^{31,36}\). At temperatures below \( \sim 1200^\circ\text{C} \), the eventual permeation of oxidizers to the silicon bond coat results in the formation of a vitreous (fused) \( \text{SiO}_2 \)\(^{37}\). Fundamental studies of the oxidation of silicon below 1200\(^\circ\text{C} \) have shown that the thickness of the thermally grown oxide (TGO) exhibits an initially linear dependence upon reaction time as the oxide layer develops to a thickness of 50-100 nm, and is followed by a transition to parabolic kinetics as further reaction requires transport through the already formed \( \text{SiO}_2 \) layer. Although the mechanism responsible for the linear region is a subject of ongoing study\(^{38}\), both regimes appear to be well modeled by the approach first proposed by Deal and Grove\(^{37}\). The rates of these reactions in dry oxygen were found to increase rapidly with reaction temperature with an activation energy of 1.99 eV in the linear regime, and 1.23 eV during parabolic growth\(^{37}\).
At temperatures above 1200°C, crystalline β-cristobalite is formed during the oxidation of silicon in gas turbine engine environments\textsuperscript{31,39}. Upon cooling, the β-cristobalite phase transforms to a higher density α-cristobalite at a temperature of ∼240°C, and is accompanied by a 4.9% volume reduction\textsuperscript{29–33}. When the SiO\textsubscript{2} layer contraction is constrained by silicon, the β→α-cristobalite phase transformation results in large tensile strains developing in the thermally grown oxide\textsuperscript{29–31}. During thermal cycling of multilayer EBC systems with a silicon bond coat, these strains result in cracking of the TGO layer, and increase the probability of coating system spallation as the TGO thickens\textsuperscript{31}. In applications where adherence of the scale and avoidance of SiO\textsubscript{2} cracking are essential, approaches for transforming β-cristobalite into a phase that remains thermo-mechanically stable on cooling, may be beneficial, especially if this phase had a coefficient of thermal expansion (CTE) similar to that of the silicon (4.1x10\textsuperscript{−6} °C\textsuperscript{−1}).

When either ZrO\textsubscript{2}, HfO\textsubscript{2}, or a mixture of both, are present during the oxidation of silicon, the formation of a SiO\textsubscript{2} TGO is expected to be accompanied by a parallel reaction between SiO\textsubscript{2} and either ZrO\textsubscript{2} or HfO\textsubscript{2} to form a zirconium or hafnium orthosilicate (ZrSiO\textsubscript{4}; zircon, or HfSiO\textsubscript{4}; hafnon) or a mixed Zr\textsubscript{x}Hf\textsubscript{1−x}SiO\textsubscript{4} orthosilicate\textsuperscript{40–45}. Since these orthosilicates are phase stable at the temperatures at which silicon bond coated EBC systems are used (currently up to 1316°C), and have reported CTE values similar to those of silicon (5.1x10\textsuperscript{−6} °C\textsuperscript{−1} for zircon, 3.6x10\textsuperscript{−6} °C\textsuperscript{−1} for hafnon)\textsuperscript{44,46}, their formation by reaction with SiO\textsubscript{2} in EBC systems would be of significant technological interest\textsuperscript{24,45,47}. However, this approach is only practical if the rate of formation of the orthosilicate was sufficiently rapid that thick SiO\textsubscript{2} layers did not develop and subsequently crack\textsuperscript{31}.

The formation of zircon by the reaction between amorphous (fused) SiO\textsubscript{2} and crystalline t-ZrO\textsubscript{2} has been investigated by Veytizou et al\textsuperscript{42} and shown to be rapid at 1300°C. However, above 1200°C crystalline SiO\textsubscript{2} is formed on silicon in the engine environment, and Ramani et al\textsuperscript{41} ob-
served a much slower reaction between quartz and tetragonal ZrO$_2$ at 1300°C. They argued that this was related to the need for a phase change from quartz to $\beta$-cristobalite via a “transitional” vitreous SiO$_2$ phase, before the formation of zircon. The rate-controlling part of the two-step reaction was not determined, and it is therefore unclear if the reaction rate is sufficiently rapid to match that of SiO$_2$ formation on silicon in an engine environment. It is also noted that the use of a ZrO$_2$ approach would be complicated by its monoclinic (m)-to-tetragonal (t) phase change at a temperature of $\sim$1200°C$^{48-50}$. Upon cooling, the t-phase undergoes a significant volume increase of $\sim$7.33% that leads to microcracking and potential coating system failure. While stabilization of ZrO$_2$ may be helpful, this allotropic transformation does not occur in m-HfO$_2$ until it is heated above $\sim$1750°C$^{48,49}$; well above the envisaged use temperature of EBC systems. If the kinetics of the $\beta$-cristobalite + m-HfO$_2$ reaction to form hafnon were sufficiently rapid, the use of HfO$_2$ to form hafnium silicate might provide the basis of a feasible approach for the avoidance of SiO$_2$ induced coating delamination.

Unfortunately, there is no reported study of the rate of the crystalline $\beta$-SiO$_2$ + m-HfO$_2$ $\rightarrow$ HfSiO$_4$ reaction in the range of temperatures of interest for EBC applications. It is, therefore, unclear if the hafnon reaction rate is sufficient to match that of SiO$_2$ formation under the environmental conditions likely to exist in EBC applications. The exploratory study reported here, therefore, seeks to measure the rate of hafnium silicate formation during solid-state reactions of mixtures of $\beta$-cristobalite SiO$_2$ and m-HfO$_2$ particles at temperatures of 1250°C to 1400°C in a dry air environment. The study identifies the existence of regions of both linear and parabolic reaction kinetics and determines the activation energies and pre-exponential factors for both reaction regimes, and discusses the mechanisms by which the reaction proceeds.
2.1 Materials and methods

2.1.1 Materials

To investigate the kinetics of the $\beta$-cristobalite SiO$_2$ phase and m-HfO$_2$ reaction, fused silica powder (-325 mesh, Atlantic Metals Inc., Stratford, CT) was annealed in lab air at 1500°C for 20 hours to convert it to $\beta$-cristobalite powder, Figure 2.1(a). Analysis of X-ray diffraction (XRD) results for the annealed powder at room temperature confirmed the formation of $\alpha$-cristobalite SiO$_2$ by high-temperature conversion of amorphous SiO$_2$ to $\beta$-cristobalite and transformation of the $\beta$-phase to the $\alpha$-allotrope on cooling to ambient. Highly porous monoclinic HfO$_2$ powder (Metco AE9930-1S, Oerlikon Metco, Westbury, NY), Figure 2.1(b), was mixed in an equimolar ratio with the cristobalite powder using a high-energy ball mill (SPEX SamplePrep 8000D, Metuchen, NJ). The HfO$_2$ powder particles were composed of partially sintered, 0.5 µm diameter grains and contained an interconnecting internal (35-40% volume fraction) pore network. After 90 minutes of milling using a DuPont Vertel XF cleaning agent to promote mixing without extensive crushing or heating of the powder particles, the blended powder was dried in air for 1 hour. Scanning electron microscopy imaging of the powder after mixing revealed some fracture of the porous m-HfO$_2$ precursor powder particles into finer grains with an average diameter of 0.5 µm. These small grains then coated the larger size silica particles, Figure 2.1(c).

![Figure 2.1](image-url)

**Figure 2.1:** SEM micrographs of a) $\alpha$-cristobalite SiO$_2$ powder and b) the m-HfO$_2$ powder that was ball-mill blended to create an equimolar cristobalite-HfO$_2$ mixture shown in (c) prior to partial consolidation.
### 2.1.2 Sample fabrication and annealing procedures

Oxygen permeable composite samples were prepared by partial consolidation of the powder mixture via spark plasma sintering (SPS) using a Thermal Technologies SPS Model 25-10 (Santa Rosa, CA, USA) machine. Consolidation was performed in an argon atmosphere at 1 atm pressure using a cylindrical 35 mm outer diameter, and a 12.7 mm (0.5 inches) inner diameter graphite die/punch system lined with 0.125 mm thick graphite foil to protect the faces of the die and punches, and simplify retrieval of samples. The samples were consolidated by heating to 1300°C while applying a pressure of 40 MPa, which was maintained for 5 minutes at the maximum temperature. The heating and cooling rates to and from the dwell temperature were 150°C/min. The partially consolidated samples were 15 mm in length, with a diameter of 12.7 mm. These were sliced into ∼2.5 mm thick, 12.7 mm (0.5 inches) diameter wafers using a diamond wafering blade, and annealed at 1050°C for 10 hours to restore oxygen stoichiometry. XRD analysis of the as-consolidated samples at room temperature showed the presence of only α-cristobalite and m-HfO$_2$, Figure 2.2. To characterize the hafnon formation reaction, the wafers were annealed in laboratory air (i.e., under an oxygen partial pressure $p_{O_2} = 0.21$ atm) in a Sentrotech ST-1600-666 bottom-loading furnace at seven temperatures (1250°C, 1280°C, 1300°C, 1316°C, 1330°C, 1350°C and 1400°C), for 1, 2, 5, 10, 15, and 20 hours. The heating and cooling rates to these temperatures were set to 10°C/min.

### 2.1.3 Characterization methods

The annealed wafers were split in half. One part was mounted in an epoxy resin (Buehler EpoKwick FC), and mechanically polished, ending with a 0.25 µm diameter diamond particle suspension. Surface analysis was performed using a Helios NanoLab DualBeam microscope (Thermo Scientific, Hillsboro, OR) operating in back-scattered electron (BSE) imaging mode using a concentric backscatter (CBS) detector. The atomic number (Z)-contrast imaging approach was used to delineate phases of different hafnium composition. Elemental microanalysis of the various phases was performed by energy dispersive spectroscopy (EDS) using an X-MaxN 150 SDD (Oxford In-
Figure 2.2: XRD spectrum of the partially consolidated and saturation annealed equimolar $\alpha$-cristobalite + m-HfO$_2$ sample indicating no hafnon was detectable prior to subsequent reaction annealing treatments.

Instruments, Concord, MA). A low accelerating voltage of 5 kV was used to limit secondary X-ray fluorescence. While use of a higher accelerating voltage (e.g. 10-15 kV) would allow one to observe the Hf L-lines, secondary X-ray fluorescence occurs due to the Hf L$_\alpha$ (7.9 kV) and Hf L$_\beta$ (9.0 kV) emissions being able to re-excite silicon to emit X-rays at its K$_\alpha$ of 1.7 kV, and results in the over-estimation of the silicon atomic fraction. EDS quantification of the composition is thus done using a lower voltage of 5 kV that only excited the silicon K$_\alpha$ and hafnium M$_\alpha$. Furthermore, during EDS data collection, the “EDX” mode on the microscope was used to reduce additional X-ray fluorescence from the sample.

The other part of the annealed wafer was crushed into a fine powder using mortar and pestle and used for X-ray diffraction (XRD) characterization. The powder was loaded on a zero-background silicon holder that was leveled using a glass microscope slide. A PANalytical Empyrean (Malvern Panalytical, Westborough, MA) X-ray diffractometer was used for the characterization. It was set-up with a Cu-K$_\alpha$ source and Bragg-Brentano optics combined with a reflection/transmission-spinner stage set-up for reflectance measurements. Diffraction angles (2$\theta$) of 15-100° were analyzed at 0.12°/s. Samples were spun at 0.25 revolutions per second to reduce the preferential
orientation of grains. Qualitative XRD analysis to identify the cristobalite peaks was performed using the PDF 00-039-1425 file for $\alpha$-cristobalite, and PDF 00-027-0605 for $\beta$-cristobalite.

2.1.4 Rietveld refinement

Rietveld refinement was used to execute quantitative phase analysis. However, this method assumes the depth of X-ray penetration is similar for all phases. In the SiO$_2$, HfO$_2$, and HfSiO$_4$ system, the mass attenuation coefficient (given by the linear attenuation coefficient, $\mu$ divided by density $\rho$) for HfO$_2$ is 136.58 cm$^2$/g, while those of hafnon and SiO$_2$ are 113.90 cm$^2$/g and 34.45 cm$^2$/g respectively.$^{51}$ The X-ray penetration depth for Cu-K$\alpha$ radiation is therefore much larger in SiO$_2$ while that of the two hafnium containing phases are similar. When an inhomogeneous powder such as that shown in Figure 2.3, where the SiO$_2$ particles are much larger than individual HfO$_2$ particles, the significant difference in X-ray penetration depth in the two phases results in an overestimation of the SiO$_2$ phase fraction when Rietveld is used. The SiO$_2$ XRD peak data was therefore not used for the determination of the hafnon phase fraction. Rietveld refinement was therefore only used to obtain the phase fractions of hafnon and HfO$_2$ in the annealed samples by fitting to the diffraction peaks of only these two phases. Even so, the smaller difference in mass attenuation coefficient between HfO$_2$ and hafnon is still sufficient to introduce an error in the Rietveld refinement, and so a calibration procedure was used to allow correction of the Rietveld refinement hafnon phase fractions, as described in section 2.5. A third order polynomial expression was fitted to the calibration data points. The standard deviation of error between the data and the polynomial fit corresponded to a hafnon molar fraction $\alpha_{\text{Hafnon}} = 0.01$. The polynomial relation was used to correct the phase fraction obtained from Rietveld refinement. The errors incurred by not using the calibration correction are shown in Figure 2.10. The calibration corrected hafnon molar fraction results subsequently reported were assigned an error of one standard deviation (68% prediction bounds) of the calibration fit.
The refinement was conducted using GSAS-II crystallographic data analysis software\textsuperscript{52} that enabled refinement for background, sample displacement, unit cell parameters, microstrain, and crystallite size. A solution was accepted only when the residual misfit (Rwp) between the predicted and the experimental data was less than 15\% for both fitted phases. An instrument parameter file was created using the GSAS-II software based on a NIST SRM 640e silicon powder standard. The hafnon peaks were fitted using PDF 01-075-1628, and the m-HfO\textsubscript{2} peaks were fitted using PDF 04-004-3850. The hafnon phase fraction $\alpha_{\text{Hafnon}}$ was calculated as the ratio of hafnon phase fraction to the sum of HfO\textsubscript{2} and hafnon phase fractions in the sample. It is noted that when the reaction of SiO\textsubscript{2} and HfO\textsubscript{2} forms stoichiometric hafnon, it can be assumed the number of moles of SiO\textsubscript{2} remains equal to that of HfO\textsubscript{2} throughout the reaction. The obtained hafnon phase fraction was then corrected using the correction described in section 2.5.

2.1.5 Data fitting

The phase fraction data were fitted to kinetic models using a bisquare weights fitting method using the Curve Fitting Toolbox in Matlab\textsuperscript{53}, rather than a standard least-squares regression method. This method was used so that data points that were far from the fitted line were assigned a lower weight factor. Thus, should there be a significant outlier in the data, its weight would be set closer to zero, while a point on a fitted line, has a weight closer to unity. This method, therefore, minimizes the effect of outliers in data sets.

2.2 Results

2.2.1 Microstructure

Micrographs of partially consolidated cristobalite-HfO\textsubscript{2} samples are shown in Figure 2.3 after (a) saturation annealing, (b) following reaction at 1250\°C for 5 hours, (c and d) after reaction at 1316\°C for 5 and 20 hours, and (e) exposure at 1400\°C for 5 hours. The HfO\textsubscript{2} particles were composed of sintered $\sim$0.5 \textmu m diameter grains which had been agglomerated into $\sim$35 \textmu m in
diameter HfO₂ particles containing significant interconnected porosity. It is evident that after partial powder consolidation and stabilization annealing, the HfO₂ microstructure retained a 35-40% micropore fraction. Unlike in an engine environment where an environmental barrier coating is applied, oxygen is allowed to continue to permeate into the powder compact. No evidence of a reaction between the HfO₂ and SiO₂ could be detected in the stabilization annealed condition. Examination of Figure 2.3 shows that samples that were annealed at higher temperatures developed a grey phase at the interface between SiO₂ and HfO₂, which increased in area as the reaction time and temperature increased. EDS analysis, Figure 2.3(f), indicates the grey phase had a Hf:Si:O ratio of 1:1:4, consistent with that of HfSiO₄. Light contrast areas within the hafnon phase are unreacted HfO₂ particulates, consistent with the growth of hafnon into the HfO₂ region. Further examination of Figure 2.3 reveals substantial densification (sintering) of the HfO₂ during annealing and the presence of cracks in the SiO₂ phase associated the approximately 4.9% volumetric shrinkage during the β→α-cristobalite phase change on cooling in a constraining HfO₂ matrix.

Upon reaction of SiO₂ with HfO₂, the original HfO₂ molar volume increases from $V_{HfO_2}^{M} = 20.82 \text{ cm}^3/\text{mol}$, to $V_{Hafnon}^{HfO_2} = 38.78 \text{ cm}^3/\text{mol}$, an expansion of 86.3% based on the ambient (298 K) temperature unit cell parameters. However, SiO₂ (β-cristobalite) is consumed in this reaction. There, since the molar volume of β-cristobalite, $V_{β-cristobalite}^{β-cristobalite} = 27.64 \text{ cm}^3/\text{mol}$ is consumed during the reaction, the effective change in molar volume when hafnon is formed is $\left(\frac{V_{Hafnon}^{HfO_2}}{V_{M}^{β-cristobalite}} + \frac{V_{HfO_2}^{HfO_2}}{V_{M}^{β-cristobalite}}\right) = 0.80$, indicating a volumetric contraction occurs as the reaction proceeds. This is consistent with the increasing presence of voids/cracks evident in Figure 2.3 as the reaction proceeded. This macroscopic behavior was accompanied by local dilation of the original HfO₂ particles, which was partially compensated here by the densification of its inter-grain microporosity.

SEM-micrographs of the SiO₂-HfO₂ interface acquired using the BSE imaging mode are shown in Figure 2.4 from (a) the saturation annealed sample, (b) at an early stage of hafnon formation.
Figure 2.3: SEM-BSE mode micrographs of a) oxygen saturation annealed sample at 1050°C for 10 hours, and after b) annealing at 1250°C for 5 hours, c) at 1316°C for 5 hours, d) at 1316°C for 20 hours, and e) at 1400°C for 20 hours. f) Shows an EDS spectrum of the grey phase indicating its composition to be that of HfSiO$_4$. 
Figure 2.4: SEM-BSE images of the α-cristobalite-HfO$_2$ interface of a) a saturation annealed sample, b) a sample annealed at 1330°C for 1 hour, and c) a sample annealed at 1330°C for 5 hours. Debonding of the SiO$_2$-HfO$_2$ interface is a result of the large contraction of the SiO$_2$ phase on cooling through the $\beta \rightarrow \alpha$ transformation.
(1 hour at 1330°C), and (c) after 5 hours at 1330°C. In Figures 2.4(b) and 2.4(c), it is shown that many of the surface grains of the HfO$_2$ phase in the saturation annealed sample were in contact with the surface of SiO$_2$ particles. It also shows the partial delamination between the SiO$_2$ and HfO$_2$ phases, consistent with a reduction in the molar volume of the reaction product, combined with shrinkage of cristobalite during cooling.

Figure 2.4(b) from a sample reacted for 1 hour at 1330°C indicates that a thin layer of hafnon had formed by conversion of the outer layer of HfO$_2$ grains to hafnon, consistent with the diffusion of SiO$_2$ into the HfO$_2$ particle. As the annealing time was increased to 5 hours, Figure 2.4(c), the reaction front progressed more deeply into the HfO$_2$ particles, consistent with the diffusion of SiO$_2$ through the hafnon reaction layer to form hafnium silicate at the advancing hafnon-HfO$_2$ interface.

EDS line scan analysis, Figure 2.5(a), shows no significant silicon in the unreacted HfO$_2$, aside from noise due to the proximity of the Hf (M$_\alpha$ = 1.646 keV) and Si (K$_\alpha$ = 1.740 keV) X-ray peak energies and the uneven HfO$_2$ particle surface. It also indicates the presence of no Hf in SiO$_2$ regions. An EDS line scan across a hafnon product layer, Figure 2.5(b), indicates the presence of no silicon within HfO$_2$ particles. It also indicates the Hf:Si ratio at a 1:1 ratio across the grey phase, indicating it to be hafnon. White particles in the hafnon phase, Figure 2.5(b) again correspond to regions of HfO$_2$ that have yet to fully react behind the advancing hafnon-HfO$_2$ reaction front that progressed through the HfO$_2$ particles.

### 2.2.2 Hafnon formation rate

Figure 2.6(a) shows that after annealing at 1316°C for 1 hour, a significant phase fraction of hafnon had formed. Figure 2.6(b) and (c) show that as the hafnon peak intensity increased with reaction time, it was accompanied by progressive decreases in the intensities of the SiO$_2$ and HfO$_2$ peaks. Rietveld refinement determined the phase fraction of hafnium silicate, $\alpha_{\text{Hafnon}}$, in all samples, as
Figure 2.5: SEM BSE mode images and EDS line-scans of samples annealed for at a) 1250°C for 5 hours showing very little hafnon formation, and b) 1400°C for 5 hours where a thick hafnon reaction layer had been formed.

described in Section 2.1.4. The hafnon phase fraction is plotted versus reaction time during annealing at 1250°C, 1316°C, and 1400°C, in Figure 2.7. The data indicates that at low temperatures, the hafnon phase fraction increased linearly with time, with a growth rate slope that increased with reaction temperature. At the lowest temperature of 1250°C, the rate of hafnon formation during the first two hours of the reaction was very low, but non-zero. For reactions at a temperature of 1280°C and above, the linear response was followed by a transition to parabolic behavior, and the reaction rate increases with temperature.
Figure 2.6: XRD spectra of α-cristobalite + m-HfO$_2$ samples annealed at 1316°C for a) 1 hour, b) 5 hours, c) 20 hours. The Rietveld refinement spectra are shown as red-dashed lines. The α-cristobalite peaks were not used for the refinement.
2.3 Discussion

The reaction rate between $\beta$-cristobalite and m-HfO$_2$ is rapid at all the temperatures investigated here. Results at 1330°C, Figure 2.4(c) show that the reaction rate is sufficiently rapid to convert about a micron of SiO$_2$ to hafnon per hour. This is well above the rate at which SiO$_2$ has been observed to form in EBC systems exposed to similar conditions$^{31}$. To model the reaction rate the experimental observations have been fitted to thermally activated transformation kinetic models and determined the activation energies of the reaction. These have then been used to explore the mechanisms by which the reaction proceeds in this system.

2.3.1 Reaction kinetics

The calibration corrected XRD derived hafnon phase fraction versus time results presented in Figure 2.7 were fitted to numerous standard solid-state reaction kinetics models, such as described by Khawam and Flanagan$^{54}$, and the comprehensive linear-parabolic model by Deal and Grove$^{37}$ on the oxidation of silicon. No satisfactory fitting could be done by a singular model. Instead, the reaction of a $\beta$-cristobalite SiO$_2$ and m-HfO$_2$ powder composite to form hafnon was found to be best fitted (with the lowest residual error) in two stages. The reaction during the first stage progressed linearly with time at a rate that increased with the reaction temperature. The phase fraction versus time data at a fixed temperature was fitted to a linear model using:

$$\alpha_{\text{Hafnon}} = k_L t$$

(2.1)

$k_L$ is a temperature-dependent linear rate constant and $t$ the reaction time. This model prediction is shown as the solid line in Figure 2.7.
Figure 2.7: The hafnon phase fraction deduced by calibrated Rietveld refinement as a function of time of annealing at a) 1250°C, b) 1316°C, and c) 1400°C. The data is fitted to a model incorporating both linear and parabolic hafnon growth kinetics.
Figure 2.8: Arrhenius plot of the parabolic rate constant $k_p$, and the linear rate constant $k_l$ values as a function of inverse temperature (1/T). The activation energy for the parabolic regime was $E_p = 5.5 \pm 1.5$ eV while that of the linear growth was $E_l = 7.8 \pm 2.1$ eV.

The linear growth rate constant for the seven temperatures studied has been plotted against inverse temperature in Figure 2.8, and found to be well fitted by an Arrhenius expression of the form:

$$k_L(T) = k_{L_0} \exp \left(-\frac{E_L}{k_B T}\right)$$  \hspace{1cm} (2.2)

where $E_L$ is the activation energy for the linear growth regime, $k_{L_0}$ a pre-exponential factor for the linear regime, $k_B$ is Boltzmann’s constant, and $T$ the absolute temperature. From the experimental data plotted in Figure 2.8, the activation energy for this linear regime is found to be $E_L = 7.8 \pm 2.1$ eV and the pre-exponential factor of $k_{L_0} = 8.3 \times 10^{22}$ mol/hour.
Reactions conducted above 1250°C exhibited a transition from a linear to parabolic dependence upon time. In the parabolic regime the hafnon phase fraction was well-fitted by a model of the form:

\[
\alpha_{\text{Hafnon}} - \alpha_{\text{Hafnon}}^L = (k_p t)^{1/2}
\]  

where \(\alpha_{\text{Hafnon}}^L\) is the hafnon phase fraction adjusted to intercept the end of the linear region, \(k_p\) is the parabolic rate constant, and \(t\) is time measured from the end of the linear region. Figure 2.7 shows a fit of this model to the XRD derived data. The value of \(k_p\) was temperature-dependent and also well fitted by an Arrhenius expression of the form:

\[
k_p(T) = k_{p0} \exp \left( \frac{-E_p}{k_B T} \right)
\]  

in which \(E_p\) is the activation energy, and \(k_{p0}\) is the pre-exponential factor for the parabolic reaction. The parabolic rate constant data for the six samples that exhibited a parabolic region, Figure 2.8, gave an activation energy of \(E_p = 5.5 (\pm 1.5)\) eV, with a pre-exponential factor of \(k_{p0} = 7.7 \times 10^{14}\) mol²/hour.

2.3.2 Reaction mechanisms

2.3.2.1 a) The parabolic reaction

Veytizou et al.\textsuperscript{42} investigated the formation of zircon (which is isomorphous with hafnon) from t-ZrO\(_2\) and vitreous SiO\(_2\). They observed a linear reaction dependence upon time at 1250°C, while at temperatures above this, the reaction rate was parabolic. They argued that the rate-limiting step in the reaction was the interstitial diffusion of Si\(^{4+}\) from SiO\(_2\) through the zircon to the t-ZrO\(_2\) phase. It was argued that the growth of new zircon occurred at the zircon-ZrO\(_2\) interface once the solubility limit of Si in ZrO\(_2\) was achieved. To maintain electroneutrality, O\(^{2-}\) diffusion from the SiO\(_2\) region to the zircon/t-ZrO\(_2\) interface must also occur, although this is not rate-limiting since
Cherniak et al.\textsuperscript{55} estimate the (dry) oxygen diffusivity in high-quality zircon single crystals to be about eight orders of magnitude higher than that of Si\textsuperscript{4+}. Zircon, therefore, formed within ZrO\textsubscript{2} regions by the coupled diffusion of Si\textsuperscript{4+} and O\textsuperscript{2−} through a zircon reaction product until one or all of the reactants were consumed.

In the SiO\textsubscript{2}-HfO\textsubscript{2} system studied here, it is evident from Figures 2.4 and 2.5 that the hafnon reaction front moves into HfO\textsubscript{2} regions. This is consistent with a hafnon growth process in which Si\textsuperscript{4+} and O\textsuperscript{2−} diffuse from SiO\textsubscript{2} regions through a HfSi\textsubscript{1+x}O\textsubscript{4−x} reaction product and reacts with HfO\textsubscript{2} at the hafnon-HfO\textsubscript{2} interface. The rate of the parabolic reaction would then be dictated by the gradient in silicon concentration across the hafnon layer and the Si\textsuperscript{4+} diffusivity within the reaction product. Veytizou et al.\textsuperscript{42} estimated the diffusivity of Si\textsuperscript{4+} during the formation of zircon and found it varied from 1.1x10\textsuperscript{−18} m\textsuperscript{2}s\textsuperscript{−1} at 1250°C to 10.6x10\textsuperscript{−18} m\textsuperscript{2}s\textsuperscript{−1} at 1400°C. This is about five orders of magnitude higher than that measured in high-quality zircon single crystals by Cherniak et al.\textsuperscript{55}, who suggested the diffusivity must therefore be highly dependent upon the local (atomic scale) structure within the transforming zircon region. No diffusion data exists for the hafnon system, but if it is assumed the diffusivities are similar to those of zircon, then the diffusion distances of Si\textsuperscript{4+} (after a 5-hour reaction time) in hafnon range from \sim 0.2 µm at 1250°C to \sim 0.6 µm at 1400°C. These are about an order of magnitude smaller than the reaction product thickness observed in Figures 2.4 and 2.5, suggesting that a faster diffusion path existed during the hafnon reaction. The activation energy for the parabolic hafnon formation reaction was found to be 5.5 (±1.5) eV, while the activation energy deduced from the Veytizou et al.\textsuperscript{42} silicon diffusion data was \sim 3.3 eV, consistent with the presence of a faster diffusion pathway in the hafnon system studied here. Examination of Figures 2.4 and 2.5 show that the hafnon reaction layer contained a high density of grain boundaries, which may have provided such a pathway.
2.3.2.2 b) The linear kinetics regime

Figure 2.7 shows that the onset of parabolic reaction kinetics was preceded by a period of linear growth. The rate of the reaction in this linear regime increased with reaction temperature. The linear regime transitioned to parabolic kinetics at a hafnon phase fraction which increased with temperature. At 1316°C the transition occurred at a hafnon phase fraction of ~0.15, while at 1400°C it occurred at a hafnon phase fraction of ~0.30. Although the hafnon phase fraction formed in the linear regime increased with temperature, the time for which linear behavior persisted decreased with increasing reaction temperature. The activation energy for the linear regime (7.8 (±2.1) eV) was higher than that of the parabolic regime, while the hafnon formation rate was also higher in this region. This is consistent with the large surface area available at the start of reaction, allowing a rapid initial hafnon formation rate.

When the reactants (Si$^{4+}$ and O$^{2-}$) diffuse into HfO$_2$ at the reaction temperatures, a local volume expansion occurs (by a factor of 1.86) as the HfO$_2$ transforms into hafnon. Due to the loss of SiO$_2$, the ratio of the molar volume of hafnon to the sum of those for HfO$_2$ and SiO$_2$ decreases to 0.80, and a contraction of the total sample volume occurs, as also discussed in Section 2.2.1. Figure 2.9 (a) and (b) schematically illustrate the consequence of these geometric effects as new contacts between a large particle of SiO$_2$ and smaller HfO$_2$ particles leads to a progressive increase in the contact area at the reaction interface. The initial reaction rate per unit area of reaction front is also likely to be high at the start of the reaction because the hafnon reaction layer is likely to be discontinuous and highly defective. Diffusion by a variety of pathways including on HfO$_2$ surfaces, along hafnon grain boundaries, and on void surfaces within the developing reaction product, is likely. As the temperature is increased, the diffusion rates of the reactants (Si$^{4+}$ and O$^{2-}$) scale exponentially with temperature according to the Arrhenius equation, thereby shortening the time required to form a less permeable, fully contiguous reaction front, and for the transition to parabolic behavior to commence, Figure 2.9(c). It is also noted that at the higher temperatures of
Figure 2.9: Schematic illustration of the high temperature solid state reaction. a) The initial state consisting of m-HfO$_2$ particles in partial contact with the surface of larger diameter β-cristobalite SiO$_2$ particles. (b) During the linear reaction stage, SiO$_2$ and HfO$_2$ rapidly react at developing areas of contact. (c) The parabolic reaction rate was governed by grain boundary, surface and bulk diffusion of Si$^{4+}$ and O$^{2-}$ through the hafnon reaction layer.
reaction used to form hafnon, the initial reaction may have also involved a contribution by vapor phase transport of SiO (g) through interparticle pore spaces to the HfO$_2$ surface. Recent studies have shown that the vapor pressure of this species is significant, especially in the presence of a small amount of free silicon$^{56}$.

Finally, it is noted that the exploratory nature of the present study has not enabled a fundamental investigation of the atomic-scale processes in play during the initial formation of hafnon. Further work will be needed to quantitatively resolve the changing nature of contact area between the reacting particles, to determine the diffusivities of the reactants in the hafnon system, and to characterize the evolving structure (and permeability) of the first formed hafnon.

### 2.4 Conclusions

The solid-state reaction between crystalline SiO$_2$ (β-cristobalite) and m-HfO$_2$ to form hafnium silicate (hafnon) at temperatures between 1250°C-1400°C has been experimentally characterized. XRD with calibration corrected Rietveld refinement enabled the hafnon formation rate to be measured as a function of reaction time and temperature. The study indicated that an initial linear kinetics regime with an activation energy of 7.8 eV switched to one with parabolic kinetics with an activation energy of 5.5 eV as either the annealing time progressed or the reaction temperature was increased. The linear reaction rate regime was consistent with an increase in the SiO$_2$-HfO$_2$ contact area with time and temperature while in the parabolic regime co-diffusion of Si$^{4+}$ and O$^{2-}$ through the reaction dominated. The rate at which hafnon is formed was observed to be well above that at which SiO$_2$ forms in EBC systems indicating that the use of HfO$_2$ to reduce the risk of delamination in EBC systems is a viable approach.
2.5 Hafnon-HfO\textsubscript{2} XRD calibration standard

Mixtures of pure, crystalline hafnon (HfSiO\textsubscript{4}) powder made by a chemical synthesis route and HfO\textsubscript{2} powder were assembled and analyzed using the same X-ray diffraction method described in Section 2.1.3, followed by the same Rietveld refinement procedure as described in Section 2.1.4, and data fitting is done as described in Section 2.1.5. The solid line in Figure 2.10 shows the result of this method using samples with the known phase fraction specified on the y-axis and the estimated phase fraction on the x-axis. It can be seen that at lower phase fractions of hafnon, a small overestimation of the amount of hafnon is found using conventional (uncalibrated) Rietveld refinement, while at higher phase fractions, the estimated phase fraction is close to that of the actual phase fraction. A third-order polynomial (ax\textsuperscript{3}+bx\textsuperscript{2}+cx+d, where a = -0.5237, b = 0.9831, c = 0.5399, and d = 0 for pure HfO\textsubscript{2} powder) was fitted to the data. The hafnon phase fraction obtained using Rietveld analysis is then set as x in the abovementioned fitted line, producing the corrected hafnon phase fraction. The results are used to produce the data plotted in Figures 2.7 and 2.8.

![Figure 2.10: The XRD calibration results used for the correction of the Rietveld refinement data. The experimental data was fitted to a third order polynomial expression (the solid curve). The standard deviation of the error between the data and the polynomial fit corresponded to a hafnon molar fraction $\alpha_{\text{Hafnon}} = 0.01$. The difference between the dashed line and solid curve at each Rietveld calculated hafnon fraction indicates the error incurred in phase fraction if no calibration correction were made.](image-url)
3 Hafnium silicate formation during oxidation of a permeable silicon + HfO$_2$ powder composite system

This chapter is published in Acta Materialia with the title "Hafnium silicate formation during oxidation of a permeable silicon + HfO$_2$ powder composite system", and can be digitally found at: http://doi.org/10.1016/j.actamat.2020.10.019

3.1 Introduction

Silicon is widely used as a bond coat material in the environmental barrier coating (EBC) systems used to reduce the risk of silicon carbide composite component oxidation and volatilization in gas turbine engines$^{3-7,9}$. The bond coat is intended to react with molecular oxygen and water vapor present in the combustion gas stream by forming a passivating SiO$_2$ thermally grown oxide (TGO) layer on the outer silicon surface, thereby impede permeation of oxidizing species to the SiC composite surface$^{8,12,13,15,16,57}$. The thickness of this TGO is dictated by the flux of oxidizing molecules reaching the silicon surface, the rate of their inward diffusion through the previously formed silicon oxide layer, and the exposure time$^{37}$.

When silicon is heated to temperatures below $\sim$1200°C in dry air, the TGO that forms is a protective vitreous form of SiO$_2$$^{37,58}$. At constant temperature, oxidation of silicon in a dry oxygen environment begins with a brief regime of linear thickening to an oxide thickness of 60-100 nm, and then transitions to a parabolic dependence upon time, provided the oxygen partial pressure exceeds that for active oxidation$^{37,59,60}$. The rate of TGO thickening in a ”wet oxygen” (water vapor rich) environment is much faster than in dry environments because of the relatively rapid transport
of hydroxyl ions through the open SiO$_2$ framework$^{37,38}$. 

Many studies of the vitreous oxidation kinetics of single crystal and polycrystalline silicon at temperatures $\leq 1200^\circ$C have shown that the rate of oxidation increases rapidly with temperature$^{37,61}$, and Deal and Grove developed a widely used kinetic model that predicts the rate of this vitreous SiO$_2$ formation$^{37}$. Their linear-parabolic oxidation model for the time dependent SiO$_2$ thickness, $x$, on silicon was of the form:

$$x^2 + Ax_0 = B(t + \tau)$$  \hspace{1cm} (3.1)

where $A$ and $B$ are constants with values that determine the linear and parabolic oxidation rate, and are dependent on the diffusivity of oxidizing species through the SiO$_2$ layer, $t$ is the oxidation time, and $\tau$ corresponds to a shift in the time coordinate to correct for the presence of the native oxide layer of thickness, $x_i$, present at the start of the process. This can also be written as: $\tau = (x_i^2 + Ax_i)/B$. Deal and Grove$^{37}$, showed that in the long time/thick oxide limit, equation 3.1 reduces to a parabolic oxidation law of the form:

$$x^2 \simeq Bt$$  \hspace{1cm} (3.2)

where $B$ is the parabolic rate constant. In the thin oxide layer limit, equation 3.1 reduces to:

$$x \simeq \frac{A}{B}(t + \tau)$$  \hspace{1cm} (3.3)

where the $B/A$ ratio is the linear rate constant of a linear oxidation law. The $B$ and $A$ coefficients, and therefore oxidation rate predictions, were determined by Deal and Grove for dry oxidation of silicon between 700-1200$^\circ$C$^{37}$. 

30
During the oxidation of silicon to form vitreous SiO$_2$, the addition of oxygen to the silicon unit cell to form randomly orientated SiO$_2$ tetrahedra, results in an increase in solid volume given by the ratio of the molar volumes of vitreous SiO$_2$ and silicon, $\frac{V^\text{vitreous}}{V^\text{M}} = 2.26$. If the silicon and SiO$_2$ are laterally constrained, growth of the oxide can only occur out of plane, and the oxidation of a 1 µm thick layer of silicon results in the formation of a 2.26 µm thick layer of vitreous SiO$_2$. Even though the coefficient of thermal expansion (CTE) of vitreous SiO$_2$ ($\sim 6 \times 10^{-7} \, ^\circ\text{C}^{-1}$)$^{62,63}$ is much less than that of silicon ($\sim 4 \times 10^{-6} \, ^\circ\text{C}^{-1}$)$^{64}$, upon cooling the compressively strained vitreous SiO$_2$ TGO rarely delaminates from the silicon surface, does not crack, and remains protective during repeated thermal cycling.

When the oxidation of silicon occurs above 1200°C, a crystalline $\beta$-cristobalite phase can form$^{29,31,39,65,66}$, especially in the presence of impurities which increase the diffusivity of oxidizing species in the oxide$^{38,58,65}$. It is unclear if the crystalline phase is formed directly, or by transformation of a transient vitreous phase. However, Breneman and Halloran$^{67}$ have shown if it occurs by the latter mechanism, the rate of the vitreous to crystalline transformation increases more rapidly with increasing temperature above 1200°C. Their data for vitreous SiO$_2$ powder transformation indicated that at 1200°C, it takes 3-5$\times 10^3$ minutes for the transformation to be completed, whereas at 1450°C it is completed in just a few minutes. In water vapor rich environments, hydroxyl (OH-) groups disrupt the SiO$_2$ structure and allow the SiO$_2$-tetrahedra to more easily transform from a random (vitreous) to an ordered crystalline state$^{65}$. However, the kinetics of silicon oxidation in the temperature regime where a crystalline oxide is formed is much less studied than that of vitreous oxide formation$^{66}$, and much remains to be understood.

Recent experiments in which a model silicon-ytterbium disilicate (Yb$_2$Si$_2$O$_7$, YbDS) EBC system was subjected to prolonged exposure to a flowing, 1 atm (90 vol% H$_2$O/10 vol% O$_2$) environment at 1316°C, found that the TGO layer thickening was rapid and appeared to be governed
by the rate of permeation of the oxidizing species through the YbDS top coat to the silicon bond coat surface\textsuperscript{31}. While the CTE of β-cristobalite (3.1x10\textsuperscript{−6} °C\textsuperscript{−1}) is quite well matched to that of silicon (∼4x10\textsuperscript{−6} °C\textsuperscript{−1}), upon cooling through ∼240°C the oxide undergoes a phase transformation to a higher density α-cristobalite phase. If the oxide is constrained from lateral shrinkage by the silicon bond coat, the ∼4.9% contraction in volume results in channel cracking, and localized delamination of thicker TGO layers\textsuperscript{29–33, 68}. The CTE of α-cristobalite (∼30x10\textsuperscript{−6} °C\textsuperscript{−1}) is also much higher than that of silicon, further raising the stored elastic strain energy in the coating system, and increasing the risk of coating delamination\textsuperscript{29, 31}.

One potential approach to mitigate coating failure is to modify the silicon bond coat composition to promote formation of an oxide that does not undergo a phase change on cooling, and that has a CTE well matched to silicon. For example, if either ZrO\textsubscript{2}, HfO\textsubscript{2}, or a mixture of both were present at the oxidizing surface of the silicon bond coat, the formation of a SiO\textsubscript{2} TGO might be followed by a reaction between SiO\textsubscript{2} and either ZrO\textsubscript{2} or HfO\textsubscript{2} to form a zirconium or hafnium orthosilicate (ZrSiO\textsubscript{4}; zircon or HfSiO\textsubscript{4}; hafnon) or a mixed Zr\textsubscript{x}Hf\textsubscript{1−x}SiO\textsubscript{4} orthosilicate. These materials are phase stable in the regime of interest, and have CTE’s that lie between those of zircon (5.1x10\textsuperscript{−6} °C\textsuperscript{−1}) and hafnon (3.6-4.5x10\textsuperscript{−6} °C\textsuperscript{−1})\textsuperscript{44, 69}, and are therefore well matched with silicon (4.1x10\textsuperscript{−6} °C\textsuperscript{−1})\textsuperscript{31}. Furthermore, the CTE of both ZrO\textsubscript{2}, and HfO\textsubscript{2} are in 6-7x10\textsuperscript{−6} °C\textsuperscript{−1} range, and their presence is therefore unlikely to pose a serious risk of thermo-mechanical failure provided they remain thin or finely dispersed. However, both ZrO\textsubscript{2} and HfO\textsubscript{2} undergo a tetragonal-to-monoclinic phase change on cooling. For ZrO\textsubscript{2} this occurs at a temperature of ∼1200°C\textsuperscript{48–50}, and upon cooling the tetragonal-to-monoclinic phase transformation is accompanied by a volume expansion of 5.18%, resulting in microcracking and potential coating failure\textsuperscript{50}. However, for m-HfO\textsubscript{2} this transformation occurs on heating through ∼1700°C; well above any proposed EBC use temperature. Since thermodynamic modelling indicates that silicon and HfO\textsubscript{2} are in equilibrium with each other up to the melting temperature of silicon (1414°C)\textsuperscript{70}, the integration of HfO\textsubscript{2} with
a silicon bond coat to dynamically convert SiO$_2$ to hafnon may be a preferred approach, provided the rate of hafnon formation is sufficiently rapid to match that of SiO$_2$ formation in the EBC application.

Such an approach has been explored by Anton et al.\textsuperscript{45}, where a PVD technique was used to deposit a mixed silicon + HfO$_2$ layer on top of a SiC substrate. Annealing of this coating system showed extensive oxidation of the silicon to form SiO$_2$, and depending on the silicon-to-HfO$_2$ ratio, sometimes consumed the entire coating layer. Harder\textsuperscript{47} also explored this concept and deposited a composite silicon+HfO$_2$ bond coat on a SiC substrate using a plasma spray-physical vapor deposition (PS-PVD) technique. He observed the oxidation of the silicon particles, followed by reaction with HfO$_2$ leading to HfSiO$_4$ formation on oxidized silicon particles distributed throughout the bond coat. However, this modified bond coat was unable to fully suppress direct oxidation of the SiC substrate and the growth of a crystalline SiO$_2$ layer upon it was observed. Unfortunately, neither study generated kinetic data for the rate of SiO$_2$ or hafnon formation within these bond coat systems, making it difficult to evaluate the benefits of this bond coat approach to the long-time survivability of the EBC system.

In chapter 2 it was shown that the solid-state reaction of $\beta$-cristobalite and m-HfO$_2$ at temperatures of 1250°C-1400°C and found rapid formation of hafnon occurs in this temperature range. The formation rate could be fitted by a combined linear plus parabolic rate kinetic model consistent with the hafnon formation reaction being controlled by the diffusion of Si$^{4+}$ through the hafnon layer. However, a two-step reaction is required to form hafnon in a silicon + HfO$_2$ composite system exposed to a dry oxidizing environment. The first oxidation step involves:

$$\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \quad (3.4)$$
This is then followed by the second reaction:

\[
\text{SiO}_2 + \text{HfO}_2 \rightarrow \text{HfSiO}_4
\]  

(3.5)

The instantaneous rate at which the oxidation of the silicon (reaction 3.4) progresses is dependent upon the partial pressure of oxygen, and is both time and temperature dependent since continuation of the reaction requires diffusion of oxidizing species through previously formed SiO₂. However, the overall kinetics for the reaction of a mixture of m-HfO₂, silicon and O₂ is expected to be more complex, since transport of the oxidizing species must permeate through the evolving HfO₂, hafnon, and SiO₂ layer system to reach silicon and reaction 3.4 to continue. This in turn depends upon the oxygen permeability of both the hafnon and SiO₂ layers. Furthermore, the thicknesses and microstructures of these materials, and their permeation rates, are expected to evolve at a rate dictated by that at which SiO₂ and HfO₂ react.

The study presented here uses a model system to experimentally investigate the two-step formation of hafnon in a silicon + m-HfO₂ system. The model system is geometrically similar to that used in chapter 2 to study reaction 3.2 where cristobalite particles were embedded in highly permeable HfO₂ powder composite\(^7\). Here the SiO₂ particles are replaced by spheroidal silicon particles. The partially consolidated, permeable silicon + HfO₂ powder composite, Figure 3.1(a), enabled rapid transport of dry air, and thus oxidation of silicon to occur upon heating, Figure 3.1(b). This is anticipated to be followed by the start of hafnon formation, Figure 3.1(c), and the reaching of a terminal state where most of the SiO₂ has been consumed resulting in a thick layer of hafnon, Figure 3.1(d), ideally impeding the continued oxidation of silicon. Since little is known on the rate of formation of crystalline SiO₂ on polycrystalline silicon particles, the study also measures this on silicon particles at temperatures of 1250°C, 1280°C, and 1316°C where \(\beta\)-cristobalite is expected to form. These results are then used to assess the difference in SiO₂ thickness in the two systems as a function of oxidation time and temperature. The study also investigates the mechanism by which
hafnon forms, and reports a SiO₂ rumpling process when its outward (radial) growth is locally constrained by HfO₂ particles.

![Figure 3.1: Schematic illustration of the model silicon-HfO₂ powder composite system used to explore the time dependent oxidation of silicon in air and dynamic conversion of SiO₂ to hafnon in the presence of HfO₂.](image)

### 3.2 Experimental procedures

#### 3.2.1 Materials

Oerlikon Metco (Westbury, NY) type M4811 silicon powder (-325 mesh, with a particle diameter of 15-53 µm), Figure 3.2(a), and agglomerated, microporous type AE 9930-1S HfO₂ powder (-325 mesh) composed of ~0.7 µm diameter sub-particles, Figure 3.2(b), were used for the study. To assess the silicon oxidation rate, the silicon particles were loosely packed into a 12.7 mm diameter pre-fired Al₂O₃ crucible. For study of the overall reaction, the silicon was dispersed in the HfO₂ powder by blending a 30/70 mol% ratio silicon/HfO₂ powder mixture using a high-energy ball mill (SPEX SamplePrep 8000D, Metuchen, NJ) for 90 minutes, using a DuPont Vertel XF cleaning agent to promote mixing without extensive milling of the powder. The blended powder was then dried in air for 1 hour in ambient air.
3.2.2 Composite sample fabrication and oxidation

The oxygen permeable composite samples were prepared by partial consolidation of the silicon + HfO₂ powder mixture via spark plasma sintering (SPS) using a Thermal Technologies SPS Model 25-10 (Santa Rosa, CA, USA) machine. Consolidation was performed in an argon atmosphere at 1 atm pressure using a cylindrical 35 mm outer diameter, and a 12.7 mm inner diameter graphite die/punch system lined with 0.125 mm thick graphite foil to protect the faces of the die and punches, and simplify retrieval of consolidated samples. The samples were consolidated by heating to 1316°C while applying a pressure of 50 MPa, and holding for 30 minutes at the maximum temperature before cooling. The heating and cooling rates were 150°C/min. Figure 3.3 shows a micrograph of the as-consolidated state indicating large diameter silicon particles in physical contact with a porous HfO₂ matrix as well as crushed silicon fragments dispersed in the HfO₂ matrix. The partially consolidated samples were sliced into ∼2.5 mm thick, 12.7 mm diameter wafers using a diamond wafering blade.

After consolidation in the very low oxygen partial pressure SPS environment, X-ray diffraction (XRD) analysis of the samples (shown later) indicated the presence of only silicon and m-HfO₂ with a 35-40% micropore fraction. To characterize both the crystalline SiO₂ formation rate on the silicon particles, and the SiO₂ and hafnon formation reaction rates in the silicon + HfO₂ powder composites, all the samples were annealed in laboratory air (i.e., under a dry oxygen partial pressure pO₂ = 0.21 atm) in a Sentrotech ST-1600-666 bottom-loading furnace at temperatures of either
1250°C, 1280°C, or 1316°C, for 1, 2, 5, 10, 15, and 20 hours. The heating and cooling rates to these temperatures was set to 10°C/min.

Figure 3.3: SEM micrograph of an as-consolidated silicon + HfO$_2$ sample showing the spheroidal silicon particles, together with fragments of silicon created during mixing, both dispersed in a highly porous, gas permeable HfO$_2$ matrix.

### 3.2.3 Characterization methods

The oxidized silicon powder was embedded in epoxy resin (Buehler EpoKwick FC) and was sectioned in half using a diamond wafering blade. The cross-section surface was mechanically polished, ending with a 0.25 µm diameter diamond particle suspension. The annealed silicon + HfO$_2$ powder composite wafers were first characterized using XRD. A PANalytical Empyrean (Malvern Panalytical, Westborough, MA) X-ray diffractometer was used for the characterization. It was set-up with a Cu-K$_\alpha$ source and Bragg-Brentano optics combined with a reflection/transmission-spinner stage set-up for reflectance measurements. Diffraction angles (2θ) of 15-100° were analyzed at a rate of 0.12°/s. Samples were spun at 0.25 revolutions per second to reduce the effects of preferential grain orientation. The cristobalite peaks were identified using the PDF 00-039-1425 for $\alpha$-cristobalite, and PDF 00-027-0605 for $\beta$-cristobalite. PDF 00-005-0565 was used to identify silicon, PDF 00-034-0104 for monoclinic HfO$_2$, and PDF 01-075-1628 for hafnon.
After XRD analysis the wafers were mounted in an epoxy resin (Buehler EpoKwick FC), and mechanically polished, ending with an 0.25 µm diameter diamond particle suspension. Surface analysis was performed using a Helios NanoLab DualBeam microscope (Thermo Scientific, Hillsboro, OR) operating in back-scattered electron (BSE) imaging mode using a concentric backscatter (CBS) detector. The atomic number (Z)-contrast imaging approach was used to delineate phases of different hafnium, silicon, and oxygen composition. SEM micrographs were used to determine the thickness of the SiO$_2$ and hafnon layers exclusively on spheroidal particles of silicon with a ferret diameter of $\sim$25 µm. The thickness was measured on at least 100 particles with ImageJ software$^{72}$, and a mean thickness standard deviation determined by including both growth parallel to the silicon particle surface and that in the protrusions within the annealed silicon + HfO$_2$ samples. Since the sectioned plane through the silicon spheres randomly sampled a region between the particle equator and a latitude of about 45°, the measured thickness on the section plane was larger than the actual thickness in the radial direction, and was therefore multiplied by a factor of cos(22.5°) = 0.924.

Elemental microanalysis of the various phases was performed by energy dispersive spectroscopy (EDS) using an X-Max$^N$ 150 SDD (Oxford Instruments, Concord, MA) detector with the Helios microscope operated in EDX mode. A low accelerating voltage of 5 kV was used to limit secondary X-ray fluorescence since a higher kV (e.g. 10-15 kV) results in a significant overestimation of the silicon atomic concentration because of secondary X-ray fluorescence (Hf L$_\alpha$ (7.9 kV) and Hf L$_\beta$ (9.0 kV)) emissions are able to re-excite silicon to emit X-rays at its K$_\alpha$ energy of 1.7 kV. Using a lower voltage of 5 kV only excites the silicon K$_\alpha$ and hafnium M$_\alpha$ lines used for EDS quantification of the composition.

After characterization of the reaction rates, some of the sectioned samples were etched in 10 M NaOH for 1.5 hours at 70°C while continuously stirred to remove the unreacted part of silicon.
particles. The samples then exposed to a slow-flowing (44 mm/s) 90 vol% \( \text{H}_2\text{O} \)/10 vol% \( \text{O}_2 \) steam environment for 2 hours at 1200°C to remove the \( \text{SiO}_2 \) layer by reaction with water vapor to form \( \text{Si(OH)}_4 \) (g), and so expose the morphology of the interface between the \( \text{SiO}_2 \) and hafnon layer.

3.2.4 Data fitting

To help ensure that data points far from a fitted line were assigned a lower weighting, all the data were fitted to kinetic models using a bi-square weights fitting method using the Curve Fitting Toolbox in Matlab\textsuperscript{53}, rather than a standard least-squares regression method. The standard deviation was determined by limiting the error output to the 68% prediction bound.

3.3 Results

3.3.1 The silicon-oxygen reaction

XRD analysis of the silicon particle samples after they were subjected to oxidation at 1316°C for 20 hours, Figure 3.4, shows the presence of both silicon and \( \alpha \)-cristobalite after cooling to ambient temperature, indicating oxidation under these conditions resulted in formation of \( \beta \)-cristobalite. The primary \( \alpha \)-cristobalite peak at \( 2\theta = 21.9^\circ \) is broadened. The origin of this is difficult to identify, but is consistent with cristobalite of very small crystallite size, the presence of regions of partial crystal ordering, and/or the presence of significant residual stress associated with the \( \beta \rightarrow \alpha \)-cristobalite phase transformation.

Micrographs of the oxidized silicon powder samples after annealing at 1316°C in atmospheric pressure air for (a) 1 hour, (b) 5 hours, and (c) 20 hours are shown in Figure 3.5. It is evident that a dense, uniformly thick, \( \text{SiO}_2 \) layer had formed on the silicon particle surface, and its thickness increased with time. The TGO layer exhibited no sign of surface deformation (rumpling), but did undergo cracking and delamination at the silicon-\( \text{SiO}_2 \) interface consistent with generation of stress during the \( \beta \rightarrow \alpha \)-cristobalite phase transformation on cooling through \( \sim 240^\circ \text{C} \). Figure 3.6 shows
Figure 3.4: XRD pattern of a gas permeable silicon powder compact after annealing at 1316°C for 20 hours. The presence of α-cristobalite peaks after cooling to room temperature is indicative of the formation of a crystalline β-cristobalite SiO$_2$ during the anneal.

Figure 3.5: SEM images of polished silicon particles after oxidation at 1316°C for a) 1 hour, b) 5 hours, and c) 20 hours. Fracture of the crystalline SiO$_2$ layer on particle surfaces is consistent with the β→α-cristobalite transformation on cooling through 240°C.

The variation of SiO$_2$ oxide layer thickness, measured as described in section 2.3, on the silicon powder (blue data) with reaction time at (a) 1250°C, (b) 1280°C, and (c) 1316°C. The thickness of the oxide increased with temperature, and at fixed temperature, increased approximately parabolically with time.

In order to investigate if the crystalline SiO$_2$ thickness grown on a polycrystalline silicon particle can be predicted by extrapolation of the Deal and Grove model, the model was first modified for oxidation of a polycrystalline silicon surface. The thickness of the oxide formed is well approximated by the average of that on the {100} (slowest oxidizing silicon plane with lowest atomic
density) and \{111\} planes (fastest oxidizing silicon plane with highest atomic density) surfaces\textsuperscript{61}. These thicknesses were determined for vitreous SiO\textsubscript{2} formation at 1250°C, 1280°C, and 1316°C, using the activation energies and pre-exponential factors from the Deal and Grove model\textsuperscript{37}, Table 3.1, and averaged to find the oxide thickness grown on a polycrystalline silicon surface. It was assumed that oxidation occurs in dry oxygen conditions at atmospheric pressure (p\textsubscript{O\textsubscript{2}} = 0.21 atm). The crystalline SiO\textsubscript{2} thickness can then be found by accounting for the volume shrinkage during crystallization of the vitreous oxide, and during conversion of the \(\beta\)-phase to \(\alpha\)-cristobalite during cooling. To convert the vitreous SiO\textsubscript{2} thickness to \(\beta\)-cristobalite, the vitreous SiO\textsubscript{2} thickness was multiplied by the ratio of the molar volume of vitreous SiO\textsubscript{2} and \(\beta\)-cristobalite \(\left(\frac{V_{\text{Vitreous}}}{V_{\text{M}}} = 0.944\right)\). This thickness was then converted to that of \(\alpha\)-cristobalite by dividing the thickness by 1.049, to account for the 4.9% volume reduction during the \(\beta\rightarrow\alpha\)-cristobalite phase transformation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Oxidation regime</th>
<th>Activation energy (eV)</th>
<th>Pre-exponential factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon {100}</td>
<td>B/A (linear)</td>
<td>2</td>
<td>3.71x10\textsuperscript{6} (µm/hr)</td>
</tr>
<tr>
<td></td>
<td>B (parabolic)</td>
<td>1.23</td>
<td>772 (µm\textsuperscript{2}/hr)</td>
</tr>
<tr>
<td>Silicon {111}</td>
<td>B/A (linear)</td>
<td>2</td>
<td>6.23x10\textsuperscript{6} (µm/hr)</td>
</tr>
<tr>
<td></td>
<td>B (parabolic)</td>
<td>1.23</td>
<td>772 (µm\textsuperscript{2}/hr)</td>
</tr>
<tr>
<td>Deal and Gove modified for (\alpha)-cristobalite</td>
<td>B (parabolic)</td>
<td>1.3</td>
<td>1.02x10\textsuperscript{3} (µm\textsuperscript{2}/hr)</td>
</tr>
</tbody>
</table>

In order to calculate temperature dependent rate constant, \(k_p\), an Arrhenius equation was used:

\[
k_p = k_0 \exp \left(-\frac{E_a}{k_B T}\right) \tag{3.6}
\]

where \(k_0\) is the pre-exponential factor, \(E_a\) is the activation energy (in eV), \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature. The activation energy and pre-exponential factor for the Deal and Grove model, modified for cristobalite formation, is noted in Table 3.1.
Figure 3.6: The measured (crystalline) SiO$_2$ layer thickness on silicon particles versus reaction time (blue). This was always less than the thickness of SiO$_2$ predicted by extension of the Deal and Grove model (black). The measured thickness of the crystalline SiO$_2$ layer on silicon particles immersed in a porous HfO$_2$ matrix is also shown (red) together with a parabolic model fit to the data beyond 5 hours.
Figure 3.6 indicates that the measured thickness of the $\alpha$-cristobalite SiO$_2$ layer formed during the oxidation of the silicon particles was always less than that predicted by this extrapolation of the Deal and Grove model$^{37}$ (black dashed line), implying that the diffusional processes necessary for crystalline oxide formation are slower in the crystalline phase.

### 3.3.2 The silicon-oxygen-HfO$_2$ reaction

Both SEM imaging (Figure 3.3) and XRD analysis (Figure 3.7(a)) of the as-consolidated silicon + HfO$_2$ powder composite indicated that the SPS process used to consolidate the powder mixture did not result in the formation of either crystalline SiO$_2$ or hafnon. Examination of the diffractionograms of samples after annealing at 1316°C for 1 hour, 5 hours, and 20 hours, Figure 4(b, c, and d), indicate an increasing intensity of the hafnon and $\alpha$-cristobalite peaks, with reaction time, accompanied by a decrease in intensity of the m-HfO$_2$ peaks.

SEM images of samples reacted at 1250°C, 1280°C, and 1316°C for 1, 5, and 20 hours, are shown in Figure 3.8. The m-HfO$_2$ matrix in which the silicon particles were embedded is seen to have remained porous, allowing oxygen to continue to permeate through the HfO$_2$ and reach the silicon particle surface. Examination of the BSE contrast images of reacted samples revealed the presence of grey and black contrast layers on the silicon particle surfaces. The darker contrast layer was in contact with the silicon surface while the lighter grey layer had formed between the dark contrast layer and the white HfO$_2$ matrix. The thickness of the grey layer increased with both time and temperature, and was always substantially thicker than the darker contrast layer. EDS line scans through the layers after reaction for 5 and 20 hours at 1316°C are compared with an as-consolidated sample in Figure 3.9. These scans indicate the dark contrast layer contained only silicon and oxygen, while the grey phase also contained hafnium and is stoichiometric HfSiO$_4$. Due to the large spot size needed to obtain a sufficient signal-to-noise ratio for the EDS data col-
Figure 3.7: XRD patterns of silicon + HfO₂ samples in the a) as-consolidated state, showing the absence of both α-cristobalite SiO₂ and hafnon. These two phases were present in samples annealed at 1316°C for b) 1 hour, c) 5 hours, and d) 20 hours. The hafnon peak intensities increased, while those of HfO₂ decreased with reaction time at this temperature.
Figure 3.8: SEM micrographs in BSE imaging mode of porous silicon + HfO$_2$ powder composite samples annealed in air for 1 hour (left column), 5 hours (middle column), and 20 hours (right column) at temperatures of 1250°C (top row), 1280°C (second row), and 1316°C (bottom row). The growth of the hafnon (intermediate grey phase) can be seen as the reaction time and temperature increased. A thin SiO$_2$ remnant layer (darkest contrast) can be seen on the silicon particles of images (c), (f) and especially (i).
lected with a low accelerating voltage of 5kV, the precise stoichiometry of the dark contrast layer in the 5-hour sample (Figure 3.9(b)) could not be obtained. For the 20-hour sample the stoichiometry of the dark contrast layer averages a Si:O stoichiometry of 1:2, indicating that the dark layer was SiO$_2$.

![Figure 3.9: SEM micrographs taken in BSE mode and EDS line-scans of silicon + HfO$_2$ samples after a) consolidation (no SiO$_2$ or hafnon were present), and after annealing at 1316°C for b) 5 hours and c) 20 hours showing the growth of a SiO$_2$ layer on the silicon particle and its reaction with HfO$_2$ to form hafnon. Note the rumpling of the SiO$_2$ layer and the local penetration of protuberances into the hafnon layer.](image)
The SiO$_2$ layer thickness is plotted versus reaction time at the three reaction temperatures in Figure 3.6. It can be seen that the SiO$_2$ oxide thickness in the silicon + HfO$_2$ powder composite samples was always substantially less than that measured on the same silicon particles in the absence of HfO$_2$. To test for parabolic reaction kinetics, the square of the hafnon layer thickness thickness (measured by randomly determining the thickness normal to particle surface including both uniform thickness and protruded regions) is plotted as a function of time at the three reaction temperatures in Figure 3.10. It can be seen that the data is well fitted by a parabolic rate law if the start of the hafnon formation reaction was delayed by approximately 3.5 hours at 1250°C. This incubation time decreased with reaction time, and was approximately 1 hour at 1316°C. Thereafter, the hafnon reaction appears to be diffusion controlled, consistent with what was seen in chapter 2 of the reaction between $\beta$-cristobalite and m-HfO$_2$.

**Figure 3.10:** Hafnon thickness (squared) versus reaction time at temperatures of 1250°C, 1280°C, and 1316°C. Hafnon formation can be seen to start after an incubation time that decreased with increasing reaction temperature.

Examination of the interface between the SiO$_2$ and hafnon layers, Figure 3.9(b) and (c), shows the presence of significant rumpling of the outer surface of the SiO$_2$ layer with many protrusions
into the hafnon region that are 0.4-0.5 µm wide when measured parallel to the silicon particle surface. This rumpling was absent on the oxidized surface of the silicon particles when partially oxidized in the absence of a HfO$_2$ particle matrix, Figure 3.5. A higher magnification view of a sample oxidized for 1 hour at 1250°C, Figure 3.11(a), indicates that the SiO$_2$ protrusions had extended the pore spaces in between HfO$_2$ particles in contact with the SiO$_2$, and were separated by about 0.5-0.7 µm, which is similar to the average diameter of HfO$_2$ particles. As the oxidation time progressed and hafnon formed, Figure 3.11(b), thin layers of hafnon developed at contacts between the HfO$_2$ particles in contact with SiO$_2$ covered silicon particle surfaces, while thicker hafnon layers formed in the voids between pairs of HfO$_2$ particles in contact with the SiO$_2$ protrusions.

To investigate this reaction mechanism further, the silicon and SiO$_2$ in a sample annealed at 1316°C for 20 hours was removed as described in Section 3.2.3, and analyzed by SEM. The exposed surface of the SiO$_2$-hafnon interface is shown in Figure 3.12. The protrusions of the SiO$_2$ into prior HfO$_2$ interparticle pores can be seen as pockets in the hafnon with a width of 0.4-0.5 µm, similar to the width of the protrusions seen in Figure 3.9. Hafnon appeared to have nucleated at the protrusions, and grain boundaries developed where adjacent hafnon eventually made contact.

Figure 3.11: High magnification SEM images of the silicon-HfO$_2$ interfaces in samples annealed for a) 1 hour and b) 5 hours at 1250°C
Figure 3.12: The hafnon-SiO$_2$ interface exposed by removal of silicon and the SiO$_2$ layer using a NaOH and steam etch where (a) a low magnification image showing hafnon surface that had been in contact with the oxidized surface of a large silicon particle, and (b) topology of the hafnon surface that had been in contact with the SiO$_2$ surface in greater detail.

3.4 Discussion

The rate at which crystalline $\beta$-cristobalite SiO$_2$ forms on silicon particles when heated to between 1250°C and 1316°C in a dry, laboratory air environment, has been measured and shown to increase with temperature. The SiO$_2$ thickness was uniform around the periphery of the particles. After cooling to ambient, XRD analysis indicated the SiO$_2$ layer was $\alpha$-cristobalite, Figure 3.4, consistent with the oxide forming at these reaction temperatures to be crystalline $\beta$-cristobalite. The oxide layer had undergone substantial microcracking consistent with the $\beta \rightarrow \alpha$-transformation of cristobalite on cooling. When HfO$_2$ particles were placed in contact with these silicon particle surfaces, XRD analysis indicated that the formation of crystalline SiO$_2$ was followed by a reaction between SiO$_2$ and HfO$_2$ to form hafnon. The net thickness of SiO$_2$ was significantly reduced compared to that formed on the same silicon particles exposed to a similar environment. The SiO$_2$ thickness on silicon particles distributed in a HfO$_2$ particle matrix was also non-uniform, with numerous SiO$_2$ layer protrusions extending into the hafnon layer.

3.4.1 Rate of SiO$_2$ formation on spheroidal silicon particles

The thickness of the SiO$_2$ layer formed on silicon particles is shown in Figure 3.6 (blue data) together with an extrapolation of the Deal and Grove model$^{37}$ for vitreous SiO$_2$ formation to the
temperatures used here, and modified to account for the higher density of the crystalline state. At
the oxidation temperatures (<1200°C) for which the Deal and Grove model was developed, an
initial 60-100 nm thick region of vitreous SiO₂ forms with a thickness that depends linearly upon
reaction time. At the temperatures used here, this thickness would be reached rapidly, well before
the acquisition of the first data in Figure 3.6. The measured SiO₂ thickness on oxidized silicon
particles was therefore well fitted by a simple parabolic model of the form;

\[ x_{\text{SiO}_2} = (k_p t)^{1/2} \]  

(3.7)

where \( x_{\text{SiO}_2} \) is the SiO₂ thickness, \( k_p \) a the parabolic rate constant, and \( t \) is the reaction time
at temperature. The value of \( k_p \) was found to be temperature-dependent and fitted an Arrhenius
expression of the form given by equation 3.6. The activation energy for the formation of crystalline
SiO₂ on these silicon particles was found to be \( E^p = 2.2 (\pm 0.2) \) eV, Table 3.2.

When the measured cristobalite layer thickness and the modified Deal and Grove prediction
are compared, Figure 3.6, the measured thickness was always less than the Deal and Grove extrap-
olation, even when the higher density of the crystalline phase was accounted for. The activation
energy for the parabolic rate constant \( B \) in the Deal and Grove model for vitreous SiO₂ growth
is 1.3 eV\(^{37} \), substantially less than that for growth of the crystalline oxide. These observations
indicate that the diffusion processes in the crystalline β-cristobalite phase are slower than those in
the less dense vitreous phase. Lamkin et al.\(^{39} \) have reviewed the diffusion of oxygen in different
phases of SiO₂, and found that the diffusivity in crystalline SiO₂ phases is 2-4 orders of magni-
itude less than that of the vitreous phase. The reduced oxygen flux transported through a more
densely packed crystalline SiO₂ phase therefore appears to be responsible for the lower rate of
β-cristobalite thickening compared to that extrapolated for a vitreous SiO₂ scale, resulting in the
smaller SiO₂ layer thickness measured in this study.
Table 3.2: Activation energies and pre-exponential factors for the formation of SiO$_2$

<table>
<thead>
<tr>
<th>System</th>
<th>Activation energy (eV)</th>
<th>Pre-exponential factor (um$^2$/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cristobalite modified Deal and Grove</td>
<td>1.3</td>
<td>1.02x10$^3$</td>
</tr>
<tr>
<td>Silicon particle oxidation</td>
<td>2.2 (± 0.2)</td>
<td>5.14x10$^5$</td>
</tr>
<tr>
<td>Silicon + HfO$_2$ composite</td>
<td>2.3 (± 0.4)</td>
<td>3.15x10$^5$</td>
</tr>
</tbody>
</table>

3.4.2 Hafnon formation in the silicon + HfO$_2$ powder composite

The squared hafnon thickness was shown as a function of reaction time in Figure 3.10 for each reaction temperature. The results are consistent with a hafnon formation rate that exhibits parabolic kinetics once an incubation time, $t_0$, is passed. The hafnon layer thickness $x_H^2$ can be fitted by a parabolic model;

$$x_H^2 = k_p^H(t-t_0^H)$$  \hspace{1cm} (3.8)

where $k_p^H$ is the parabolic rate constant for hafnon formation in the silicon + HfO$_2$ system, and $t_0^H$ is the incubation time until hafnon starts to form. This time decreased rapidly with increasing reaction temperature. The parabolic rate constants and incubation time for the parabolic model fits to the hafnon data are given in Table 3.3. The activation energy for hafnon formation in this system was 5.0 (±0.6) eV, consistent with the value of 5.5 (±1.5) eV found in chapter 2 by hafnon formation by the reaction of $\beta$-cristobalite and HfO$_2$ powders.

Table 3.3: Fitting parameters for equation 3.8 for the growth of hafnon, and equation 3.9 for the net growth of SiO$_2$ during hafnon formation

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$k_p^H$ (µm$^2$/hr)</th>
<th>$t_0^H$ (hr)</th>
<th>$k_p^{SiO_2}$ (µm$^2$/hr)</th>
<th>$t_0^{SiO_2}$ (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>4.745x10$^{-2}$</td>
<td>4.3</td>
<td>6.862x10$^{-3}$</td>
<td>1.4</td>
</tr>
<tr>
<td>1280</td>
<td>7.007x10$^{-2}$</td>
<td>1.2</td>
<td>9.723x10$^{-3}$</td>
<td>2.2</td>
</tr>
<tr>
<td>1316</td>
<td>1.623x10$^{-1}$</td>
<td>1.1</td>
<td>1.428x10$^{-2}$</td>
<td>1.8</td>
</tr>
</tbody>
</table>

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3.4.3 Net SiO$_2$ thickening rate in a permeable silicon-HfO$_2$ powder composite

The oxidation of the partially consolidated silicon + HfO$_2$ system has resulted in the formation of crystalline SiO$_2$ and hafnon shells surrounding the spheroidal silicon particles similar to that schematically illustrated in Figure 3.1. The measured (net) SiO$_2$ layer thickness resulted from a competition between the rate of SiO$_2$ formation and its loss by reaction with HfO$_2$ to form hafnon. Both the oxide layer thickness for spheroidal silicon particles (blue data) and for those in contact with HfO$_2$ (red data) are plotted in Figure 3.6. The experimental data indicate that the rate of hafnon formation was sufficient to significantly reduce the SiO$_2$ layer thickness when HfO$_2$ was in contact with SiO$_2$, even in the high oxygen flux environment of this experiment. It also indicates that the difference between the net SiO$_2$ thickness and that forming on silicon increased with both reaction time and temperature.

The data points (in red) in Figure 3.6 show that for all three temperatures, a transient net oxide thickness regime is found that continued until a thickness of $\sim$200 nm was established. At 1250°C oxide thickening rate temporarily ceased, while at 1280°C and 1316°C it is seen to reverse sign before increasing again. The time at which this transient in net SiO$_2$ thickness occurs approximately coincides with the incubation time for hafnon formation, Figure 3.10. This suggests that initially, SiO$_2$ grows on silicon particles in places where it is not in contact with HfO$_2$ (i.e. into the pores between HfO$_2$ particles). Once SiO$_2$ contacts HfO$_2$, the ensuing hafnon formation reaction is rapid, consistent with the initial stages of a parabolic rate law. At 1316°C, Figure 3.6(c), this rapid increase in hafnon formation (and thus loss of SiO$_2$) results in a drop in SiO$_2$ thickness.

Following this transient regime, competition between SiO$_2$ formation and SiO$_2$ loss by hafnon formation resulted in a net positive rate of SiO$_2$ formation that could be empirically fitted by a parabolic model of the form:

$$x_{\text{SiO}_2}^2 = k_p(t-t_0^{\text{SiO}_2}) \quad (3.9)$$
where $t_0^{SiO_2}$ corresponds to a shift in time to exclude the transient regime. Once the competition between oxidation and hafnon formation was established, the net parabolic rate $k_p^{SiO_2}$ had an activation energy of 2.3 ($\pm$0.4) eV, similar to that for the formation of cristobalite SiO$_2$ although with a different pre-exponential factor, given in Table 3.2.

### 3.4.4 The total SiO$_2$ growth rate in the silicon + HfO$_2$ powder composite system

The net SiO$_2$ thickness measured in the silicon + HfO$_2$ powder composite system, Figure 3.6, is not indicative of the total amount of SiO$_2$ formed during oxidation since it does not account for the SiO$_2$ that was consumed to form hafnon. It is important to determine how much SiO$_2$ had formed in total in order to predict the required silicon layer thickness for a duplex silicon + HfO$_2$ bond coat. The total thickness of SiO$_2$ created during oxidation is:

$$t_{SiO_2}^{total} = t_{SiO_2}^{net} + t_{SiO_2}^{conv} \tag{3.10}$$

where $t_{SiO_2}^{net}$ is the net (measured) SiO$_2$ thickness presented in Figure 3.6, and $t_{SiO_2}^{conv}$ is the thickness of SiO$_2$ converted to hafnon. The converted thickness can be determined by converting the volume of a hollow, spherical hafnon shell with thickness $t_{Hafnon}$, Figure 3.10, surrounding a SiO$_2$ layer coated silicon particle, Figure 3.1(c), to that of the SiO$_2$ required to form it. During silicon particle oxidation, the average net silicon particle radius $r_{Si}^{net}$ decreases compared to the average initial silicon particle radius $\bar{r}_{Si}$, since silicon is also lost as it oxidizes to form SiO$_2$.

The volume of an annular spherical hafnon shell is given by:

$$V_H = \frac{4}{3} \pi (r_H^3 - r_{SiO_2}^{net}^3) \tag{3.11}$$

where the outer radius of the hafnon shell, $r_H = r_{Si}^{net} + r_{SiO_2}^{net} + t_H$, and $r_{SiO_2}^{net} = r_{Si}^{net} + t_{SiO_2}^{conv}$. Appendix 3.A provides a procedure for the calculation of $r_{Si}^{net}$. Substitution of $r_H$ and $r_{Si}^{net}$ into equation 3.11 gives the volume of the hollow hafnon shell:
\[ V_H = \frac{4}{3} \pi \left[ (\bar{r}_{\text{Si}} + 0.565t_{\text{netSiO}_2} + t_H)^3 - (\bar{r}_{\text{Si}} + 0.565t_{\text{netSiO}_2})^3 \right] \] (3.12)

The volume of the SiO\(_2\) shell that was converted to hafnon can then be found by multiplying \( V_H \) by the ratio of the molar volumes of \( \beta\)-cristobalite (\( V_{\beta M}^M = 25.78 \text{ cm}^3/\text{mol} \)) and hafnon (\( V_{H M}^M = 38.79 \text{ cm}^3/\text{mol} \)), \( \frac{V_{H M}^M}{V_{\beta M}^M} = 0.664 \), and converted to \( \alpha\)-cristobalite by accounting for the 4.9% volume shrinkage (multiplying by a factor of 0.951), so that the volume of SiO\(_2\) converted to hafnon equals:

\[ V_{\text{SiO}_2}^{\text{conv}} = 0.631V_H \] (3.13)

The thickness of the shell surrounding the net silicon particle and net (measured) SiO\(_2\) layer is then:

\[ t_{\text{SiO}_2}^{\text{conv}} = \left[ \frac{3V_{\text{SiO}_2}^{\text{conv}}}{4\pi} + (\bar{r}_{\text{Si}} + 0.565t_{\text{netSiO}_2})^3 \right]^{\frac{1}{3}} - \bar{r}_{\text{Si}} - 0.565t_{\text{netSiO}_2} \] (3.14)

The SiO\(_2\) thickness converted to hafnon obtained from equation 3.14 has been substituted into equation 3.10 to find the total thickness of SiO\(_2\) formed during oxidation and conversion to hafnon in this system.

The thickness of SiO\(_2\) converted to hafnon (black data) together with the sum of the hafnon converted and the measured (net) SiO\(_2\) thickness is plotted in red in Figure 3.13, and compared to the measured SiO\(_2\) layer thickness on silicon particles when HfO\(_2\) was not present (blue data). For the reactions at 1250°C, Figure 3.13(a), the thickness of SiO\(_2\) that was converted to hafnon after the incubation time for the hafnon reaction was exceeded, was approximately the same as the measured net SiO\(_2\) thickness in the experiment. About a half of the SiO\(_2\) was converted to hafnon by reaction with HfO\(_2\). At this temperature, the total SiO\(_2\) thickness created during silicon oxidation and simultaneous conversion to hafnon was about the same as that measured on silicon particles when no HfO\(_2\) was present.
Figure 3.13: The measured thickness of SiO$_2$ on silicon particles (blue), the thickness of SiO$_2$ used in the formation of hafnon (black) and the total thickness of SiO$_2$ formed during silicon oxidation and hafnon formation (red), at a) 1250°C, b) 1280°C, and c) 1316°C
As the temperature and the rate of the hafnon formation reaction increased, both the thickness of SiO₂ formed during oxidation and the thickness of SiO₂ converted to hafnon increased, Figures 3.13 (b) and (c). At 1316°C, Figure 3.13(c), the thickness of SiO₂ converted to hafnon was comparable to the thickness of SiO₂ formed on silicon particles without HfO₂ present, and the total SiO₂ formed by oxidation and hafnon formation was approximately 1.5 times that measured on the silicon particles. This increase in total SiO₂ formation rate is consistent with a higher oxygen permeability through the always thinner SiO₂ layer that exists when hafnon was being formed, and a hafnon layer morphology that was relatively ineffective at impeding oxygen transport to the SiO₂ surface.

With increasing reaction temperature, the formation of the two phase SiO₂/hafnon reaction layer consumed significantly more silicon, and was less protective compared to the SiO₂ layer that forms on silicon without HfO₂ present. This implies that if HfO₂ particles were added to the silicon bond coat of an EBC system, the total amount of SiO₂ formed during oxidation of the silicon bond coat at 1316°C for a fixed time, increasing the amount of silicon consumed compared to a conventional silicon bond coat.

The reduction in the net SiO₂ thickness remaining after reaction is approximately halved in this study, but actual results in an EBC system would be dependent on the rate of supply of oxidizing species to the silicon. This is influenced by the permeability of the EBC layer applied over the silicon + HfO₂ bond coat and the volume fraction of HfO₂ in the duplex bond coat since oxidizer diffusion through HfO₂ is much faster than via other routes. Since SiO₂ is the primary source of the thermal mismatch strain energy on cooling, and this strain energy scales linearly with SiO₂ thickness, the decrease in its thickness is anticipated to reduce the thermo-mechanical stresses and stored elastic strain energy by the thickness reduction ratio during thermal cycling⁷³, and therefore extend the delamination lifetime.
3.4.5 Microstructural evolution and reaction mechanisms

The proposed transport mechanisms responsible for the formation of hafnon are schematically illustrated in Figure 3.14, and are similar to those of Veytizou et al.\textsuperscript{42} for the formation of zircon. In this case, the formation of hafnon at the interface between a silicon and HfO\textsubscript{2} particle begins after the permeation of molecular oxygen (O\textsubscript{2}) through the highly permeable HfO\textsubscript{2} to the silicon surface where it forms SiO\textsubscript{2}. This SiO\textsubscript{2} then reacts with HfO\textsubscript{2} to form a first hafnon layer. Once a first complete layer of hafnon has formed, both atomic and molecular oxygen must diffuse through the newly formed hafnon to continue the reactions. Data for oxygen diffusivity in hafnon has not been reported, but if it is taken to be similar to the diffusion of oxygen through single crystal zircon, the lattice diffusivity of oxygen in hafnon would be about $\sim 10^{-19}$ m\textsuperscript{2}/s at 1300°C\textsuperscript{74}. In this study, the rapid formation of hafnon that has been observed does not agree with such a low rate of diffusion, and we infer that lattice defects and grain boundaries play a significant role in oxygen transport within hafnon. Once oxygen diffuses through hafnon, it then diffuses through the SiO\textsubscript{2} to continue the oxidation of silicon, and the continuing growth of SiO\textsubscript{2} protrusions.

The formation of hafnon requires the diffusive transport of silicon (presumably interstitially as Si\textsuperscript{4+}) from the SiO\textsubscript{2} through the previously formed hafnon layer, while molecular oxygen (O\textsubscript{2}) is supplied at the hafnon-HfO\textsubscript{2} interface from the environment. The atomic oxygen (2O\textsuperscript{2−}) created as Si\textsuperscript{4+} is transported through the SiO\textsubscript{2}, is then taken to diffuse through the SiO\textsubscript{2} layer towards the silicon surface, where it reacts to form SiO\textsubscript{2}. To preserve charge neutrality, four electrons created in this way at the silicon/SiO\textsubscript{2} interface are then transported through the SiO\textsubscript{2} and hafnon layers to the hafnon/HfO\textsubscript{2} interface to reduce O\textsubscript{2} to 2O\textsuperscript{2−}. The interstitial diffusion of Si\textsuperscript{4+} to form hafnon leads to a reaction rate that exhibits diffusion-limited kinetics, and therefore parabolic reaction kinetics governed by equations 3.7 and 3.8.
Figure 3.14: The proposed transport processes during oxidation and hafnon formation in the silicon + HfO$_2$ system, showing separation of SiO$_2$ into Si$^{4+}$ and 2O$^{2-}$, followed by Si$^{4+}$ interstitial diffusion through HfSiO$_4$ to the HfSiO$_4$/HfO$_2$ interface. The 2O$^{2-}$ diffuses through SiO$_2$ to oxidize silicon. Diffusion of oxygen species from the environment through HfO$_2$ to the hafnon-HfO$_2$ interface reacts with Si$^{4+}$ and HfO$_2$ to form HfSiO$_4$.

To better understand the mechanisms controlling the SiO$_2$ and hafnon reactions, and the hafnon morphology that developed during oxidation of the binary silicon + HfO$_2$ system, SEM analysis was used to examine the evolution of the interfaces of the reaction products, Figures 3.9 and 3.11. Use of a highly porous HfO$_2$ microstructure allowed oxygen to rapidly permeate to the silicon surface. As silicon was oxidized, and the volume of the system increased, the radial growth of the SiO$_2$ was mechanically constrained at locations where silicon was in contact with HfO$_2$ particles, leading to the non-uniform growth of SiO$_2$ protrusions into the pore spaces between adjacent HfO$_2$ particles. The time required for these SiO$_2$ protrusions to grow until contact was made with HfO$_2$ surfaces is then taken to correspond to the incubation time for hafnon formation reported in Figure 3.10 and summarized in Table 3.3.

After removal of both the silicon spheres and the SiO$_2$, Figure 3.12 reveals the presence of both pores in the hafnon layer at locations that were originally occupied by the SiO$_2$ protrusions, and the presence of hafnon grain boundaries intersecting the hafnon on the SiO$_2$ surface. Examination of Figure 3.11(b) indicates that the prior location of SiO$_2$ protrusions (now pores) was near the center
of the hafnon grains; consistent with being the region from which hafnon formation was initiated. This process is schematically illustrated in Figure 3.15, where the initial as-consolidated state is shown in Figure 3.15(a), followed by a regime where SiO₂ protrusions form in the gaps between HfO₂ particles, Figure 3.15(b). Hafnon then grew outward from the protrusions into HfO₂ particles, Figure 3.15(c) and (d), until the hafnon reaction fronts from adjacent protrusions impinged upon each other, leading to the formation of a grain boundaries oriented approximately normal to the SiO₂ surface, Figure 3.15(e), and therefore promoted grain boundary transport of oxygen through the hafnon layer.

The interfacial area between SiO₂ and HfO₂ influences the hafnon formation rate, as illustrated in Figure 3.15. Larger contact areas grow bigger hafnon grains, and so the spacing of protrusions from the SiO₂ layer played an important role in determining the direction of hafnon grain boundary growth. In the experiments described in this study, a small HfO₂ particle size was used, resulting in a high density of SiO₂ protuberances, a large interfacial area between SiO₂ and HfO₂, and small distance between grain boundaries. Additionally, hafnon was found to grow outward from the silicon particles, and into the HfO₂ particles. Implementation of a duplex silicon-HfO₂ bond coat in EBC systems might therefore be best achieved using a dense, bilayer architecture, rather than a HfO₂ particle-based approach. In this way, the hafnon layer can grow outward and potential thermo-mechanical stresses generated by protrusions growing into the hafnon/HfO₂ layer can be minimized. The continued oxidation of silicon would then require diffusion through both the hafnon and SiO₂ layers, and therefore more effectively reduce the overall rate of oxidation.

### 3.5 Conclusions

The oxidation of spheroidal silicon particles at 1250°C, 1280°C, and 1316°C, in atmospheric pressure air (pO₂ = 0.21 atm) results in the formation of β-cristobalite SiO₂, which then transforms to α-cristobalite upon cooling. The growth of this crystalline SiO₂ layer on silicon particles was well-
Figure 3.15: Schematic illustration of the interfacial reaction mechanisms between silicon and HfO$_2$ particles. a) The initial silicon + HfO$_2$ state. b) SiO$_2$ formation on silicon particles in pores between HfO$_2$ particles leading to the start of rumpling. c) Early stage hafnon formation on the surface of SiO$_2$ protrusions. d) Growth of hafnon into HfO$_2$ particles. e) The late stage showing hafnon grain boundaries at locations of adjacent hafnon reaction front impingement.
modelled by parabolic kinetics with an activation energy of 2.2 (±0.2) eV. This activation energy is greater than the value of 1.3 eV deduced for vitreous SiO$_2$ formation at lower temperatures. The crystalline SiO$_2$ thickness was also less than that predicted by extrapolation of Deal and Grove model for vitreous SiO$_2$ formation$^{37}$, consistent with a decrease in oxygen diffusion in the more closely packed, crystalline SiO$_2$ phase. When these spheroidal silicon particles were dispersed in a porous HfO$_2$ matrix, silicon oxidation was followed by its dynamic conversion to hafnium silicate (HfSiO$_4$, hafnon). The study of this model system has shown that:

1. When spheroidal silicon particles were immersed in a partially consolidated, porous m-HfO$_2$ matrix, SiO$_2$ formation on silicon particles was accompanied by reaction with the m-HfO$_2$ particles to form hafnon. The net thickness of SiO$_2$ was decreased by at least a factor of two compared that observed on silicon particles without m-HfO$_2$ present.

2. The total amount of silicon converted to SiO$_2$ when HfO$_2$ was present was found to be significantly greater than that formed in the absence of HfO$_2$. This increase in SiO$_2$ formation rate was consistent with a higher oxygen permeability through the always-thinner SiO$_2$ layer that exists when hafnon has formed, and a high oxygen diffusivity in the hafnon phase.

3. The SiO$_2$ formed on silicon particles immersed in a porous m-HfO$_2$ matrix exhibited severe rumpling. However, no rumpling was observed in the absence of a m-HfO$_2$ particle-matrix. Rumpling only occurred when the radial expansion of an SiO$_2$ layer on spheroidal silicon particles was partially constrained by contact with HfO$_2$ particles, and was found to grow into pores between m-HfO$_2$ particles.

4. The results indicate that a HfO$_2$ modified silicon bond coat is a potential coating candidate for use in environmental barrier coating systems, since the reduction in thickness of a crystalline SiO$_2$ TGO by the dynamic formation of a hafnon layer is expected to reduce the risk of coating system delamination.
3.A Derivations for the idealized spherical model

The spherical particle model, Figure 1(c), places hollow shells around a silicon particle, where the inner shell is the measured SiO$_2$ layer with net thickness $t_{\text{net}}^\text{SiO}_2$, and the outer shell is the hafnon layer with thickness $t_H$. The volume of the hafnon layer can be found using equation 3.11, in which the net radius of the silicon particle (after some of the silicon is lost during oxidation) is denoted as $r_{\text{net}}^\text{Si}$:

$$r_{\text{net}}^\text{Si} = \bar{r}_\text{Si} - t_{\text{Si}}^\text{Lost} \quad \text{(3.A1)}$$

where $\bar{r}_\text{Si}$ is the average silicon particle radius (12.5 µm) prior to any oxidation, and $t_{\text{Si}}^\text{Lost}$ is the thickness of the silicon lost due to oxidation. This thickness can be found by converting the net (measured) thickness of SiO$_2$ $t_{\text{Net}}^\text{SiO}_2$ by the ratio of molar volumes of silicon ($V_M^\text{Si} = 12.106 \text{ cm}^3/\text{mol}$) and $\beta$-cristobalite ($V_M^\beta = 26.469 \text{ cm}^3/\text{mol}$), and the volume change ($\Delta V^\beta \rightarrow \alpha = 0.951$) during the $\beta \rightarrow \alpha$-cristobalite phase transformation:

$$t_{\text{Si}}^\text{Lost} = \frac{V_M^\text{Si}}{V_M^\beta \Delta V^\beta \rightarrow \alpha t_{\text{Net}}^\text{SiO}_2} = 0.435 t_{\text{Net}}^\text{SiO}_2 \quad \text{(3.A2)}$$

Substitution of equation 3.2 into equation 3.1 gives:

$$r_{\text{Net}}^\text{Si} = \bar{r}_\text{Si} - 0.435 t_{\text{Net}}^\text{SiO}_2 \quad \text{(3.A3)}$$

The volume of the hafnon shell, $V_H$, is found using equation 3.11:

$$V_H = \frac{4}{3} \pi (r_H^3 - r_{\text{net}}^\text{SiO}_2^3) \quad \text{(3.11)}$$

where the outer radius of the hafnon shell, $r_H = r_{\text{net}}^\text{Si} + t_{\text{net}}^\text{SiO}_2 + t_H$, and $r_{\text{net}}^\text{Si} = r_{\text{net}}^\text{Si} + t_{\text{net}}^\text{SiO}_2$. This results in;
\[ V_H = \frac{4}{3} \pi \left[ (r_{\text{net Si}} + t_{\text{net SiO}_2} + t_H)^3 - (r_{\text{Si}} + t_{\text{net SiO}_2})^3 \right] \]  

(3.A4)

Substitution of equation 3.A3 into equation 3.A4 results in equation 3.12 for the volume of the hollow hafnon shell:

\[ V_H = \frac{4}{3} \pi \left[ (\bar{r}_{\text{Si}} + 0.565t_{\text{net SiO}_2} + t_H)^3 - (\bar{r}_{\text{Si}} + 0.565t_{\text{net SiO}_2})^3 \right] \]  

(3.12)

In order to find the thickness of the \( \text{SiO}_2 \) layer converted to hafnon \( t_{\text{conv SiO}_2} \), equation 3.14, the volume of the hollow sphere of \( \text{SiO}_2 \) converted to hafnon is:

\[ V_{\text{conv SiO}_2} = \frac{4}{3} \pi \left( r_{\text{conv SiO}_2}^3 - r_{\text{net SiO}_2}^3 \right) \]  

(3.A5)

where \( r_{\text{conv SiO}_2} = r_{\text{Si}} + t_{\text{net SiO}_2} + t_{\text{conv SiO}_2} \), and \( r_{\text{net SiO}_2} = r_{\text{Si}} + t_{\text{net SiO}_2} \). This results in:

\[ V_{\text{conv SiO}_2} = \frac{4}{3} \pi \left[ (r_{\text{net Si}} + t_{\text{net SiO}_2} + t_{\text{conv SiO}_2})^3 - (r_{\text{Si}} + t_{\text{net SiO}_2})^3 \right] \]  

(3.A6)

Substitution of equation 3.A3 into 3.A6 gives:

\[ V_{\text{conv SiO}_2} = \frac{4}{3} \pi \left[ (\bar{r}_{\text{Si}} + 0.565t_{\text{net SiO}_2} + t_{\text{conv SiO}_2})^3 - (\bar{r}_{\text{Si}} + 0.565t_{\text{net SiO}_2})^3 \right] \]  

(3.A7)

Substitution of equation 3.13 into equation 3.A7, and rearranging the equation for \( t_{\text{conv SiO}_2} \), gives equation 3.14:

\[ t_{\text{conv SiO}_2} = \left[ \frac{3V_{\text{conv SiO}_2}}{4\pi} + (\bar{r}_{\text{Si}} + 0.565t_{\text{net SiO}_2})^3 \right]^{\frac{1}{3}} - \bar{r}_{\text{Si}} - 0.565t_{\text{net SiO}_2} \]  

(3.14)
Formation of a hafnon thermally grown oxide in the silicon-HfO$_2$-Yb$_2$Si$_2$O$_7$ EBC system

4.1 Introduction

Silicon carbide composites based upon fibers such as Hi-Nicalon Type S$^{1,2}$ and silicon carbide matrices (CMCs) made from preceramic polymers, densified by silicon melt infiltration$^3$, are beginning to be used in the hottest sections of aero-gas turbine engines$^4$-$^9$. For non-stressed applications, the use time at temperature is determined by their rate of oxidization and steam volatilization$^{12,13,57}$. These rates are governed by the combustion gas temperature, pressure, composition, and flow speed dependent rates of chemical reactions between residual oxygen and water vapor in the gas stream and the surface of the SiC components$^{12,13,57}$. When unprotected SiC composites are exposed to this environment, rapid SiC oxidation initially results in formation of SiO$_2$ (s) and CO (g), and is accompanied by volatilization of the SiO$_2$ by reaction with high temperature steam to form gaseous Si(OH)$_4$ and related species$^{12-14}$. This results in recession of the composite at rates of 1-10 µm/hour at gas temperatures of 1300°C-1500°C$^{15}$. Engine component surfaces exposed to this reactive gas flow are therefore protected with an environmental barrier coating (EBC) systems whose function is to eliminate the flux of oxidizing species reaching the SiC composite surface and avoid volatilization of the oxidized surface$^{16-20}$.

A schematic illustration of an EBC system applied to a SiC-based CMC component is shown in Figure 4.1. Since the erosion rate of coating materials has been shown to scale with their SiO$_2$ activity$^{14,27}$, the outer layer of an EBC system is typically made from a material with a SiO$_2$ activity substantially less than that of SiC. Rare earth disilicates such Yb$_2$Si$_2$O$_7$ (ytterbium disilicate, YbDS), whose water vapor volatility rate is at least $\frac{1}{4}$ that of SiC, are currently used for this$^{75}$. This layer is also intended to reduce the permeation of molecular oxygen and water towards the
SiC composite. Even so, these oxidizing species eventually permeate through the layer, and so current EBC systems use a bond coat whose function is to react with the oxidizing species to form a thermally grown oxide whose oxygen diffusion coefficient is low, and that avoids the formation of a gaseous phase such as CO \((g)\)\textsuperscript{29–31}.

Many materials have been proposed for use as a bond coat\textsuperscript{16–18}. Since the bond coat is applied directly to the SiC composite, it must be thermochemically compatible with the composite and the environmental barrier. Since the EBC system suffers very large temperature changes during its use, the bond coat must have a coefficient of thermal expansion (CTE) \(\alpha_{BC}\), close to that of the composite \(\alpha_{SiC}\), otherwise large elastic stresses develop during cooling\textsuperscript{73}. In that case, the stored elastic strain energy \(G_{SS}\), which increases with the bond coat thickness, the square of its thermal mismatch strain with the substrate, and the change in temperature, can lead to delamination or channel cracking (if stresses are tensile). If a phase changes in the use temperature range and
causes a change in volume, this can also contribute to an increased risk of delamination or channel cracking of the coating. Begley and Hutchinson\textsuperscript{73} have shown that in the absence of relaxation processes to reduce the stresses, the stored elastic strain energy in a coating takes the form;

\[
G_{SS} = \frac{\pi}{2} (1 - \nu^2) Eh[(\alpha_1 - \alpha_2)\Delta T + \varepsilon_L]^2 g(\alpha, \beta, \ldots)
\]  

(4.1)

where $\nu$ is the Poisson’s ratio for the coating layer, $E$ is the Young’s modulus, $h$ is the coating layer thickness, $\alpha_1$ and $\alpha_2$ are the CTE of the coating layer and the thick substrate, respectively, and $\Delta T$ is the temperature difference between the stress free and current temperature. The factor $g(\alpha, \beta, \ldots)$ is dependent on the mode and method of cracking\textsuperscript{73,76}. $\varepsilon_L$ is the linear strain due to a phase transformation during cooling, where $\varepsilon_L$ is one-third the volumetric strain accompanying the transformation ($\frac{1}{3} \varepsilon_V$). When the stored strain energy is sufficiently high, crack propagation is energetically favorable. The type and method of crack propagation (e.g. channel cracking, bifurcation, or delamination) is then dependent on the size and shape of flaws, the properties of the coating layers, and the type of strain in the coating layers (i.e. tensile or compressive strain)\textsuperscript{29–31,73,77}.

The presence of temperature gradients through a coating system or abrupt changes in surface temperature resulting in thermal shock must also be addressed in bond coat design. A high thermal conductivity and low CTE difference reduce thermal gradient stresses, while the thermal shock resistance of a bond coat material increases with $\frac{\sigma_y \kappa}{E \alpha_{BC}}$, where $\sigma_y$ is the materials yield strength, $\kappa$ its thermal conductivity and $E$ its Young’s modulus\textsuperscript{73,78}. Bond coat materials with high thermal conductivity, in combination with low Young’s moduli and thermal expansion coefficients are therefore preferred. In addition, the bond coat and its TGO must be thermochemically compatible with the environmental barrier layer\textsuperscript{19}.

The good match of silicon with SiC composites and rare earth disilicates such YbDS, combined with the stability of a protective vitreous SiO\textsubscript{2} TGO with YbDS, have led to its widespread
use as a bond coat material, and is typically applied to SiC composites using thermal spray methods. For vitreous SiO$_2$ TGO layers, the combination of a low oxygen diffusivity and very low oxygen activity beneath a SiO$_2$ (s) TGO layer ($\sim 10^{17}$ at/cm$^3$ O in silicon with respect to $5\times10^{22}$ Si at/cm$^3$) greatly limits the flux of oxygen that can reach the composite surface. The combination of a stable SiO$_2$ TGO, a good CTE match with SiC, a high thermal conductivity (and therefore high thermal shock resistance), a highly protective TGO, and avoidance of the formation of a gaseous phase, has led to the adoption of silicon as the bond coat material of choice in EBC systems intended to operate up to about 1320°C (within approximately 95°C of its melting temperature of 1414°C). However, in applications where the bond coat surface exceeds a temperature of $\sim 1200$°C, a $\beta$-cristobalite phase SiO$_2$ TGO is formed. Upon cooling, the CTE of $\beta$-cristobalite ($3.1\times10^{-6}$ °C$^{-1}$) is similar to that of silicon ($4.1\times10^{-6}$ °C$^{-1}$) and little thermal stress is created until the temperature reaches $\sim 240$°C, whereupon a $\beta\rightarrow\alpha$-cristobalite transformation occurs with a 4.9% reduction in volume. The $\alpha$-phase of cristobalite also has a much higher CTE ($30\times10^{-6}$ °C$^{-1}$) than that of silicon. The resulting tensile strains in the SiO$_2$ TGO after the temperature drops below the $\beta\rightarrow\alpha$ transition temperature have been observed to lead to channel cracking of the TGO and delamination of the silicon-TGO interface, and eventual loss of the coating.

One approach to the suppression of this delamination mechanism is to reduce the thermomechanical stresses that develop upon cooling. In Chapter 3 the potential of a duplex silicon-HfO$_2$ bond coat was identified for this. It was shown that the oxidation of silicon particles dispersed in a HfO$_2$ matrix was accompanied by a parallel reaction with HfO$_2$ to form hafnium orthosilicate (HfSiO$_4$, hafnon), which has a CTE ($3.6\times10^{-6}$ °C$^{-1}$) close to that of silicon ($4.1\times10^{-6}$ °C$^{-1}$) and SiC ($4.67\times10^{-6}$ °C$^{-1}$). Here, we investigate the thermomechanical stresses developed in candidate duplex bond coat systems, and identify a potentially robust silicon-HfO$_2$ coating design. We deposit the silicon-HfO$_2$-YbDS EBC system using a combination of thermal spray and vapor depo-
sition methods and investigate its response to prolonged thermal cycling in a flowing steam/oxygen environment between temperatures of 110°C and 1316°C.

4.2 Duplex bond coat design

The energy release rates (ERR) driving crack propagation in a duplex silicon-HfO$_2$ bond coat EBC system can be estimated using the LayerSlayer code developed by Begley$^{73}$. Using material properties given in Table 4.1, Figure 2(a) shows the ERR available to drive delamination at each interface in a silicon-SiO$_2$-YbDS system after cooling to ambient from an (assumed) stress-free temperature of 1316°C as a function of temperature during cooling assuming a 5 µm thick SiO$_2$ layer, equal to the thickness of the SiO$_2$ TGO expected to grow over 2000 1-hours steam cycles at 1316°C such as previously shown by Richards et al.$^{31}$ The large increase in ERR can be seen to exceed 10 J/m$^2$ at the silicon/SiO$_2$ interface. The toughness of a silicon–SiO$_2$ TGO interface has not been reported, but is unlikely to be higher than $\sim$10 J/m$^2$ since plasticity and other toughening mechanisms in the silicon and SiO$_2$ layers are unlikely at the low temperature (240°C), at which the strain energy rapidly develops$^{81}$. In Figure 2(b), where the ERR is plotted for each interface as a function of the $\beta$-cristobalite SiO$_2$ thickness, indicates the risk of delamination at the silicon-TGO interface rapidly rises as the TGO thickness increases beyond 4 µm. The onset silicon-SiO$_2$ interfacial delamination has also been reported by Anton et al.$^{45}$ as the SiO$_2$ layer thickness reached 5 µm.

| Table 4.1: Material properties for LayerSlayer calculations |
|------------------|------------------|------------------|------------------|
| Material         | Young’s modulus (GPa) | Poisson’s ratio | CTE x10$^{-6}$ (°C$^{-1}$) | Growth strain (-) |
| SiC              | 430              | 0.14            | 4.67            | 0               |
| Silicon          | 70              | 0.223           | 4.1             | 0               |
| SiO$_2$ ($\beta$-cristobalite) | 70            | -0.042 (<240°C) | 30 (<240°C)     | -0.015 (<240°C) |
| SiO$_2$ ($\alpha$-cristobalite) | 70            | -0.164 (≥240°C) | 3.1 (≥240°C)    | 0 (≥240°C)      |
| Yb$_2$Si$_2$O$_7$ | 90              | 0.27            | 4.1             | 0               |
| HfSiO$_4$        | 282             | 0.30            | 3.6             | 0               |
| HfO$_2$          | 166             | 0.36            | 6.1             | 0               |
| F$_{SS}$ (5 mol% Yb$_2$O$_3$-stabilized HfO$_2$) | 200             | 0.30            | 11.3            | 0               |
Figure 4.2: Energy release rates at the interfaces of a silicon-SiO$_2$-YbDS coating system after cooling from a stress free temperature of 1316°C. (a) Shows the log of the ERR in the 25°C to 500°C temperature interval highlighting the abrupt increase in ERR during the $\beta \rightarrow \alpha$-cristobalite phase transformation at 240°C on cooling. (b) Shows the effect of the $\beta$-cristobalite SiO$_2$ TGO layer thickness after cooling to 25°C, assuming the SiO$_2$ had transformed to $\alpha$-cristobalite without stress relief.

One approach to the implementation of a hafnon conversion bond coat has been explored by Anton et al.$^{45}$ They deposited a two-phase silicon and HfO$_2$ bond coat using an electron beam – physical vapor deposition (EB-PVD) technique. It resulted in a silicon matrix-HfO$_2$ particle composite whose particle volume fraction was varied between 36 and 60 vol%. Following furnace annealing in air, they observed oxidation of the silicon located between HfO$_2$ particles and its subsequent reaction to form hafnon. While the SiO$_2$–HfO$_2$–HfSiO$_4$ mixed TGO did not exhibit channel cracking or delamination, the presence of HfO$_2$ particles in contact with the silicon coating either had little influence upon the TGO growth rate (in the 36 vol% HfO$_2$ case) or greatly accelerated the oxidation when the HfO$_2$ particles formed a percolation network through the bond coat. This was consistent with rapid diffusive transport of oxygen through the HfO$_2$ network$^{82}$.

To avoid the existence of oxidizer percolation pathways throughout the silicon+HfO$_2$ bond coat, the approach explored here seeks to deposit a continuous layer of HfO$_2$ upon the outer surface of a silicon bond coat, and then allow dynamic conversion of the SiO$_2$, that forms by dif-
fusion of oxidizers through HfO$_2$, to hafnon, Figure 4.3. In Chapter 3, the oxidation of a model silicon+HfO$_2$ particulate composite indicated that the conversion of SiO$_2$ to hafnon was sufficiently rapid at the temperatures of EBC application interest (1250°C-1316°C), reducing the SiO$_2$ layer thickness by about a factor of two during oxidation in air. During these reactions, the silicon from the SiO$_2$ diffused through the hafnon to react at the hafnon-HfO$_2$ interface, and consequently the morphology of the hafnon was inherited from that of the contacting HfO$_2$ material. While there are volume changes associated both the conversion of silicon to SiO$_2$ and its subsequent reaction to form hafnon, at least some of these can be accommodated by changes in thickness of a layered system, and since these all occur at high temperature, the stresses resulting from in-plane contributions to the volume changes are likely to be relieved by creep relaxation.

**Figure 4.3:** The simultaneous oxidation of silicon to form SiO$_2$ and its reaction with HfO$_2$ to form HfSiO$_4$

Figure 4.4, shows the ERR between the interfaces in the silicon-hafnon-YbDS coating system as a function of the hafnon layer thickness, calculated using material properties given in Table 4.1. The hafnon TGO replaces the β-cristobalite SiO$_2$ TGO on a silicon bond coat. It can be seen that the ERR in this case remains below 2 J/m$^2$, even for a TGO thickness of more than 10 µm. The use
of a silicon-based bond that forms a hafnon TGO is therefore predicted to result in a thermomechanically robust EBC system that is susceptible to neither channel cracking (and loss of protection to oxidizer transport) nor delamination, potentially providing a route to increased coating lifetime.

Figure 4.4: Energy release rates at the interfaces of a silicon-HfSiO$_4$-YbDS system as a function of HfSiO$_4$ thickness.

The thickness, Young’s modulus, and CTE of the layers determines the thermomechanical stresses that are developed in a duplex silicon-HfO$_2$ bond coat EBC system. The CTE of m-HfO$_2$ (6.1x10$^{-6}$ °C$^{-1}$) is reasonably well matched to that of SiC, but slightly greater than that of the other EBC system materials, raising the possibility of coating system failure as the HfO$_2$ layer thickness increases. The calculated ERR as a function of HfO$_2$ layer thickness upon cooling from a deposition temperature of 1200°C using material properties summarized in Table 4.1, is shown in Figure 5(a). The ERR is calculated assuming a fully dense HfO$_2$ layer, and increases rapidly to 12 J/m$^2$ as the coating thickness approaches 20 µm. Since coatings deposited using PVD-type techniques have some form of porosity and generally do not have a Young’s modulus equal to that of a fully dense material, the ERR reduces linearly according to equation 4.1, Figure 5(b). When the Young’s modulus is $\frac{1}{2}$ that of the fully dense value, the ERR is equivalent to that found for a
10 µm thick HfO\textsubscript{2} layer. As such, the same thermomechanical benefit can be achieved by either halving the HfO\textsubscript{2} layer thickness, or halving the Young’s modulus, as per equation 4.1. Since the in-plane Young’s modulus of PVD-type coatings typically range from $\frac{1}{5}$ of the fully dense value in the as-deposited state when columnar, to $\frac{1}{2}$ of the fully dense value when annealed, ERR values can be reduced significantly\textsuperscript{83,84}. As such, the ERR of the HfO\textsubscript{2} layer can be reduced by about half when densely deposited, simulating an annealed situation, and still equal $\sim$5 J/m\textsuperscript{2}, reducing the chance of delamination significantly.

![Figure 4.5](image)

**Figure 4.5:** Energy release rate as a function of (a) HfO\textsubscript{2} thickness in a silicon/HfO\textsubscript{2}/YbDS coating system applied to a SiC substrate, and (b) the HfO\textsubscript{2} Young’s modulus fraction for a 20 µm thick HfO\textsubscript{2} layer. With increasing porosity, Young’s modulus decreases.

The hafnon, SiO\textsubscript{2}, and HfO\textsubscript{2} thicknesses, all change with time as hafnon grows and the reactants are consumed during the use of a duplex bond coat EBC. To investigate this, we considered a scenario where an initially 2 µm thick SiO\textsubscript{2} TGO layer was present between the silicon bond coat, and a 5 µm thick fully dense HfO\textsubscript{2} layer. To account for the 20% decrease in molar volume when hafnon is formed from SiO\textsubscript{2} and HfO\textsubscript{2}, it is assumed that as the SiO\textsubscript{2} layer is converted into hafnon, a 1 µm loss of thickness of both SiO\textsubscript{2} and HfO\textsubscript{2} results in the formation of 0.8 µm thick layer of hafnon\textsuperscript{71}. Figure 4.6 shows that the risk of delamination is again highest at the silicon/SiO\textsubscript{2}
interface in the starting condition prior to the formation of hafnon. As the initially 2 µm thick SiO$_2$ layer is progressively converted to hafnon, the ERR for the silicon-SiO$_2$ and SiC-silicon interfaces both continuously decrease. The ERRs for all other interfaces are small (on the order of 1 J/m$^2$) and also decrease with SiO$_2$ conversion, indicating that the use of a silicon/HfO$_2$ duplex bond coat to promote conversion of SiO$_2$ into hafnon is a thermomechanically viable route to a delamination resistant EBC system.

Figure 4.6: Energy release rate versus thickness of SiO$_2$ converted to hafnon for a SiC-Si-SiO$_2$-hafnon-HfO$_2$-YbDS system. The initial SiO$_2$ layer was 2 µm thick and was located under a 5 µm thick HfO$_2$ layer.

4.3 Experimental procedures

To experimentally explore the duplex bond coat concept, an atmospheric plasma spray (APS) process was used to deposit silicon bond coats on SiC substrates$^{31,34,79}$. A thin layer of segmented structure HfO$_2$ was then deposited through a mask to the central region of the outer surface of a silicon using a coaxial plasma directed vapor deposition (CP-DVD) technique. The response of the duplex bond coat to oxidation in air was used to first confirm the viability of the coating concept and method of deposition. A $\sim$150 µm thick YbDS top layer was then deposited on three addi-
tional duplex bond coat samples using APS with identical spray same parameters to those used previously by Richards et al.\textsuperscript{31} for the deposition of YbDS on a similar silicon bond coat deposited on a SiC substrate. The SiC/silicon-HfO\textsubscript{2}/YbDS samples were then steam cycled at 1316°C for up to 1000 cycles in the same manner used by Richards et al.\textsuperscript{31} in order to be able to compare results with their system.

### 4.3.1 Coating deposition

Samples with duplex bond coats were prepared by using an APS process to deposit a \( \sim 50 \, \mu\text{m} \) thick silicon bond coat on rectangular CVD-SiC substrates of 25.4 mm x 12.7 mm x 4.8 mm thick (Chand Associates, Inc., Plymouth, MA, USA), with 45° chamfered edges to allow for coating over-spray to reduce edge delamination. They were surface roughened using 60-grit SiC abrasive medium (White Abrasives, Niagara Falls, Canada) resulting in an average roughness \( R_a = 1 \, \mu\text{m} \).

For the silicon deposition, four substrates were placed in a deposition furnace and heated to 1200°C in a 20 slm argon flow to reduce oxidation in the furnace. A \( \sim 50 \, \mu\text{m} \) silicon layer was deposited using a Praxair SG-100 torch set-up with the standard 03083-175 anode configuration for APS and APS grade SL-111 silicon powder (Micron Metals, Bergenfield, NJ, USA). The torch power was 16.1 kW achieved using an arc current of 350 A, with a primary argon gas flow of 77.87 slm and a secondary H\textsubscript{2} gas flow of 1.42 slm. The silicon powder was fed at a rate of 31.0 g/min with an argon carrier gas flow rate of 4.72 slm. The traverse speed of the torch was constant at 610 mm/s, with a standoff distance of 150 mm (whereof the first 25 mm of the plasma plume was outside the furnace to allow for sufficient clearance between the torch and furnace).

After deposition of the silicon layer, a thin HfO\textsubscript{2} layer was deposited using the CP-DVD technique through a rectangular stainless-steel mask with an 8x20 mm opening, Figure 4.7, that resulted in HfO\textsubscript{2} deposition in only the central region of the sample. The substrate was electrically connected to a conducting substrate bias plate and placed against a boron nitride substrate holder.
with a tungsten heating element, and heated to 1000°C under a base vacuum pressure of 0.05-0.1 Pa, Figure 4.8. A 12.5 mm diameter HfO$_2$ source rod (TCI Ceramics Inc., Bethlehem, PA, USA) of 4” length was used for evaporation of the HfO$_2$. Evaporation of the HfO$_2$ was accomplished using a 70 kV electron beam gun using an electron beam current of 30 mA (and electron beam power of 2.1 kW). To correct for loss of oxygen during evaporation and transport of the vapor, the HfO$_2$ layer was deposited on the substrates by transport in 10 slm He/1 slm O$_2$ gas jet.

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To increase the coating density, a hollow cathode plasma assistance method was used, Figure 4.8. The hollow cathodes used a 0.2 slm argon flow to assist the transport of low voltage electrons and Ar$^+$ ions from four hollow cathodes coaxially oriented with the vapor plume in the deposition chamber. Opposing pairs of cathodes were alternatingly electrically biased so that one of the cathodes transiently acted as an anode to accelerate the electrons from the other and induce efficient ionization. By circulating the voltage around the four cathodes, an intense 3.4 kW plasma was cre-

![Figure 4.7:](image-url)

**Figure 4.7:** (a) Schematic illustration of the sample geometry. (b) Cross-section of test samples showing the masked region through which HfO$_2$ was vapor deposited, and the use of YbDS overspray at the edges to reduce edge silicon oxidation and steam volatilization.
The substrate was electrically biased to -300V, allowing attraction of positively charged Ar\(^+\) ions towards the substrate, aiding densification of the HfO\(_2\) coating. During coating deposition, the chamber pressure was 8 Pa. Deposition was conducted for 3 minutes resulting in a coating thickness of 2-5 µm.

The YbDS environmental barrier layer was deposited using the same APS system used for silicon bond coat deposition. A ~150 µm thick YbDS top layer was deposited using the same plasma torch setup as for the silicon layer, resulting in a torch power of 14.7 kW using an arc current of 275 A, a primary argon gas flow of 84.95 slm and a secondary H\(_2\) gas flow of 1.42 slm.
The YbDS powder (Treibacher Industrie Inc., Toronto, ON, Canada) was fed at a rate of 41.5 g/min with an argon carrier gas flow rate of 4.72 slm. It is noted that after deposition, roughly 1.5 mol% of the YbDS coating consisted of a secondary YbMS phase resulting from the presence of YbMS in the powder, and loss of SiO$_2$ from the YbDS phase during coating deposition$^{79,85}$.

4.3.2 Oxidation and steam cycling set-up

Substrates coated only with the silicon/HfO$_2$ bond coat were furnace annealed in laboratory air (i.e., in dry oxygen with a partial oxygen pressure, $p_{O_2} = 0.21$ atm) in a Sentrotech ST-1600-666 bottom-loading furnace for 20 hours at 1316°C. Substrates coated with the silicon/HfO$_2$/YbDS coating system were thermally cycled in a slowly flowing (44 mm/s), 90 vol% H$_2$O/10 vol% O$_2$ steam environment. During a cycle, the specimens spent 60 minutes in the hot furnace position (1316°C), and 5 minutes in the cold position ($\sim$110°C). Up to four samples were suspended in the furnace using a Pt/10Rh wire. The setup and flow conditions are similar to those previously used for steam cycling studies and approximate the H$_2$O partial pressure during lean hydrocarbon combustion at a total pressure of 10 atm$^{29,31}$. During steam cycling, gaseous Si(OH)$_4$ was formed by reaction of the high temperature H$_2$O with the uncoated backside of the oxidizing SiC surface via SiC (s) + 3 H$_2$O (g) $\rightarrow$ 3 H$_2$ (g) + CO (g) + SiO$_2$, and SiO$_2$ + 2 H$_2$O $\rightleftharpoons$ Si(OH)$_4$ (g)) and with Yb$_2$Si$_2$O$_7$ (via Yb$_2$Si$_2$O$_7$ + 2 H$_2$O $\rightleftharpoons$ Yb$_2$SiO$_5$ + Si(OH)$_4$ (g))$^{31,75}$. Samples were removed after 75, 250, 500, and 1000 cycles.

4.3.3 Characterization methods

After oxidation and steam cycling, metallography was performed on samples by embedding them in epoxy resin (Buehler EpoKwick FC), and sectioning embedded samples in two using a diamond wafering blade. This was followed by mechanically polishing, ending with a 0.25 µm diamond particle suspension. Surface analysis was performed using a Helios NanoLab DualBeam scanning electron microscope (Thermo Scientific, Hillsboro, OR, USA). To enable atomic number
(Z)-contrast imaging for delineation of phases with different atomic composition, it was operated in the back-scattered electron (BSE) mode using a concentric backscatter (CBS) detector. Images were taken using an accelerating voltage of 5 kV in order to reduce the penetration depth of electrons and get better delineation of lower Z-element phases such as silicon and SiO$_2$ in the sample. Additional images were taken at 15kV in order to penetrate deeper into the sample and obtain better images of porosity. The SiO$_2$ TGO thickness of samples steam cycled for 75, 250, 500, and 1000 cycles was measured in areas with and without HfO$_2$ present. The TGO thickness was measured for at least 40 different locations in both regions. The TGO thickness in the as-deposited sample was too thin to be measured.

Elemental microanalysis of the various phase was performed using energy dispersive spectroscopy (EDS) using an X-Max$^N$ 150 SDD (Oxford Instruments, Concord, MA) detector. A low accelerating voltage of 5 kV was used to limit secondary X-ray fluorescence. While use of a higher accelerating voltage (e.g. 10-15 kV) would allow one to observe the Hf L-lines, secondary X-ray fluorescence occurs due to the Hf L$_\alpha$ (7.9 kV) and Hf L$_\beta$ (9.0 kV) emissions being able to re-excite silicon to emit X-rays at its K$_{\alpha}$ of 1.7 kV, and results in the over-estimation of the silicon atomic fraction. EDS quantification of the composition is thus done using a lower voltage of 5 kV that only excited the silicon K$_\alpha$ and hafnium M$_\alpha$. Furthermore, during EDS data collection, the "EDX" mode on the microscope was used to reduce additional X-ray fluorescence from the sample.

X-ray diffraction (XRD) analysis was performed using a PANalytical Empyrean (Malvern Panalytical, Westborough, MA, USA) set-up with a Cu-K$_\alpha$ source and Bragg-Brentano optics. This was combined with a reflection/transmission spinner stage set-up for reflectance measurements. Diffraction angles (2$\theta$) of 15-90$^\circ$ were analyzed at a rate of 0.12$^\circ$/s. Preferential orientation was minimized by spinning the samples at 0.25 revolutions per second.
Foil specimens for transmission electron microscopy (TEM) were prepared using the ion beam of a Helios NanoLab DualBeam microscope. A foil was extracted from the polished as-deposited silicon/HfO$_2$/YbDS sample, and the sample steam cycled for 1000 hours. Each foil was approximately 12x 50 µm in area and 0.2 µm thick. They contained the silicon bond coat, the original HfO$_2$ layer and hafnon region for the steam cycled sample, and part of the YbDS top layer. TEM analysis was conducted using a Thermo Scientific (Hillsboro, OR, USA) Titan microscope equipped with a double-tilt specimen holder and operated at 300 keV.

4.4 Results

4.4.1 Oxidation of a silicon/HfO$_2$ coating system

A SEM micrograph of the cross-section of the as-deposited sample taken using the BSE imaging mode is shown in Figure 4.9(a). In the as-deposited condition, the (white) HfO$_2$ layer had a columnar microstructure with a column width of 150 nm at the silicon-HfO$_2$ interface that increased with distance from the silicon surface to 400 (± 50) nm at the HfO$_2$ surface. No delamination of the coating was observed after cooling from the deposition temperature, and the experiment therefore confirms the thermomechanical prediction (Section 2) that thin HfO$_2$ layers are unlikely to delaminate during cooling from high temperatures.

After oxidation in air for 20 hours at 1316°C, Figure 4.9(b), the HfO$_2$ layer is seen to have densified, and evolved into a more equiaxed structure. A wide crack-like vertical pore had formed in the top half of the layer to accommodate some of the lateral contraction associated with this densification. In addition, a light grey phase had appeared in the HfO$_2$ layer near its interface with silicon. EDS point analysis indicated it has the composition of HfSiO$_4$, Figure 4.9(b). Examination of the silicon bond coat indicated the presence of a ∼1 µm thick (black) layer containing only silicon and oxygen, and is taken to be SiO$_2$. A dashed line denotes its smooth interface with the silicon. No evidence of channel cracking or delamination was evident. The SiO$_2$-hafnon interface
Figure 4.9: (a) Shows the approximately 4 µm thick vapor deposited HfO$_2$ layer with a columnar structure on a silicon bond coat. b) Shows a similar duplex bond coat after furnace annealing for 20 hours at 1316°C in laboratory air. Note the presence of hafnon (light grey phase) and formation of a (darkest contrast) SiO$_2$ TGO. Sintering of the HfO$_2$ resulted in the formation of the vertical pore in the HfO$_2$ region of the coating.

was observed to exhibit periodic protuberances with a spacing of 338 ($\pm$ 166) nm, consistent with the growth of SiO$_2$ into the intercolumnar spaces in the HfO$_2$ layer as seen in Chapter 3.

The reaction of SiO$_2$ and HfO$_2$ to form hafnon resulted in the formation of a thin continuous layer of the hafnon phase at the HfO$_2$ and SiO$_2$ interface, and regions of hafnon had extended several microns into the prior HfO$_2$ layer. This hafnon occupied $\sim$61% of the lower half area of the HfO$_2$ layer near its interface with SiO$_2$.

4.4.2 Steam cycling of a silicon/HfO$_2$/YbDS coating system

Photographs of the partially transparent (translucent) YbDS coating surface of three samples that had been steam cycled for 250, 500, and 1000 1-hour cycles are shown in Figure 4.10. The region where the HfO$_2$ was present is slightly lighter in contrast since the diffuse reflectivity from the HfO$_2$ layer is much greater than that from the silicon bond coat. As the number of steam cycles increased, several dark spots began to develop on the surface of the YbDS coating layer, corresponding with regions where surface cracks formed in the YbDS. The white regions at the edges of the three samples correspond to regions of local delamination at the silicon-SiO$_2$ interface. The delamination distance from the edge of the samples increased with the number of cycles. Some of
the delaminated region on the right side of the sample cycled for 1000 cycles had fractured, Figure 4.10(c), exposing the silicon coated substrate underneath to rapid oxidation.

Examination of cross-sectional images of the duplex bond coated region of samples in the as-deposited and four steam cycled conditions are shown in Figure 4.11 (using accelerating voltages of both 5 and 15 keV), together with EDS line scans across the HfO$_2$ layer. The images indicate good adherence between the silicon and HfO$_2$, and HfO$_2$ and YbDS layers. No evidence of delamination is present in any of these images, consistent with the thermomechanical predictions, Figures 4.5 and 4.6. The average width of the HfO$_2$ columns in the as-deposited state was 40 (± 7) nm, Figure 4.11(a), while the average width of gaps between column clusters was ~150 nm.
As steam cycling progressed, the morphology of the HfO$_2$ layer region changed. Sintering of the HfO$_2$ resulted in the emergence of widely spaced crack-like voids spaced 2-3 µm apart, oriented normal to the coating surface with average void separations of 300-400 nm. They were most frequent in the sample subjected to 250 thermal cycles and gradually disappeared as the cycling time was further increased.

As the number of steam cycles increased, the regions between the crack-like voids densified, and a light grey phase began to develop in the HfO$_2$ layer. The growth of a (dark grey) SiO$_2$ TGO layer can be seen between the silicon surface and the light grey phase in Figure 4.11(e). EDS analysis showed that the dark grey phase contained silicon, but little hafnium, and is taken to be SiO$_2$. The grey phase in the SEM images contained both hafnium and silicon, and corresponds to HfSiO$_4$. The EDS analysis also indicates the presence of a low concentration of ytterbium throughout all the HfO$_2$ layers, and a small concentration of hafnium in the YbDS layer, indicative of counter-diffusion of ytterbium and hafnium accompanied the silicon oxidation and hafnon formation reactions.

The thickness of the SiO$_2$ layer was measured and is plotted as a function of the number of steam thermal cycles in Figure 4.12. Measurements were made in duplex regions where the silicon had been coated with HfO$_2$ (black data points), and outside the duplex bond coat region where the silicon bond coat was in contact with only YbDS (red data points). These results indicate that the SiO$_2$ thickness in the duplex bond coat region was about one half that for the silicon bond coat. In contrast to the work of Richards et al.\textsuperscript{31}, no evidence of SiO$_2$ channel cracking was observed after 1000 steam cycles at 1316°C.

TEM analysis of the TGO-region of the silicon/HfO$_2$/YbDS coating was used to identify the phases observed during SEM imaging and EDS analysis. Electron transparent (~0.2 µm thick)
Figure 4.11: SEM micrographs of the cross section of silicon-HfO$_2$-Yb$_2$Si$_2$O$_7$ EBC system together with EDS composition profiles. a) The as-deposited condition, and after steam thermal cycling for b) 75, c) 250 cycles, d) 500 cycles, and e) 1000 1-hour cycles.
foils were lifted out of the as-deposited sample and the sample steam cycled for 1000 hours and analyzed by TEM. A high-angle annular dark-field (HAADF) image of the as-deposited sample, Figure 4.13(a), shows the YbDS, HfO$_2$ and silicon bond coat layers and their interfaces. Grain boundaries can be seen in the silicon bond coat indicating its grains to be several microns in diameter. A selected area electron diffraction (SAED) pattern was taken on a large grain in the YbDS layer, Figure 4.13(b), and indicates this region is YbDS (C2/m, PDF 01-074-2071) and contained none of the 1.5 mol% YbMS present in the APS powder. A SEAD pattern collected from within the HfO$_2$ layer, Figure 4.13(c), indicates it to be monoclinic HfO$_2$ (P2$_1$/a, 00-034-0104). The HfO$_2$ layer was composed of narrow columnar grains that grew out from the silicon surface. The average column width was between 30 and 40 nm. The interface between the HfO$_2$ layer and the silicon bond coat was smooth.
A HAADF image of the sample steam cycled for 1000 hours 110°C and 1316°C is shown in Figure 4.14(a), together with SAED patterns collected in or just beneath the HfO$_2$ layer. The SAED data from the region closest to the YbDS coating layer, Figure 4.14(b), indicates this to be a cubic fluorite phase, consistent with an Yb$_2$O$_3$-stabilized HfO$_2$ solid solution (F$_{\text{ss}}$, Fm$3\overline{m}$, PDF 00-053-0560), which was also reported by Poerschke et al.$^{86}$ A SAED pattern taken in the grey layer between the HfO$_2$ layer and the silicon bond coat, Figure 4.14(c), indicated it to be hafnon (I$4_1$/amd, PDF 01-075-1628). A SAED pattern taken within the black layer, Figure 4.14(d), indicated it to be $\alpha$-cristobalite (P4$_1$2$_1$2, PDF 00-039-1425). The YbDS EBC layer in this sample
contained had a 2-3 µm wide YbDS layer free of YbMS precipitates near the HfO$_2$ layer. Beyond this region, the YbDS layer contained a substantial volume fraction of YbMS precipitates that nucleated inside the YbDS coating, due the presence of YbMS (1.5 mol%) in the original powder used for coating synthesis and loss of SiO$_2$ during spray deposition. The silicon-SiO$_2$ interface can be seen to be smooth, whereas the SiO$_2$-hafnon interface can be seen to have SiO$_2$ protuberances extending into the hafnon, Figure 4.14(a). The presence and morphology of the hafnon deep within the prior HfO$_2$ layer is consistent with rapid diffusion of SiO$_2$ along the columnar growth surfaces of the segmented HfO$_2$ layer.

**Figure 4.14:** (a) TEM HAADF image of the silicon-HfO$_2$-YbDS system after cycling for 1000 cycles between 110°C and 1316°C. Selective-area electron diffraction patterns of (b) cubic fluorite Yb$_2$O$_3$-stabilized HfO$_2$ (F$_{SS}$, Fm$ar{3}$m), (c) HfSiO$_4$ (I4$_1$/amd), and (d) $\alpha$-cristobalite (P4$_1$2$_1$2$_1$).
4.5 Discussion

The study presented here has compared the response of a conventional silicon-YbDS EBC system with one that used a two-layer (duplex) silicon-HfO$_2$ bond coat concept intended to dynamically convert SiO$_2$ formed during the oxidation of silicon, to hafnon. The presence and morphology of the hafnon deep within the prior HfO$_2$ layer is consistent with rapid diffusion of SiO$_2$ along the columnar growth surfaces of the segmented HfO$_2$ layer, Chapter 3.

The ratio of molar volumes of hafnon and $\beta$-cristobalite ($\frac{V_{\beta}}{V_{\text{Hafnon}}} = 0.665$) can be used to convert the estimated thickness of the hafnon layer (0.73 µm) in Figure 4.9(b), to the thickness of SiO$_2$ used to form it. By then correcting for the volume change of the $\beta \rightarrow \alpha$-cristobalite phase transformation (4.9% volume reduction) of the remaining SiO$_2$, it is estimated that about 0.46 µm of SiO$_2$ had been converted to hafnon during this rapid oxidation test. Since the rate of silicon oxidation, but not the formation rate of hafnon, is expected to decrease when an YbDS environmental barrier layer is present, this preliminary test indicated that further exploration of the duplex bond coat EBC system in a representative steam/air environment was merited.

After depositing an YbDS environmental barrier on the duplex bond coat, and subjecting the samples to steam thermal cycling, the thickness of the SiO$_2$ TGO was approximately half that of the TGO formed on the conventional silicon only bond coat, Figure 4.12. After deposition of the YbDS EBC layer, a SiO$_2$ TGO $\leq$100 nm was observed in between the silicon and HfO$_2$ layers. Since oxidation of the silicon bond coat requires diffusion of oxidizing species through the YbDS EBC layer, the HfO$_2$ layer, and the SiO$_2$ TGO layer, the SiO$_2$ TGO thickness $x$ was fitted to a parabolic relation of the form:

$$x^2 = k_0t + x_0$$  \hspace{1cm} (4.2)
where $k_p$ is the parabolic rate constant, $t$ is the oxidation time, and $x_0$ is the initial oxide thickness in the as-deposited state ($t = 0$)\(^{37}\). The measured SiO$_2$ TGO thickness for the duplex bond coat section, Figure 3.12 (black data), represents the net amount of SiO$_2$ present in the system after SiO$_2$ formation and conversion to hafnon. The total thickness of SiO$_2$ formed, can be determined by adding the thickness of SiO$_2$ necessary to form the hafnon layer to the net SiO$_2$ thickness reported in Figure 4.12. As an example, consider the sample that underwent 1000 1-hour steam cycles, Figure 4.11(e). The difference in BSE imaging mode contrast between hafnon and HfO$_2$ enables the area fraction of each phase to be estimated using the ImageJ software package\(^{72}\). Hafnon was found to occupy 40.9% of the area, and HfO$_2$ the remainder. The average measured thickness of the HfO$_2$ + hafnon layer in this sample after reaction was 2.35 µm, and so the equivalent hafnon layer thickness is 0.96 µm if all hafnon had been created as a single continuous layer. The thickness of the $\alpha$-cristobalite used to create this hafnon layer can be found by multiplying the hafnon thickness by the ratio of molar volumes ($\frac{V_{Hafnon}}{V_{HfO_2}} = 0.665$), and correcting for a volume reduction of 4.9% during the $\beta \rightarrow \alpha$-cristobalite phase transformation. This gives a thickness of the SiO$_2$ used to form hafnon of 0.68 µm. Adding the measured (net) thickness (0.24 µm) to that used to form hafnon, gives a total SiO$_2$ thickness of 0.92 µm. This is roughly twice that of the measured (net) SiO$_2$ thickness for the conventional bond coat system (0.414 µm). Thus, even though the measured (net) thickness of the duplex bond coat system is half that of the conventional bond coat system, the total thickness of SiO$_2$ formed was more than twice that on the conventional silicon bond coat. If the actual (net) SiO$_2$ layer thickness remains thin, the oxidation rate of the silicon will be high as the thickness will be close to the inflection point between the linear and early parabolic oxidation regimes\(^{37}\). Even though the formation rate of SiO$_2$ has increased, the hafnon formation is rapid enough to suppress excessive SiO$_2$ growth, although it is not rapid enough to overcome the rapid oxidation regime and completely consume the SiO$_2$ layer.

The initially porous, columnar structured HfO$_2$ layer underwent sintering upon initial heating
to 1316°C, resulting in the formation of isolated pores and periodic vertical crack-like flaws, Figure 4.11(b) and (c). As the duration of high temperature exposure increased, the cross-section of the sample cycled for 1000 1-hour cycles at 1316°C shows densification of the coating and the presence of hafnon growth within it, Figure 4.11(c). Densification may have been promoted by hafnon formation, since the addition of Si$^{4+}$ and 2O$^{2−}$ to the m-HfO$_2$ unit cell results in an increase in volume given by the ratio of molar volumes of hafnon and m-HfO$_2$ ($\frac{V_{\text{Hafnon}}}{V_{\text{HfO}_2}} = 1.86$)\(^{71}\). As the thermal cycling time increased, lateral shrinkage of the HfO$_2$ layer was accommodated by vertical crack-like pores and development of voids within the layer between them. However, as hafnon was formed in this layer, the associated increase in volume was accommodated by filling of these features, and the coating appeared to densify as the reaction time increased.

The TEM observation of a steam cycled sample, Figure 4.14, indicates that the HfO$_2$ layer had been converted from a monoclinic phase to a cubic fluorite (F$_{SS}$) structure during the 1,000 hours of annealing at 1316°C. The phase equilibria study of Poerschke et al.\(^{86}\) indicates that m-HfO$_2$ reacts with both YbDS and YbMS to form the F$_{SS}$ phase. The EDS results shown in Figure 4.11(e) indicate about 10 at% ytterbium and 90 at% hafnium in the white, non-reacted spots. This equates to 5 mol% Yb$_2$O$_3$, and upon reaction of Yb$_2$O$_3$ and HfO$_2$ to form F$_{SS}$, the volume shrinks according to the ratio of molar volumes ($\frac{V_{F_{SS}}}{0.95V_{\text{HfO}_2}+0.05V_{YbO}_3} = 0.91$), resulting in shrinkage of the material and generation of tensile strain in the surrounding material. This tensile strain will aid surface and lattice diffusion at high temperatures, promoting sintering and densification. This increases the relative Young’s modulus of the material compared to the porous, columnar microstructure\(^{83,84}\). The CTE, reported in the section 4.7, also increases from the m-HfO$_2$ value of 6.1x10$^{-6}$ °C$^{-1}$ to 11.1x10$^{-6}$ °C$^{-1}$ for the 5 mol% Yb$_2$O$_3$-stabilized HfO$_2$ F$_{SS}$ phase. This implies that the ERR predictions for the coating system may change.

The transformation of m-HfO$_2$ to the F$_{SS}$ phase also results in the formation of an YbMS-free
region that forms in the YbDS coating of the silicon/HfO$_2$/YbDS coating system as the number of cycles increases. Olson et al.\textsuperscript{87} recently reported that an YbMS-free zone formed in YbDS due to reaction of SiO$_2$ from the TGO with YbMS inclusions in the top layer to form YbDS. Since the SiO$_2$ TGO is separated from the top layer here by a HfO$_2$ layer, and during reaction any SiO$_2$ in the HfO$_2$ is most likely to form hafnon, it appears that the YbMS in the EBC layer dissociates into Yb$_2$O$_3$ and SiO$_2$, with the Yb$_2$O$_3$ then available to react with the HfO$_2$ to form the F$_{SS}$ phase, and the SiO$_2$ to either react with the remaining YbMS to form YbDS, or with the HfO$_2$ to form hafnon.

At 1000 cycles, $\sim$25\% of the mixed layer was found to consist of hafnon, and a remainder of the F$_{SS}$ phase. The predicted ERR of the silicon/SiO$_2$/hafnon/mixed hafnon+F$_{SS}$/YbDS coating system is shown in Figure 4.15 for a 2 $\mu$m thick F$_{SS}$ layer that converts to hafnon. The material properties used for this calculation are shown in Table 4.1. For the ERR calculation it is assumed that the effective Young’s modulus consists of 25\% hafnon, and 75\% rare-earth-stabilized HfO$_2$ in the cubic fluorite form. The same ratio is used to calculate the CTE of this mixture. The maximum ERR in the coating system in this situation is predicted to be 2.5 J/m$^2$ at the silicon/SiO$_2$ interface, similar to the ERR found in a 2 $\mu$m thick cristobalite TGO found after 2000 steam cycles as calculated by Richards et al.\textsuperscript{31}. If the remaining F$_{SS}$ phase in the coating system continues to be converted to hafnon, the ERR can be found to continuously drop, Figure 4.15, and the maximum ERR after full consumption of the high CTE F$_{SS}$ layer does not surpass 1 J/m$^2$. Combined with the predictions done in section 4.2, Figure 4.6, and no delamination of the duplex bond coat up to 1000 1-hour steam cycles, this approach proves to be promising to reduce or even prevent coating failure due to cracking of the cristobalite SiO$_2$ TGO.
4.6 Conclusions

Oxidation of a silicon/HfO$_2$ in lab air at 1316°C resulted in the formation of hafnon parallel to the coating surface along the SiO$_2$/HfO$_2$ interface, and perpendicular to the coating surface along grain boundaries. Steam cycling of a silicon/HfO$_2$/YbDS coating system at 1316°C showed the formation of hafnon in the same fashion. It was concluded that:

1. YbMS from the YbDS environmental barrier reacts with the monoclinic HfO$_2$ layer to form cubic fluorite Yb$_2$O$_3$-stabilized HfO$_2$, hafnon, and further consume YbMS to form YbDS.

2. Extensive sintering occurred due to the formation of hafnon and cubic HfO$_2$, resulting in densification of the hafnon/HfO$_2$ layer over the course of 1000 steam cycles at 1316°C.

3. The measured (net) SiO$_2$ thickness on the silicon bond coat was significantly reduced in the silicon/HfO$_2$/YbDS coating system compared to the TGO on the conventional silicon bond coat, and exhibits parabolic growth.
4. The thickness of the cristobalite SiO$_2$ TGO at the edges of the sample where no HfO$_2$ was present, so that the coating system locally resembles the conventional silicon/YbDS examined by Richards et al.$^{31}$, showed a significant reduction in TGO thickness compared to previous work on the conventional silicon/YbDS EBC system, and exhibited parabolic growth.

5. thermomechanical modelling using the software package LayerSlayer indicated that even though densification of the coating occurred, as well as a significant increase in CTE as monoclinic HfO$_2$ transformed into cubic fluorite (F$_{SS}$) HfO$_2$, the ERR is predicted to remain below 4 J/m$^2$. As more of the HfO$_2$ layer is consumed the ERR is reduced below 1 J/m$^2$.

The application of a thin ($\leq$3 µm) HfO$_2$ layer in between the silicon and YbDS coating layers is thus deemed very beneficial and will potentially increase the longevity of the silicon/YbDS-based environmental barrier coating systems.

### 4.7 Thermal expansion of the binary Yb$_2$O$_3$-HfO$_2$ system

#### 4.7.1 Determination of the CTE of the Yb$_2$O$_3$-HfO$_2$ system

Since no data on the CTE of the Yb$_2$O$_3$-HfO$_2$ system is available, the impact of stabilization of the HfO$_2$ on the change in CTE of the material cannot be determined. As such, potential channel cracking and delamination of coating systems cannot be determined. In this section, the CTE of the Yb$_2$O$_3$-HfO$_2$ binary system is described. A mixture of HfO$_2$ and YbDS was compressed and annealed in order to investigate what reaction products form at the YbDS-HfO$_2$ interface, such as found in Figure 4.15.

#### 4.7.2 Sample fabrication and annealing

HfO$_2$ powder (-325 mesh, AE9930-1S, Oerlikon Metco, Westbury, NY, USA) and Yb$_2$O$_3$ powder (-325 mesh, Elemental Metals, Randolph, NJ, USA) were mixed in the molar ratios listed in Table 4.2 using a high-speed ball mill (SPEX SamplePrep 8000D) for 90 minutes, using a DuPont Vertel
XF milling fluid. After drying, this powder mixture was consolidated by spark plasma sintering (SPS) using a Thermal Technologies SPS Model 25-10, into a pellet of 12.7 mm diameter and 3mm thickness by heating to 1500°C and holding for 5 minutes using a pressure of 40 MPa. Sintering of the samples was done using a graphite die/punch system, lined with 0.125 mm thick graphite foil to protect the faces of the die and punches and to make retrieval of samples easier.

The samples made for this study are summarized in Table 4.2. These samples include a monoclinic HfO₂ sample without Yb₂O₃ added, a 100% Yb₂O₃ sample without HfO₂ added, and a sample with 15.8 mol% which has a eutectoid fluorite to monoclinic/delta phase change at ∼620°C according to the binary Yb₂O₃-HfO₂ phase diagram⁸⁶.

Table 4.2: Summary of samples and their properties found. The phases are based on the phase diagrams by Poerschke et al.⁸⁶,⁸⁸, where M = monoclinic, F = fluorite (HfO₂-rich cubic phase), δ = Yb₄Hf₃O₁₂, H₃ = Yb₆Hf₃O₁₁, and C = Yb₂O₃-rich cubic phase

<table>
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<tr>
<th>Mol% Yb₂O₃</th>
<th>0</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>15.8</th>
<th>28.6</th>
<th>35</th>
<th>45</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE x10⁻⁶ °C⁻¹</td>
<td>6.1</td>
<td>7.2</td>
<td>9.2</td>
<td>11.1</td>
<td>11.3</td>
<td>11.5</td>
<td>12.3</td>
<td>10.9</td>
<td>10.4</td>
<td>10.3</td>
<td>9.8</td>
<td>9</td>
</tr>
<tr>
<td>Expected phase(s)</td>
<td>M</td>
<td>M</td>
<td>M+F</td>
<td>M+F</td>
<td>M+F</td>
<td>F</td>
<td>F+δ</td>
<td>H₃+δ</td>
<td>H₃</td>
<td>C+H₃</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>Phase(s) detected</td>
<td>M</td>
<td>M+F</td>
<td>M+F</td>
<td>M+F</td>
<td>M+F</td>
<td>F</td>
<td>F+δ</td>
<td>F+δ</td>
<td>δ+H₃</td>
<td>C+H₃</td>
<td>C</td>
<td></td>
</tr>
</tbody>
</table>

Pellets were then put in pre-fired Al₂O₃ crucibles lined with Pt-10Rh foil in order to avoid reaction between the pellets and the crucible, and annealed in air at 1400°C for 10 hours in lab air in order to restore oxygen stoichiometry and allow for homogenization of the sample. The pellets were then polished up to a 0.25 µm diamond suspension, and examined using a Quanta 650 FE scanning electron microscope (ThermoFisher Scientific, Hillsboro, OR) using the backscattered electron (BSE) mode in low vacuum conditions. The atomic Z-number imaging approach was used in order to use the differences in contrast to differentiate between different concentrations of ytterbium and hafnium across grains. Energy dispersive spectroscopy (EDS) was used for elemental microanalysis (X-MaxN 150 SDD, Oxford Instruments, Concord, MA).
Analysis of phase structure was done using X-ray diffraction (XRD) using a PANalytical Empyrean (PANalytical, Almelo, The Netherlands). It was set-up with a Cu-Kα source and Bragg-Brentano optics combined with a reflection/transmission-spinner stage set-up for reflectance measurements. Diffraction angles (2θ) of 15-100° were analyzed at a rate of 0.12°/s. Samples were spun at 0.25 revolutions per second to reduce the effects of preferential grain orientation. Monoclinic HfO₂ was identified using PDF 00-034-0104, cubic (fluorite) HfO₂ using PDF 00-053-0560, the δ-Yb₄Hf₃O₁₂ phase using PDF 04-002-0212, the H₃-phase using PDF 04-006-0134, and the cubic Yb₂O₃ phase using PDF 01-082-2417.

Coefficient of thermal expansion was measured using a Netzsch DIL 402C dilatometer which was calibrated between room temperature and 1200°C using a cylindrical, 10 mm long, Al₂O₃ calibration standard. Pellets were cut into ~10x3x3mm squared rods, and a constant 25cN force was applied during the process while heating samples up to 1200°C at a rate of 5°C/min. A 30-minute dwell period was used at 1200°C, followed by cooling down to room temperature at a rate of 5°C/min.

4.7.3 Dilatometry results

The CTE as a function of Yb₂O₃ mol% with remainder HfO₂ is presented in Table 4.2 and Figure 4.16. It can be seen that each regime, this being a pure phase or a mixture of two, each has a specific rate for change in CTE per mol% Yb₂O₃. Between 0-5 mol% Yb₂O₃, the CTE increases linearly from 6.1x10⁻⁶ °C⁻¹ for monoclinic HfO₂, to 11.1x10⁻⁶ °C⁻¹ for 5 mol% Yb₂O₃-stabilized HfO₂, increasing 1x10⁻⁶ °C⁻¹ per mol% Yb₂O₃ added. When the amount of Yb₂O₃ is increased, the CTE is seen to increase until a pure fluorite phase is found at 15.8 mol% Yb₂O₃-stabilized HfO₂. Between 5 mol% and 15.8 mol%, the rate of CTE increase is 0.11x10⁻⁶ °C⁻¹ per mol%, one order of magnitude less compared to the previous regime. The highest CTE found in the bi-
binary Yb$_2$O$_3$-HfO$_2$ system is measured for pure fluorite at 15.8 mol% Yb$_2$O$_3$-stabilized HfO$_2$, at 12.3x10^{-6} ^\circ C^{-1}. Once more Yb$_2$O$_3$ is added after this, the CTE decreases at the same rate as before, 0.11x10^{-6} ^\circ C^{-1}, until a bit after the cubic δ-hafnate (Yb$_4$Hf$_3$O$_{12}$) has formed with a CTE of 10.3x10^{-6} ^\circ C^{-1}. The CTE then only slightly decreases until no HfO$_2$ is left in the mixture, with Yb$_2$O$_3$ having a CTE of 9x10^{-6} ^\circ C^{-1}.

![Figure 4.16: CTE as a function of Yb$_2$O$_3$ fraction in the Yb$_2$O$_3$-HfO$_2$ system. Phase boundaries of the binary phase diagram at the 1500°C are shown in the background together with the F $\rightarrow$ M+δ eutectoid decompostion that occurs at a temperature of of $\sim$600°C.](image)

**4.7.4 Phase analysis**

Phase analysis done using XRD showed that most phases predicted to be found were also found in practice. Two exceptions were found at 28.55 mol%, where some additional fluorite was found aside from the δ-phase, and at 45 mol%, where some additional δ-phase was found aside from the H$_3$ phase. Figure 17(a) shows the combined XRD diagrams for the 1-9 mol% Yb$_2$O$_3$-stabilized
HfO$_2$ samples, and Figure 17(b) shows the combined XRD diagrams for the samples $\geq$15.8 mol% Yb$_2$O$_3$-HfO$_2$.

(a) Monoclinic HfO$_2$ containing samples (1-9 mol% Yb$_2$O$_3$)

(b) Samples including fluorite (F), $\delta$-phase, H$_3$-phase, and cubic Yb$_2$O$_3$

**Figure 4.17:** XRD diagrams of all samples with the major XRD peaks are indexed, where a) samples between 1-9 mol% Yb$_2$O$_3$ in HfO$_2$, and b) samples with $\geq$15.8 mol% Yb$_2$O$_3$ in HfO$_2$
4.7.4.1 Impact of CTE on the ERR in the duplex bond coat + YbDS EBC system

The CTE of 5 mol% Yb₂O₃-stabilized HfO₂ was found to be roughly 11.1x10⁻⁶ °C⁻¹, which is almost twice as high as the CTE of monoclinic HfO₂ (6.1x10⁻⁶ °C⁻¹). Using Equation 4.1 it can be shown that the difference in CTE is one of the factors that has the most profound impact on the ERR as \( \Delta \alpha \), or \( \alpha_1 - \alpha_2 \), is squared. Assuming \( \alpha_2 = \alpha_{SiC} = 4.67 \times 10^{-6} \text{ °C}^{-1} \), the squared difference in CTE for monoclinic HfO₂ equals 2.0. For cubic HfO₂ (F_{SS}) this equals 41.3, an increase in ERR by almost a factor of 20 over that of monoclinic HfO₂, increasing the chance of failure significantly. This does not include the aforementioned change in Young’s modulus, as the Young’s modulus of the 5 mol% Yb₂O₃-stabilized HfO₂ is unknown.

4.8 Reaction of a HfO₂ + YbDS powder mixture

In order to investigate the reaction between monoclinic HfO₂ and YbDS, HfO₂ powder (-325 mesh, AE 9930-1S, Oerlikon Metco, Westbury, NY) was mixed in equimolar ratio with YbDS powder (Metco 6157, Oerlikon Metco, Westbury, NY, USA) using a high-energy ball mill (SPEX SamplePrep 8000D, Metuchen, NJ) for 90 minutes, using a DuPont Vertel XF cleaning agent to promote mixing without extensive milling of the powder. The blended powder was then dried in air for 1 hour in ambient air. This mixture was subsequently cold-pressed into a 12.5 mm diameter x 3 mm thick pellet using 40 MPa, loaded in an pre-fired alumina crucible and then annealed at 1316°C for 20 hours in a Sentrotech ST-1600-666 bottom-loading furnace.

The as-mixed and annealed states of the powder mixture were analyzed using XRD and the results of this are shown in Figure 4.17. In the as-mixed state a mixture of YbDS, some YbMS, and monoclinic HfO₂ is detected. After annealing at 1316°C for 20 hours it can be seen that a significant amount of cubic (fluorite, F_{SS}) HfO₂ is found, and the YbMS peaks have almost disappeared. The YbDS peaks increased compared to the as-mixed state, likely due to the as-received powder
not being fully crystalline. Using the ternary HfO$_2$-YbO$_{1.5}$-SiO$_2$ phase diagram from Poerschke et al., Figure 5.2, it can be seen that monoclinic HfO$_2$ and both YbMS and YbDS are not thermo-chemically compatible at 1500°C, but instead react to form both HfSiO$_4$ and cubic HfO$_2$, denoted as F$_{SS}$ on the phase diagram. It has to be noted that in the XRD diagram, Figure 4.17, no HfSiO$_4$ was detected. Instead the amount of YbMS decreased, suggesting that it is likely that either YbDS or YbMS decomposed into Yb$_2$O$_3$ and SiO$_2$, where the Yb$_2$O$_3$ reacted with the monoclinic HfO$_2$ to form Yb$_2$O$_3$-stabilized HfO$_2$ (F$_{SS}$), and the remaining SiO$_2$ reacted with some of the remaining YbMS to form YbDS. Since no thermodynamic data are available for the Yb$_2$O$_3$-SiO$_2$ system, it is not possible to calculate which of the two reactions is more preferential in terms of Gibbs free energy ($\Delta$G), but we observe that it is more likely that the silicon-poor YbMS decomposes. As such, aside from SiO$_2$ reacting with the HfO$_2$ to form hafnon, the HfO$_2$ reacts with the YbDS/YbMS composite top layer to form F$_{SS}$. 
Figure 4.18: The as-mixed and annealed (1316°C for 20 hours) XRD diagrams of the 50/50 mol% YbDS/m-HfO$_2$ powder, indicating the loss of m-HfO$_2$ (m) and YbMS (MS), and growth of some hafnon (h) and cubic fluorite (F$_{SS}$) HfO$_2$. YbDS (DS) sees a change in preferential orientation.
5 HfO$_2$-based thermal barrier coatings for the silicon-Yb$_2$Si$_2$O$_7$

environmental barrier coating system

5.1 Introduction

Gas turbine engines have started to make use of SiC-based ceramic matrix composites (CMCs) in combustion gas flows that raise their surface temperatures to 1300°C and above$^{4-9}$. At these temperatures residual oxygen and water vapor oxidize the silicon carbide, forming CO(g) and a protective SiO$_2$ thermally grown oxide (TGO)$^{12,13,57}$. However, in the presence of the water vapor, SiO$_2$ reacts to form a volatile Si(OH)$_4$ gas species, volatilizing the oxide and eventually the SiC$^{15,27}$. To avoid this, SiC components are protected by environmental barrier coating (EBC) systems that seek to reduce the flux of the oxidizing species reaching the components’ surface, and eliminate oxidation of the SiC and subsequent volatilization of the oxide$^{16-20}$.

Current EBC systems use a silicon bond coat that does not form a CO gas species upon oxidation. Instead, only a SiO$_2$ TGO forms, which at bond coat temperatures above $\sim$1200°C crystallizes into $\beta$-cristobalite$^{29,31,39,65,66}$. This phase transforms into a higher density $\alpha$-phase upon cooling at 240°C, resulting in a 4.9% volume reduction. This volume reduction produces a significant strain on the material, increasing the risk of delamination as the thickness increases. To reduce the rate of oxide thickening, a rare-earth disilicate EBC layer with low silica volatility is applied to the silicon surface. In order to reduce the risk of cracking or delamination during thermal cycling, the EBC layer must also have a coefficient of thermal expansion (CTE) that matches that of the SiC-based substrate ($4.67\times10^{-6}$ °C$^{-1}$) and the silicon bond coat ($4.1\times10^{-6}$ °C$^{-1}$)$^{20,29,31,89}$. The material presently used is ytterbium disilicate (Yb$_2$Si$_2$O$_7$, YbDS), which has a CTE of $4.0\times10^{-6}$ °C$^{-1}$. This EBC system has been subjected to up to 2000 1-hour thermal cycles (1 hour “hot” at 1316°C, and 10 minutes “cold” at $\sim$110°C) in a slowly flowing (44 mm/s) 90 vol% H$_2$O (steam)/10 vol% O$_2$
steam environment\textsuperscript{31}, whereupon delamination of the coating began due to increasing stored strain energy at the silicon/SiO\textsubscript{2} interface as the SiO\textsubscript{2} layer thickness increased.

During thermal cycling in steam, YbDS EBC layers react with water vapor to form Si(OH)\textsubscript{4} (g) and ytterbium monosilicate (Yb\textsubscript{2}SiO\textsubscript{5}, YbMS). After 2000 1-hour steam cycles to a maximum temperature of 1316°C, a \textasciitilde 15 \textmu m thick layer of the YbDS EBC layer surface had been converted to YbMS due to loss of SiO\textsubscript{2}. The loss in volume of coating surface results in the formation of voids and cracks, and combined with the relatively high CTE of YbMS (7.2x10\textsuperscript{-6} °C\textsuperscript{-1}) compared to SiC, silicon, and YbDS, can cause it to crack and spall off upon cooling, increasing the effective rate of recession\textsuperscript{29,30,35,36}. Experiments conducted at different temperatures, steam flow speeds, steam partial pressures and total pressures, indicate that the recession rate increases with all of these variables\textsuperscript{75,90}. Additionally, rare-earth silicates, and specifically ytterbium silicates, have shown to have a low resistance to interactions with molten calcium magnesium alumino-silicates (CMAS), resulting in dissolution of the EBC layer into the CMAS melt, eventually resulting in crack formation and delamination of the coating system\textsuperscript{20,91–93}.

One approach to extending the life of the coating system is to lower the temperature across the coating, since steam volatility at the YbDS surface and transport of oxidizing species through it, together with the oxidation rate of the silicon bond coat itself, all decrease with a reduction of temperature\textsuperscript{37}. Furthermore, if the silicon outer surface temperature could be reduced to less than 1200°C, the TGO is more likely to be vitreous instead of forming the crystalline $\beta$-cristobalite phase, thereby reducing the risk of delamination\textsuperscript{67}. Rare-earth disilicates have thermal conductivities of 4-9 W m\textsuperscript{-1} K\textsuperscript{-1} at room temperature, which reduces to \textasciitilde 2-3 W m\textsuperscript{-1} K\textsuperscript{-1} at temperatures $\geq$400°C\textsuperscript{20,92}, so active cooling of the SiC substrate to create a thermal gradient across the coating system would lower the temperature of the silicon bond coat. However, this does not reduce the outer YbDS surface temperature, and thus the rate of EBC layer recession. The deposition of a
thermal barrier coating (TBC) on the EBC surface to create a thermal and environmental barrier coating (T-EBC) system could significantly reduce both the surface temperature of the bond coat, delaying thermomechanical failure induced by TGO growth, and reduce the temperature and steam flow rate over the outer YbDS surface, potentially reducing the rate at which water vapor can react with YbDS to form Si(OH)$_4$ and thereby extending the life of the EBC system. A schematic illustration of the proposed T-EBC system is shown in Figure 5.1.

![Schematic illustration of a T-EBC system concept](image)

**Figure 5.1:** Schematic illustration of a T-EBC system concept applied to an actively cooled SiC composite substrate during exposure to a representative gas turbine engine combustion gas flow.

The design and implementation of a thermal barrier coating system for a T-EBC system is very challenging. There are many different TBC systems that could be proposed, and numerous approaches for their deposition on an EBC surface are available. To identify a viable system, it is important to ensure the TBC material and deposition approach result in a low thermal conductivity.
in the coating though thickness, and optical opacity, that are sufficient to provide a large tempera-
ture drop between the gas flow and EBC outer surface. Since the outer surface of the coating may
be in contact with the combustion gas flow (whose temperature can currently be up to $\sim 1500^\circ$C),
the TBC material must have a melting temperature well above that of the combustion gas to avoid
melting and evaporation, and to slow the rate of sintering of the typically porous layer. Addi-
tionally, it should also have a very low steam volatility rate, must be able to survive the intense
thermomechanical cycling of the application environment, and either exhibit sufficient thermo-
chemical stability with the EBC material, or undergo reaction with it at a rate that is sufficiently
low to not compromise the integrity of the T-EBC system. However, the absence of thermochemi-
cal databases for many of the candidate systems is a serious handicap to this.

Motivated by concerns about molten silicate interactions with T-EBC systems, Poerschke et
al.\textsuperscript{86,95} proposed the application of a $\delta$-Yb$_4$Hf$_3$O$_{12}$ or H$_3$-Yb$_6$HfO$_{11}$ (Yb-hafnate) TBC to the
YbDS layer. Their thermochemical analysis of a Yb-hafnate in contact with a YbDS EBC layer
showed that an adverse reaction occurs between the two, requiring a YbMS layer to be placed be-
tween the YbDS and Yb-hafnate in order to ensure thermochemical stability. However, Richards
et al.\textsuperscript{29} have shown that the high CTE of YbMS results in channel cracking when applied to mate-
rials with a CTE in the 4-5$x 10^{-6}$ $^\circ$C$^{-1}$ range (silicon, YbDS and SiC), with the cracks providing
a fast reactant transport path to layers underneath. Since Yb-hafnates have been shown to have a
CTE on the order of 9-11$x 10^{-6}$ $^\circ$C$^{-1}$, the risk of cracking and delamination is increased further, as
described in Chapter 4. While a method for vapor depositing a Yb-hafnate TBC was successfully
demonstrated\textsuperscript{95}, the response of the coating (or indeed any TBC coated EBC) to thermal cycling in
a water vapor environment was not investigated.

The intent of the study reported here is to begin an exploration of the failure modes of T-EBC
systems during thermal cycling in a steam environment. A very high melting temperature, steam
volatility resistant monoclinic HfO\textsubscript{2} TBC material applied to a silicon/YbDS EBC is used as a model TBC system. It is one of the few systems for which basic thermochemical assessments have been reported. Poerschke et al.\textsuperscript{86} had investigated some aspects of the thermochemical stability between YbDS and m-HfO\textsubscript{2}, and proposed a ternary phase diagram for the SiO\textsubscript{2}-HfO\textsubscript{2}-YbO\textsubscript{1.5} system at 1500°C. They found that a mixture of m-HfO\textsubscript{2}, a HfO\textsubscript{2}-rich solid-solution cubic fluorite (F\textsubscript{SS}, Fm\textbar m) phase, HfSiO\textsubscript{4} (hafnon), YbDS, and/or YbMS would form. Figure 5.2 shows the proposed ternary phase diagram for the SiO\textsubscript{2}-HfO\textsubscript{2}-Yb\textsubscript{2}O\textsubscript{3} system, modified by replacing YbO\textsubscript{1.5} from Poerschke et al.\textsuperscript{86} with Yb\textsubscript{2}O\textsubscript{3}. The modified diagram is consistent with the binary HfO\textsubscript{2}-Yb\textsubscript{2}O\textsubscript{3} phase diagram of Duran et al.\textsuperscript{96}. We explore the thermomechanical compatibility of a model monoclinic (m, p\textsubscript{2}1/c) HfO\textsubscript{2} TBC with a CTE of 6.1x10^{-6} °C\textsuperscript{-1} on a silicon-YbDS EBC system, investigate the thermomechanical requirements that drive the method of deposition, and evaluate the thermochemical response between the m-HfO\textsubscript{2} TBC and YbDS EBC layer during thermal annealing and thermal cycling in a high temperature (1316°C) steam environment.

Figure 5.2: Phase equilibria at 1500°C in the SiO\textsubscript{2}-HfO\textsubscript{2}-Yb\textsubscript{2}O\textsubscript{3} system, adapted from the SiO\textsubscript{2}-HfO\textsubscript{2}-YbO\textsubscript{1.5} phase equilibrium diagram as proposed by Poerschke et al.\textsuperscript{86}
5.2 Thermomechanical considerations

The difference in CTE between the m-HfO$_2$ TBC (6.1x10$^{-6}$ °C$^{-1}$) and the SiC substrate (4.67x10$^{-6}$ °C$^{-1}$) generates a stored elastic strain energy in the coating layer$^{73,76}$. Begley and Hutchinson$^{73}$ have shown that the steady-state energy release rate (ERR), $G_{SS}$, that is then available to drive interfacial delamination of a bi-layer system during cooling from a stress free temperature can be estimated using:

$$G_{SS} = \frac{\pi}{2} (1 - \nu^2) E h [(\alpha_1 - \alpha_2) \Delta T]^2 g(\alpha, \beta, ..)$$  \hspace{1cm} (5.1)

where $\nu$ is the Poisson’s ratio for the coating layer, $E$ is the Young’s modulus, $h$ is the coating layer thickness, $\alpha_1$ and $\alpha_2$ are the CTE of the coating layer and the thick substrate, respectively, and $\Delta T$ is the temperature difference between the stress free and current temperature. The factor $g(\alpha, \beta, ..)$ is dependent on the mode and method of cracking$^{73,76}$. Increases in temperature change and CTE difference between the coating and substrate affect the ERR more significantly than changes in the Young’s modulus and thickness of the coating layer. Nevertheless, the available energy increases linearly with the layer modulus and thickness. Previous work has shown that the incorporation of porosity in 7YSZ coatings lowers the Young’s modulus of the TBC layers. However, studies have shown that as the porous coating sinters during subsequent high temperature use, the pore fraction is reduced over time, and the modulus can then increase towards the dense value$^{83,84}$.

The stored elastic strain energy is able to drive delamination or cracking of the coating, especially at geometric features that locally raise the stress (e.g. a crack tip or coating edge)$^{73,76}$. Many different modes of cracking exist, and compete for dominance$^{97-99}$. Using material properties summarized in Table 5.1, the LayerSlayer software package$^{73}$ can be used to calculate the plane strain ERR as a function of the HfO$_2$ TBC thickness for the interfaces in a silicon/YbDS/HfO$_2$ coating system. The ERR estimates provide a means for estimating the risk of delamination when inter-
Table 5.1: Material properties for materials used in ERR predictions using LayerSlayer

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio (-)</th>
<th>CTE (x10^{-6} °C^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>430</td>
<td>0.14</td>
<td>4.67</td>
</tr>
<tr>
<td>Silicon (APS)</td>
<td>70</td>
<td>0.223</td>
<td>4.1</td>
</tr>
<tr>
<td>Yb$_2$Si$_2$O$_7$ (APS)</td>
<td>90</td>
<td>0.27</td>
<td>4.0</td>
</tr>
<tr>
<td>m-HfO$_2$ (fully dense)</td>
<td>166</td>
<td>0.36</td>
<td>6.1</td>
</tr>
<tr>
<td>F$_{SS}$ (16 mol% Yb$_2$O$_3$-stabilized HfO$_2$)</td>
<td>200</td>
<td>0.30</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Facial toughness values are available. These have not been reported for the systems of interest in T-EBC systems, but are expected to lie in the 5-10 J/m$^2$ range. Figure 3(a) shows the ERR for a fully dense HfO$_2$ layer. It is noted that in the limit of zero TBC layer thickness, the ERR at the silicon/YbDS was found to be $\leq 1$ J/m$^2$ for the EBC thicknesses used here, and delamination at this location is thus unlikely, as previously demonstrated by Richards et al. Figure 3(a) shows that the ERR at all interfaces increase rapidly as the TBC thickness increases. However, the highest ERR always occurred at the EBC-TBC interface.

The TBCs deposited using either air plasma spray or physical vapor deposition methods are often porous, and the coatings deposited by these methods can have Young’s moduli between $\frac{1}{5}$-th and $\frac{1}{2}$ that of the dense Young’s modulus. To investigate the consequence of this, the ERR of a silicon/YbDS/HfO$_2$ system with a 100 µm thick HfO$_2$ TBC was calculated as a function of the HfO$_2$ Young’s modulus, Figure 3(b). Consistent with Equation 5.1, the ERR at the HfO$_2$-YbDS interface is linearly dependent on the HfO$_2$ layer Young’s modulus. While Equation 5.1 indicates that reducing the TBC thickness also reduces the ERR in a similar way, this would reduce the temperature difference between the YbDS surface and the hot gas environment. Segmentation of the coating, and thus reduction of its Young’s modulus, is a preferred route for T-EBC applications since the increase in porosity increases the temperature difference across the TBC while reducing the ERR.
Figure 5.3: The energy release rate available to drive delamination in a silicon/YbDS/HfO$_2$ T-EBC system as a function of (a) m-HfO$_2$ TBC thickness assuming a solid HfO$_2$ Young’s modulus, and (b) as the function of the HfO$_2$ Young’s modulus fraction, which can be reduced by segmentation or incorporation of porosity in a HfO$_2$ TBC, assuming a fixed 100 µm TBC layer thickness. (c) Shows the uniaxial stress in the coating system.

CTE mismatch will also result in tensile or compressive thermal stresses being generated, which will influence the expected cracking modes$^{73}$. Layers with CTE lower than that of the thick substrate will be compressed (e.g. silicon and YbDS), while layers with CTE higher than that of the thick substrate will be in tension (e.g. the m-HfO$_2$ TBC), Figure 3(c). The HfO$_2$ TBC layer is predicted to have high tensile stresses that can lead to the formation of channel cracking, while the underlaying YbDS and silicon layers are in compression. If a channel crack would grow in the
HfO₂ TBC, and into the YbDS layer, it would likely bifurcate in the same fashion as previously shown by Richards et al. in the tri-layer silicon/mullite/YbMS EBC system²⁹,³⁰.

5.3 Methods

Two approaches to deposit a m-HfO₂ TBC on a silicon/YbDS have been investigated. In one approach, the HfO₂ TBC was deposited using atmospheric plasma spray (APS), which resulted in a dense, but vertical channel cracked TBC. The second approach sought to create a highly porous columnar coating using an electron beam, directed vapor deposition (EB-DVD) technique. This approach resulted in a more strain-tolerant, coating similar in pore morphology and volume fraction to the yttria stabilized zirconia counterparts used for thermal protection of superalloy components in current gas turbine engines⁹⁴.

5.3.1 Deposition of silicon/YbDS EBC system

Each of the T-EBC systems investigated in this study utilized a silicon bond coat and YbDS EBC layer deposited using atmospheric plasma spray (APS). The EBC systems were deposited on 25.4 mm long x 12.7 mm wide x 4.8 mm thick CVD-SiC substrates (Chand Associates, Inc., Plymouth, MA, USA). The substrates had 45° chamfered edges to allow for over-spray and reduce the risk of edge-delamination. The substrates were surface roughened (Rₐ = 1 µm) using 60-grit SiC abrasive medium (White Abrasives, Niagara Falls, Canada) before deposition and cleaned with high-pressure air and ethanol.

APS deposition was performed using a Praxair SG-100 torch, set-up with the standard 03083-175 anode configuration, mounted on an ABB IRB 140 6-axis robot arm. Prior to deposition, the samples were placed in a deposition furnace at 1200°C, while flowing 20 slm argon at all times samples were inside the furnace in order to avoid oxidation of the SiC substrates. A ~50 µm thick silicon layer was deposited with a torch power of 16.1 kW using an arc current of 350 A, using
a primary argon gas flow of 77.87 slm, and a secondary H2 gas flow of 1.42 slm. The silicon powder (APS grade SL-111 silicon powder, Micron Metals, Bergenfield, NJ, USA) was fed at a rate of 31.0 g/min with an argon carrier gas flow rate of 4.72 slm. A ∼130 µm thick YbDS EBC layer was deposited with a torch power of 14.7 kW using an arc current of 275 A, using a primary argon gas flow rate of 84.95 slm, and a secondary H2 gas flow rate of 1.42 slm. The YbDS powder (Treibacher Industrie Inc., Toronto, ON, Canada) with 1.5 mol% YbMS impurity was fed at a rate of 41.5 g/min with an argon carrier gas flow rate of 4.72 slm. The traverse speed of the torch was constant at 610 mm/s, with a standoff distance of 150 mm (whereof the first 25 mm of the plasma plume was outside the furnace to allow for sufficient clearance between the torch and furnace).

**5.3.2 APS TBC deposition**

A ∼150 µm thick HfO$_2$ (-325 mesh, AE 9930-1S, Oerlikon Metco, Westbury, NY) TBC layer was deposited onto four silicon/YbDS EBC systems that were previously deposited onto SiC substrates. The coated substrates were placed in the deposition furnace prior to deposition, and held at 1200°C for at least three minutes to allow the substrates to sufficiently heat up, while flowing 20 slm of argon into the furnace to minimize oxidation of the SiC substrate and silicon bond coat. Initial trials for HfO$_2$ deposition using APS on top of the YbDS coating without the deposition furnace were unsuccessful, resulting in spallation of the HfO$_2$ from the YbDS layer during or immediately after deposition. Instead, deposition into the furnace at 1200°C, the same method used for the deposition of the silicon and YbDS layers, allowed the partially molten HfO$_2$ to solidify at a slower rate due to the smaller ΔT compared to deposition outside of the furnace (at room temperature). Deposition at a higher temperature also allowed for thermal diffusion of the coating materials, resulting in better adhesion of the HfO$_2$ to the YbDS layer. Deposition of the HfO$_2$ was done using the standard “730”-anode setup acquired from Praxair TAFA, which is designed for conventional 7YSZ deposition using the Praxair SG-100 plasma torch. Deposition was done with a torch power of 31.5 kW and a 750 A arc current, using a primary argon gas flow of 42.48 slm, and a secondary
He gas flow of 20.77 slm. The HfO$_2$ powder was fed at a rate of 83.0 g/min with an argon carrier gas flow rate of 4.72 slm. The traverse speed of the torch was constant at 610 mm/s, with a standoff distance of 150 mm (whereof the first 25 mm of the plasma plume was outside the furnace to allow for sufficient clearance between the torch and furnace).

### 5.3.3 EB-DVD TBC deposition

Four SiC substrates coated with a silicon/YbDS EBC system were used to deposit porous, columnar HfO$_2$ TBC layers onto using electron-beam directed vapor deposition (EB-DVD). The substrates were fixed on a rotation arm surrounded by a clamshell heater, allowing for heating of the samples up to $\sim$1000°C by radiative heating. The set-up of the EB-DVD system is illustrated in Figure 5.4. A single 12.5 mm diameter HfO$_2$ source rod (TCI Ceramics Inc., Bethlehem, PA, USA) of 4” length was used for deposition of the HfO$_2$ layer. Prior to deposition and during sample heating to $\sim$1000°C the chamber had a base vacuum of 0.05-0.1 Pa. During deposition a He/O$_2$ gas jet was established using 10 slm He and 1 slm O$_2$. Since the HfO$_2$ concentration across the projected area of the vapor plume decreases radially from the center of plume, the HfO$_2$ deposition rate decreases radially from the center of the vapor plume. The HfO$_2$ TBC thickness of each of the samples, and the purpose of these samples, are noted in Table 5.2.

### 5.3.4 Steam cycling furnace

Samples were suspended in a vertical tube furnace using a Pt-10Rh wire. Thermal cycling entailed a 1-hour hot cycle at 1316°C, followed by a cold cycle at $\sim$110°C for 5 minutes. A high-
Figure 5.4: The EB-DVD system used for the deposition of the porous HfO$_2$ TBC layer. During deposition, only one of the four 12.5 mm diameter sources in the multi-source crucible was used for the HfO$_2$ deposition. To compensate for loss of oxygen from the evaporated HfO$_2$ source, a He+10 vol% O$_2$ gas mixture was used to transport the vapor to the heated substrate.

temperature water vapor mixture consisting of 90 vol% H$_2$O/10 vol% O$_2$ flowed through the tube at a speed of 44 mm/s. The setup and flow conditions are similar to those previously used for steam cycling studies$^{31}$ and approximate the H$_2$O partial pressure during lean hydrocarbon combustion at a pressure of 10 atm. During steam cycling it is expected that Si(OH)$_4$ forms due to reaction of the high temperature steam with the uncoated backside of the SiC and subsequent reaction with the SiO$_2$ that forms. The two samples that were located towards the center of the vapor plume, samples 2 and 3, were thermally cycled (1 hour at 1316°C, then 5 minutes at $\sim$110°C) by moving the furnace around the stationary sample. Sample 2 was cycled for 103 cycles until visual inspection indicated spallation of the HfO$_2$ layer occurred. Sample 3 was cycled for 750 cycles until this
sample also showed visible spallation.

One of the two samples furthest away from the center of the vapor plume, sample 1, was used for isothermal annealing (without thermal cycling) at 1316°C for 500 hours. The exact same steam environment was used in order to solely observe thermochemical effects in the same environment as the thermally cycled samples without influence of thermomechanical responses of the coating system. Sample 4 was used as a control for characterizing the as-deposited condition of the complete coating system.

5.3.5 Characterization methods

Samples were embedded in epoxy resin (Buehler EpoKwick FC) in order to preserve the coherence of the coating layers during sample preparation, and were subsequently sectioned in half using a diamond wafering blade. The cross-section was mechanically polished, ending with a 0.25 µm diamond particle suspension.

Scanning electron microscopy (SEM) was performed using a Quanta 650 field emission scanning electron microscope (Thermo Scientific, Hillsboro, OR, USA) or a Helios NanoLab Dual-Beam microscope (Thermo Scientific, Hillsboro, OR, USA) in combination with back-scattered electron (BSE) mode imaging using a concentric backscatter (CBS) detector. This is done to allow for atomic number (Z)-contrast imaging in order to delineate variations in atomic composition. Elemental microanalysis was done using energy dispersive spectroscopy (EDS) using an X-MaxN 150 SDD (Oxford Instruments, Concord, MA) detector. During EDS data collection, the “EDX” mode on the microscope was applied in order to reduce detection of secondary X-ray signals. The atom fraction of ytterbium found in reaction layers using EDS are converted to the equivalent mol fraction of Yb$_2$O$_3$ using $y = \frac{x}{2 - x}$, where $x$ is the at% of Yb, and $y$ is the mol% of Yb$_2$O$_3$.

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5.4 The plasma spray deposited m-HfO$_2$ TBC

The APS deposited HfO$_2$ TBC remained adherent to the underlying YbDS EBC layer immediately after deposition, Figure 5.5(a). The porosity of the HfO$_2$ TBC cross-section was determined to be 11% in the as-deposited state using the ImageJ software package$^{72}$. Although this is on the same order of conventional 7YSZ coatings (5-20%)$^{94}$, the porosity in 7YSZ coatings is usually more uniformly dispersed throughout the coating compared to the HfO$_2$ coating shown in Figure 5.5$^{17,94}$. Typical 7YSZ coatings are sprayed without utilization of a deposition furnace, resulting in less clustering ("sticking together") of the powder upon deposition. This clustering effect has led to a variation in porosity throughout the coating, with stress concentrations forming around the large pores in the HfO$_2$ coating. Vertical cracking of the TBC layer with a periodic spacing of $\sim$300 $\mu$m was also evident. These vertical cracks passed through the HfO$_2$-YbDS interface and bifurcated into the YbDS layer, Figure 5.5(b). The bifurcated cracks followed grain and splat boundaries in the YbDS EBC layer. Thermal cycling of this coating system resulted in almost immediate spallation of the HfO$_2$ TBC within a few cycles so that no results could be gathered regarding the thermochemical stability between the YbDS and HfO$_2$ coating layers.

The periodicity of the vertical channel cracking is governed by the same variables used in Equation 5.1, as well as the sharp features present in the coating, which have been found to decrease the periodic spacing distance between vertical cracks$^{101}$. When these vertical cracks reach the HfO$_2$-YbDS interface, the tips can be seen to bifurcate at several locations, Figure 5.5, as was predicted by the calculated stresses in the silicon/YbDS/HfO$_2$ system, Figure 3(c). The same bifurcation process was observed by Richards et al.$^{30}$ during the thermal cycling of the silicon/mullite/YbMS EBC system, where the vertical crack originated in the YbMS top layer, and penetrated through the mullite layer into the compressively stressed silicon layer. Bifurcation then appears to become the most energetically favorable cracking mode in these compressed coatings, instead of continuing as a single (vertical) crack$^{31,73}$. 

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Figure 5.5: SEM micrographs of a silicon/YbDS T-EBC with an \( \sim 100 \) µm thick APS deposited HfO\(_2\) TBC. (a) Shows vertical channel cracks spaced approximately 300 µm apart in the TBC. They bifurcated upon penetration into the compressively stressed YbDS layer. (b) Shows a detail of the channel crack tip region seen to the right of (a).

Even though the porosity of the HfO\(_2\) coating is at the same order of conventional 7YSZ coatings, deposition of the HfO\(_2\) at high temperature results in clustering, and not many inter-splat cracks and pores are found in the coating. Due to this localized higher density of the HfO\(_2\) layer, the Young’s modulus is assumed to be closer to that of annealed 7YSZ with a Young’s modulus at 50% of the fully dense value. Since the average thickness of the APS TBC is \( \sim 150 \) µm, half of
the predicted ERR in Figure 3(a) (solid blue line) can be used as an estimate (∼100 J/m^2). The high ERR throughout the coating suggests that crack propagation is very likely, which was seen in practice by the APS-deposited HfO₂ coatings spalling almost immediately when subjected to thermal cycling. The channel cracking and bifurcation after deposition left sharp flaws in the coating, which during heating and cooling rapidly propagated. As a result, no thermochemical data on the stability between the YbDS EBC layer and m-HfO₂ TBC layer could be gathered in the APS-deposited coatings.

By reducing the crack tip opening angle, and thus creating more blunted crack tips, the propensity for cracking could be reduced significantly^{73,99}. A potential method for this is to apply a columnar PVD-type coating instead, where the gaps between columns have a smaller crack tip opening angle^{17,94,102}. This decreases the stress field around the crack tips, lowering the propensity for crack propagation as relatively more energy is required for crack propagation to occur compared to the sharp flaws found in the HfO₂ APS TBC. As such, it was decided to deposit a HfO₂ TBC using electron beam directed vapor deposition (EB-DVD), aided by substrate heating in order to ensure sufficient adhesion between the YbDS EBC layer and the HfO₂ TBC layer.

5.5 **EB-DVD deposited m-HfO₂ TBC**

5.5.1 **Coating characterizing**

Four samples were coated with a porous, columnar m-HfO₂ TBC using EB-DVD. Due to the dispersed positioning of the samples with respect to the center of the vapor plume, the HfO₂ deposition rate on samples 1 and 4 was lower compared to samples 2 and 3. SEM analysis of sample 4 in the as-deposited condition, revealed a TBC layer with a thickness of ∼35 µm, and a feathery, columnar microstructure with a porosity of 12.2%, Figure 5.6. The average width of the columns was measured to be 282 (± 93) nm closer to the HfO₂-YbDS interface, and 436 (± 149) nm closer to the coating surface. SEM analysis of samples 2 and 3 after thermal cycling revealed a coating
thickness of \( \sim 85 \, \mu m \) due to the increased flux of HfO\(_2\) during deposition as these samples were positioned closer to the center of the vapor plume.

![Image](image.png)

**Figure 5.6:** SEM micrograph of the vapor deposited HfO\(_2\) TBC showing its fine (\( \sim 1 \, \mu m \) wide) columnar microstructure.

### 5.5.2 Isothermal annealing of the vapor deposited HfO\(_2\) TBC

Sample 1 was isothermally annealed in steam at 1316°C for 500 hours, Figure 5.7, in order to evaluate the thermochemical stability between the HfO\(_2\) TBC and YbDS EBC layers without thermomechanical influences such as crack growth and delamination that can occur during thermal cycling. In Figure 5.7(a) it can be seen that after 500 hours the HfO\(_2\) had sintered together significantly at the surface of the TBC layer, and had partially delaminated at the YbDS-HfO\(_2\) interface. The column width had increased significantly compared to the as-deposited state, averaging 841 (\( \pm \) 359) nm close to the top surface of the HfO\(_2\) TBC layer, and 725 (\( \pm \) 277) nm closer to the HfO\(_2\)-YbDS interface. Due to sintering of the columns, the pore gap width visibly increased, increasing the porosity of the coating to 18.0%. A densely sintered HfO\(_2\) layer with a thickness of 3.2 (\( \pm \) 0.4) \( \mu m \) is present along the HfO\(_2\)-YbDS interface, with pores and cracks forming along the interface. A segmented TBC structure remained as parts of the TBC layer had delaminated.
lamination cracks are visible at the edges of the remaining segments, and the coating can be seen to uplift slightly at the edges, Figure 5.7(a). Thin cracks are seen running parallel to the YbDS-HfO₂ interface through the YbDS, Figure 5.7(b).

Four EDS line scans were done across the YbDS-HfO₂ interface, the reaction layer, and the lower part of the remaining columnar HfO₂ TBC, Figure 5.7(c), showing an average of 26.2 (± 2.6) at% ytterbium in the reaction layer. No significant amount of hafnium was detected in the EBC layer, this indicates diffusion of ytterbium from the EBC layer into the TBC layer, resulting in a reaction between the YbDS EBC and HfO₂ TBC. The YbDS EBC layer normally contains 1.5 mol% YbMS dispersed throughout the coating, although after annealing a YbDS layer free of YbMS precipitates is measured adjacent to the YbDS-HfO₂ interface, averaging 4.5 (± 1.1) µm, Table 5.3. This suggests a loss of YbMS from the EBC layer, rather than loss of YbDS. Poerschke et al.⁸⁶ determined that a thermochemical instability between both YbDS and YbMS, and m-HfO₂, Figure 5.2. They showed that the dissolution of Yb₂O₃ in m-HfO₂ results in formation of a cubic fluorite, F₃SS phase with a Yb₂O₃ content of 5-15%. It is noted that the measured 26.2 at% ytterbium fraction in the reaction layer is equivalent to the dissolution of ~15 mol% Yb₂O₃ in HfO₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>State</th>
<th>YbDS layer (µm)</th>
<th>Reaction layer (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500 hours isothermal</td>
<td>4.50 (± 1.06)</td>
<td>3.17 (± 0.39)</td>
</tr>
<tr>
<td>2</td>
<td>103 1-hr cycles</td>
<td>3.08 (± 0.70)</td>
<td>0.83 (± 0.08)</td>
</tr>
<tr>
<td>3</td>
<td>750 1-hr cycles</td>
<td>4.04 (± 0.62)</td>
<td>0.90 (± 0.08)</td>
</tr>
</tbody>
</table>

5.5.3 Steam cycling of the vapor deposited HfO₂ TBC

Samples 2 and 3 were steam cycled concurrently (60 minutes at 1316°C, then 5 minutes at ~110°C). Sample 2 was removed from the furnace when it visibly started to show spallation after 103 cycles. Figure 5.8 shows cross-sectional images of sample 2, where an increase in pore width between
Figure 5.7: Isothermally annealed sample 1 after a 500-hour furnace anneal in a 90 vol% H₂O/10% O₂ steam environment at 1316°C. a) Example of HfO₂ growth column sintering, fracture of some growth columns, development of a dense reaction layer and interfacial cracks at the YbDS-HfO₂ interface. b) Detail of the YbDS-HfO₂ interface showing delamination between the reaction layer and the YbDS. (c) An EDS line scan along the orange line shown in (b) indicating the reaction layer contained ∼30 at% ytterbium and 70 at% hafnium, consistent with the Yb₂O₃-stabilized cubic fluorite (F₃₅) HfO₂ phase.
columns is evident compared to the as-deposited state, Figure 5.6, with a porosity of 17.9%. The columns densified slightly as well, Table 5.3, averaging 796 (± 220) nm at the top of the HfO$_2$ TBC, and averaging 654 (± 225) nm at the bottom of the layer. A densified HfO$_2$ layer is found on top of the YbDS EBC layer with a thickness of 0.8 (± 0.1) µm. The columnar HfO$_2$ layer is found to be mostly delaminated from the densified layer. At several spots on the coating the delamination crack was found to pass through this densified layer into the YbDS coating, Figure 5.8(b). In locations, the delamination crack penetrated into the YbDS layer via periodic channel cracks in the densified layer, and in one instance coalesced into a bigger crack, Figure 5.8(c). Similar to the isothermally annealed sample, a YbDS layer free of YbMS precipitates is found immediately below the YbDS-HfO$_2$ interface with a thickness of 3.1 (± 0.7) µm. Four EDS line scans across the reaction layer indicate an average of 27.9 (± 3.4) at% ytterbium, averaging ∼16 mol% Yb$_2$O$_3$.

Sample 3 was removed from the furnace when spallation of the coating became visible after 750 steam cycles, Figure 5.9. The columnar HfO$_2$ TBC was found to be mostly intact and adhering to the YbDS EBC layer, Figure 5.9(a), although showing more densification at the bottom of the layer compared to sample 2. The column width averaged 797 (± 208) nm at the bottom, and 613 (± 208) nm at the top of the HfO$_2$ layer, thinner compared to sample 2. The porosity of the sample increased further to 25.8%, as measured on the adhering coating segments and excluding gaps created by spalled off segments. The densified HfO$_2$ layer at the YbDS-HfO$_2$ interface has a thickness of 0.9 (± 0.1) µm, only marginally higher compared to sample 2, and shows periodic channel cracking every 5-10 µm. The thickness of the YbDS layer free of YbMS precipitates averaged 4.0 (± 0.6) µm, and showed formation of pores in the YbMS-free layer. There is no indication that such porosity occurs in the underlying YbDS coating where YbMS is present, so it appears that the reactions that consume YbMS locally results in loss of volume, and thus creation of pores. An EDS line scan done across the YbDS-HfO$_2$ interface, the densified layer, and partially into the columnar HfO$_2$ TBC, Figure 5.9(c), reveals that the densified layer has an average of 27.4
Figure 5.8: SEM images of (a) the HfO₂ TBC layer of sample 2 after 103 steam cycles between 110°C and 1316°C. (b) A higher magnification view of the YbDS-HfO₂ interface showing the reaction layer with channel cracks, and delamination cracks. (c) A higher magnification view of a region where a delamination crack and channel crack coalesced, and the channel crack penetrated into the YbDS layer and bifurcated.
(±2.9) at% ytterbium, equaling ∼16 mol% of the FSS phase, similar to that of sample 2. In sample 3, several cracking modes can be observed, Figure 5.9(b), such as delamination of the YbDS-FSS interface, which also results in kinking of the crack into the YbDS EBC layer. Additionally, a delamination crack can be seen ∼8 µm from the FSS-TBC interface, indicating cracking is not solely limited to the layer interfaces.

5.5.4 Formation of a Yb$_2$O$_3$-stabilized HfO$_2$ reaction layer

Poerschke et al.$^{86}$ showed that at 1500°C neither YbDS nor YbMS are thermochemically stable when in contact with monoclinic HfO$_2$, forming a mixture of FSS and hafnon instead. Since no thermodynamic data are available, predictions of which reaction products will form cannot be made. Chapter 4 showed that a mixture of the YbDS (including 1.5 mol% YbMS) and HfO$_2$ APS powders was annealed at 1316°C for 20 hours in lab air, indicated complete consumption of the YbMS, and formation of HfSiO$_4$ (hafnon) and the FSS phase. All samples annealed at 1316°C in this work confirm that a nominal YbDS EBC layer (containing ∼1.5 mol% YbMS) also reacts with the monoclinic HfO$_2$ TBC to form a FSS reaction layer, and was accompanied by a loss of YbMS from the EBC layer adjacent to the YbDS-HfO$_2$ interface, resulting in a reaction: 2x Yb$_2$SiO$_5$ + (1-x) HfO$_2$ → (Yb$_2$O$_3$)$_x$ (HfO$_2$)$_{1-x}$ + x Yb$_2$Si$_2$O$_7$. This is consistent with YbMS being the preferred source of the Yb$_2$O$_3$ in the FSS layer rather than YbDS. Since BSE imaging and EDS analysis did not reveal any direct evidence of hafnon formation, it is possible that the remaining SiO$_2$ reacted with other YbMS inclusions to form YbDS instead.

The concentration of Yb$_2$O$_3$ reached a maximum of 16 mol% Yb$_2$O$_3$ in the FSS layer in all samples, independent on the thickness of the reaction layer. Crack growth between the FSS and TBC layers interrupted the growth of the reaction layer, but the maximum Yb$_2$O$_3$ concentration of 16 mol% was not exceeded. According to the binary Yb$_2$O$_3$-HfO$_2$ phase diagram$^{96}$, a eutectoid point between the FSS phase and the combined M+δ phase region is present, and addition of more
Figure 5.9: SEM images of sample 3 subjected to 750 steam cycles between 110°C and 1316°C. (a) Shows the presence of wide gaps in the HfO$_2$ TBC layer and the presence of a reaction layer at the YbDS-HfO$_2$ interface. (b) Shows a higher magnification view of the channel cracked reaction layer that formed in the TBC-EBC interface and the presence of pores in the YbDS layer. (c) Shows an EDS line scan through the reaction layer indicating an ytterbium concentration of \(~26\) at% in the reaction layer.
Yb$_2$O$_3$ would result in formation of the $\delta$-Yb$_4$Hf$_3$O$_{12}$ phase. Poerschke et al.\textsuperscript{86} showed that such a composition would result in the formation of YbDS, YbMS, and the F$_{SS}$ phase instead, suggesting that it is not thermodynamically favorable for more Yb$_2$O$_3$ to be included. It is noted that that even after relatively short times at a temperature of 1316°C (sample 2, exposed to 103 1-hour steam cycles), the predicted maximum Yb$_2$O$_3$ concentration (16 mol% Yb$_2$O$_3$) in the F$_{SS}$ layer was attained, indicating that the predicted cubic stabilization of m-HfO$_2$, Figure 5.2, occurs quite rapidly.

5.5.5 Thermomechanical implications of the F$_{SS}$ layer during thermal cycling

Figure 3(b) showed that the ERR at the m-HfO$_2$-YbDS interface in a silicon/YbDS/HfO$_2$ system with a 100 µm thick EB-DVD deposited TBC with a Young’s modulus assumed to be $\frac{1}{5}$th of the solid Young’s modulus was $\sim$30 J/m$^2$. Since the ERR scales linearly with coating thickness, Equation 5.1, the ERR was $\sim$10 J/m$^2$ (50 J/m$^2$ times $\frac{1}{5}$th of the fully dense Young’s modulus) for samples 1 and 4, which had a 35 µm thick TBC, and $\sim$25 J/m$^2$ (125 J/m$^2$ times $\frac{1}{5}$th of the fully dense Young’s modulus) for samples 2 and 3 with 85 µm thick layers. This reduction in Young’s modulus is possible due to the columnar and feathery microstructure of the vapor deposited HfO$_2$ TBC\textsuperscript{83,84,94}. Since the as-deposited coatings did not delaminate upon cooling, it appears the interfacial toughness’s exceeded 25 J/m$^2$ in the as-deposited state.

As the porous HfO$_2$ was subjected to annealing, it gradually densified, resulting in the formation of wide gaps in the TBC layer and uplifting of the edges near the YbDS-TBC interface as the top of the m-HfO$_2$ columns sintered together. However, before this led to failure of the coating system, Figures 5.7, 5.8, and 5.9 showed that the F$_{SS}$ phase developed between the YbDS and m-HfO$_2$ TBC. Figure 5.8(a) shows that the emergence of an $\sim$1 µm thick F$_{SS}$ reaction layer primarily resulted in delamination of the $\sim$85 µm thick TBC at the F$_{SS}$-HfO$_2$ interface after 103 steam cycles. However, Figure 5.9 showed that a HfO$_2$ TBC of similar thickness only partially
delaminated, and some regions remained well bonded at both the $F_{SS}$-TBC and YbDS-$F_{SS}$ interfaces. It is noted that both steam-cycled samples (2 and 3) suffered from channel cracking of the $F_{SS}$ layer, followed by very thin cracks penetrating into the YbDS layer, Figures 5.8(c) and 5.9(b). Some of these cracks apparently continued to grow as cycling continued, resulting in coalescing of these cracks and eventually uplifting the delaminated parts away from the underlaying coating.

To investigate the thermomechanical driving force for delamination, the LayerSlayer code was used to model the ERR in a TBC system containing a 1 $\mu$m thick $F_{SS}$ layer. The CTE of this phase was measured (Chapter 4 to be 12.3x10$^{-6}$ $^\circ$C$^{-1}$, i.e. more than double that of the m-HfO$_2$ TBC (6.1x10$^{-6}$ $^\circ$C$^{-1}$) and triple the YbDS (4.0x10$^{-6}$ $^\circ$C$^{-1}$) layers. Using these data, and that for the other constituents given in Table 5.1, the ERR for m-HfO$_2$ TBC as a function of its thickness (assuming the TBC layer modulus was $\frac{1}{2}$ that of the fully dense HfO$_2$ Young’s modulus) is shown in Figure 5.10. The highest ERR in the thermally cycled samples 2 and 3 (with a m-HfO$_2$ TBC thickness of 85 $\mu$m) existed at the YbDS-$F_{SS}$ interface ($\sim$65 J/m$^2$). However, the YbDS-$F_{SS}$ interfacial ERR was also high ($\sim$55 J/m$^2$), indicating a potentially high risk of delamination at either interface. Equation 5.1 indicates that these ERR values are likely to increase with increase in HfO$_2$ modulus (i.e. as sintering of the TBC progresses) and with thickness of a growing $F_{SS}$ layer.

It has to be noted that the plane of delamination in samples 2 and 3 was usually the YbDS-$F_{SS}$ interface, whose ERR was slightly less than that of the $F_{SS}$-HfO$_2$ interface. As such, it appears that the location of failure was dictated by either the interfacial toughness, or failure nucleated by stress concentrating features such as pores and sharp flaws. Careful examination of the delaminated regions, Figures 5.8 and 5.9, shows that delamination at the $F_{SS}$-TBC interface was associated with regions of very high HfO$_2$ layer porosity. Since the toughness is consistent with $G = E^{-1} K_{IC}^2$, where $K_{IC}$ is the mode I fracture toughness, it appears that the presence of pores at this interface may have significantly influenced the final plane of delamination since both $E$ and $K_{IC}$ decrease.
Figure 5.10: The calculated ERR in a silicon-YbDS-FSS-HfO$_2$ system as a function of the HfO$_2$ thickness (annealed) with a 1 µm thick FSS layer, assuming the m-HfO$_2$ TBC has $\frac{1}{2}$ of the fully dense Young’s modulus

with increase in porosity. It is noted that delamination cracks in regions of TBC well above the interface (8-10 µm) were also seen, Figure 5.9(b), consistent with this phenomenon.

Further examination of sample 3 (750 cycles), Figure 5.9(b), shows two major mechanical failure modes:

1. Frequent, periodic channel cracking of the FSS layer

2. Crack growth, bifurcation, and crack coalescence into the YbDS layer

Channel cracking stems from the large CTE of the FSS layer on top of the lower CTE YbDS layer. As the FSS layer attempts to shrink more during cooling due to its high CTE, stresses are relieved by channel cracking instead. Since the YbDS EBC layer is brittle in nature, the channel cracks that form continue into the YbDS layer in the same fashion as was described by Richards et al.$^{30}$, resulting in the second failure mode. Due to the YbDS EBC layer having a lower CTE than
the thick SiC substrate, the EBC layer will be in compression. As such, the cracks that form into the YbDS layer tend to either be arrested, bifurcate, or travel upward back towards the FSS layer. This effect can be seen in Figure 5.11(a), where two cracks have coalesced. Continued thermal cycling would have exacerbated this further, resulting in ejection of the cracked segment from the coating system, which was visually observed during periodic inspection of the coating surface during the steam cycling process.

![Diagram](image)

**Figure 5.11:** Schematic illustration of the mechanisms of fracture in sample 2 and 3, including the CTE of the various layers.

Delamination along the YbDS-FSS interface occurred in the isothermally annealed sample 1, Figure 5.7. This sample had sintered significantly more throughout the TBC compared to the thermally cycled samples, lowering the strain tolerance of the coating compared to the columnar microstructure of the as-deposited and thermally cycled samples.\(^9^4\) As the sample cooled down and thermal strain was generated in the TBC layer due to its higher CTE compared to the underlaying layers, a bending moment was created inside the layer.\(^7^3\) Due to the rigidity of the thick substrate, the HfO\(_2\) TBC layer was not able to bend, and thus preferentially cracked and partially delaminated instead, Figure 5.7(a). Since no repeated cycling had occurred in sample 1, flaws along the
The formation of the FSS layer is deemed one of the biggest downfalls of this coating system. In order to stop the formation of the high CTE FSS layer due to reaction of the YbDS EBC with the monoclinic HfO₂ TBC, a fully stabilized, 16 mol% Yb₂O₃-stabilized HfO₂ TBC would have to be deposited instead. The predicted ERR for such a silicon/YbDS/FSS coating system is shown in Figure 5.12, as a function of the FSS layer thickness. It can be seen that the ERR linearly increases rapidly and sufficient energy is available for crack propagation throughout the coating (including in the silicon and YbDS layer), suggesting the usage of a 16 mol% Yb₂O₃-stabilized HfO₂ FSS phase is unlikely to be thermomechanically viable on top of a silicon/YbDS EBC system.

Figure 5.12: ERR of the interfaces in the silicon/YbDS/FSS system as a function of the FSS layer thickness
5.6 Conclusions

Deposition of a m-HfO$_2$ thermal barrier coating (TBC) with clustered porosity using atmospheric plasma spray (APS) on top of a silicon/Yb$_2$Si$_2$O$_7$ (YbDS) environmental barrier coating (EBC) system showed channel cracking of the TBC immediately after deposition, where cracks were deflected and bifurcated at the YbDS-HfO$_2$ interface. Within several thermal cycles the coatings completely spalled off.

Deposition of a m-HfO$_2$ TBC using electron beam directed vapor deposition (EB-DVD) resulted in a columnar and porous microstructure without any crack formation in the coating system. All the samples annealed in steam at 1316°C showed reaction of the EBC layer with the TBC to form Yb$_2$O$_3$-stabilized HfO$_2$ (F$_{SS}$) with a high coefficient of thermal expansion (CTE), which densified upon reaction. Loss of YbMS precipitates near the YbDS-HfO$_2$ interface was also observed. The thickness of both layers increased with time. Two samples that were thermally cycled for 103 and 750 cycles showed delamination of the columnar HfO$_2$ TBC from the densified reaction layer, as well as some cracks penetrating through the reaction layer into the YbDS EBC. One sample isothermally annealed for 500 hours showed a much thicker reaction layer, partial delamination along the YbDS-F$_{SS}$ interface, and ejection of HfO$_2$ columns after cooling. The composition of the F$_{SS}$ reaction layer averaged 16 mol% Yb$_2$O$_3$ with a CTE of 12.3x10$^{-6}$ °C$^{-1}$ in all of reaction layers.

Prediction of the energy release rate (ERR) indicates that the formation of the high CTE reaction layer results in a significant increase in ERR along the YbDS-F$_{SS}$ interface, making delamination along this interface energetically favorable due to the combination of densification and the significant increase in CTE. Three major fracture mechanisms were observed as a result of the formation of the F$_{SS}$ reaction layer, that eventually result in failure of the TBC layer. Contraction of the high CTE F$_{SS}$ layer during cooling resulted in (1) the formation of channel cracks in the F$_{SS}$
layer. These cracks then continued into the YbDS EBC layer, resulting in (2) the formation of hairline cracks, bifurcation, and eventual cracks coalescing in the EBC layer. Finally, (3) differential contraction between the FSS layer and m-HfO$_2$ TBC, combined with contraction and segmentation of the m-HfO$_2$ TBC, resulted in the shearing off of the TBC from the FSS layer. In order to make the use of a HfO$_2$-based TBC, reaction between the YbDS and monoclinic HfO$_2$ layers should be actively avoided.
6 Multi-component rare-earth disilicates for tunable properties of T-EBC systems

6.1 Introduction

Silicon carbide based ceramic matrix composites (CMCs) are beginning to be implemented in the hottest regions of gas turbine engines where surface temperatures are on the order of $\sim 1300^\circ C$. Using film cooling and other thermal management approaches, CMC operating temperatures can be increased to $\sim 1500^\circ C$. Under these conditions, the surface of silicon carbide oxidizes to form CO gas species and a crystalline SiO$_2$ layer. In the presence of abundant water vapor in the gas flow, the SiO$_2$ (s) reacts to form volatile reaction products such as Si(OH)$_4$ (g), resulting in recession of SiC at the composite surface at rates of $\geq 1$ µm/hour. An environmental barrier coating (EBC) system that reduces the flux of oxidizing species to the SiC-based substrate is therefore utilized to limit oxidation and volatilization of the SiC.

EBC systems in current use are designed to function at temperatures up to 1316°C (2400°F), and utilize a Yb$_2$Si$_2$O$_7$ (ytterbium disilicate; YbDS) rare-earth disilicate environmental barrier layer whose silica volatility (rate of steam volatility) is $\sim 1/4$ that of SiO$_2$. The environmental barrier is applied to a silicon bond coat that functions as an oxidation barrier, by forming a SiO$_2$ thermally grown oxide (TGO) when oxidizing species reach its surface. This silicon layer also increases adhesion between the EBC layer and the SiC-based substrate. An example of such an EBC system is shown in Figure 6.1. Given the brittle nature of the materials used in this protection strategy, it is essential that the thermal expansion and contraction of all coating layers be similar to that of the SiC composite substrate to which it is applied. YbDS and silicon have coefficients of thermal expansion (CTE) ($\alpha_{\text{YbDS}} = 4.0 \times 10^{-6}$ °C$^{-1}$, and $\alpha_{\text{Si}} = 4.1 \times 10^{-6}$ °C$^{-1}$, respectively) matching quite well to that of pure SiC ($\alpha_{\text{SiC}} = 4.5 \times 10^{-6}$ °C$^{-1}$), and the layered system has
shown excellent thermo-mechanical stability during thermal cycling when applied to a thick SiC substrate\textsuperscript{31}.

**Figure 6.1:** Schematic illustration of an environmental barrier coating system applied to an air-cooled SiC CMC exposed to a high temperature (1316°C, high pressure, and high flow speed) combustion gas environment.

When oxidizing species reach the bond coat surface, they react with silicon to form crystalline \( \beta \)-cristobalite when the bond coat surface temperature is above \( \sim 1200^\circ\text{C} \), at a rate that increases exponentially with temperature\textsuperscript{37}. When YbDS is applied as a dense layer on the silicon bond coat, the YbDS reduces the flux of oxidizing species that permeate to the bond coat, thereby reducing the growth rate of the SiO\textsubscript{2} TGO layer\textsuperscript{31}. While the CTE of \( \beta \)-cristobalite (3.1x10\textsuperscript{-6} °C\textsuperscript{-1})\textsuperscript{103} is quite well matched to other components of the system a \( \beta \rightarrow \alpha \)-cristobalite transition occurs on cooling through 240°C, resulting in a 4.9% decrease in TGO volume, and the development of large stored elastic strain energy in the coating system. Failure of the coating system has been predicted to oc-
cur when the TGO layer thickness reaches a critical value, whereupon delamination of the coating at the silicon-SiO$_2$ interface is energetically favorable occurs$^{31}$.

The rate of growth of the TGO layer depends upon both the flux of oxidizer species at the bond coat surface, and the rate of its diffusion through the TGO layer to form new oxide at the silicon-SiO$_2$ interface. At high temperatures, where diffusion through the TGO layer is fast, Richards et al.$^{31}$ showed that the TGO grew at a rate that appeared to be governed by permeation of the oxidizing species through the YbDS layer rather than the TGO layer. As the environmental barrier layer suffers steam volatility, the effective distance of oxidizer permeation decreases, and it would be expected that flux would increase over time. While Richards et al.$^{31}$ found that the delamination of the silicon-YbDS system does not occur for at least 2,000 hours at 1316°C while exposed to steam (90 vol% H$_2$O/10 vol% O$_2$, 44 mm/s) and thermally cycled (60 minutes hot at 1316°C, 10 minutes cold at $\sim$110°C), about 15 µm of the environmental barrier had been transformed, raising concern that the oxidizer flux would eventually cease to be rate limiting.

Other materials, such as barium-strontium-aluminosilicates (BSAS), alumino-silicate (mullite), and ytterbium monosilicate (Yb$_2$SiO$_5$, YbMS) have been proposed for use as EBC materials. However, their CTE’s are not well matched to that of the SiC-based components ($\alpha_{BSAS} = 7.5 \times 10^{-6}$ °C$^{-1}$, $\alpha_{Mullite} = 5.5 \times 10^{-6}$ °C$^{-1}$, $\alpha_{YbMS} = 7.2 \times 10^{-6}$ °C$^{-1}$)$^{17,20,29,30,104}$. This results in channel cracking and failure of the coating system during thermal cycling$^{29,30}$, and creation of a fast path for oxidizer permeation through the cracked region of the coating. The CTE of these materials, together with many other silicates and oxides, is plotted against their melting temperature in Figure 6.2. It shows that the Sc-, Lu-, Y-, Er- and Yb-disilicates and the ZrSiO$_4$ and HfSiO$_4$ orthosilicates all have CTE values and melting temperatures in the ranges needed for EBC applications, which is indicated as a yellow highlighted zone in Figure 6.2. The use of materials with a lower permeation rate and good CTE match may therefore lead to new EBC systems with improved durability.
A second approach to increased durability is to reduce the temperature of the TGO, and therefore attempt to make diffusion of oxidizers through the TGO the life determining design approach. In a typical gas turbine application, thermal management concepts are employed to create a thermal gradient across the coating system, thereby reducing the temperature of the underlying coating layers and component. Since the TGO growth rate at the surface of the silicon bond coat increases exponentially with temperature, a reduction of temperature could extend the coating life by decreasing the rate of TGO thickening, and possibly avoid the formation of a crystalline SiO$_2$ TGO if the temperature of the bond coat surface was reduced below $\sim$1200°C\[37,67\]. If a SiC composite was cooled as indicated in Figure 6.1, the YbDS layer would provide some thermal protection.
of the bond coat since its ambient thermal conductivity, $\kappa_{\text{YbDS}} = 4.5-8 \text{ W m}^{-1} \text{ K}^{-1}$, would be sufficient to create a thermal gradient in an internally cooled application\textsuperscript{87}. Backside cooling also lowers the average temperature within the YbDS, thus lowering the contribution of thermally activated diffusion to the rate of permeation of oxidizing species through the layer, and thus the oxidizer flux at the bond coat. The discovery of an EBC layer materials with low steam volatility, a CTE in the $4-5\times10^{-6} \text{ °C}^{-1}$ range, and a lower thermal conductivity than YbDS, could therefore have a significant consequence for EBC system development, especially if the material had good resistance to other relevant engine failure modes (e.g. particle impact and molten silicate reaction resistance)\textsuperscript{16, 17, 26, 94, 105}.

The average bulk thermal conductivity in polycrystalline materials versus the CTE for candidate materials for use in EBC systems is shown in Figure 6.3. In general, the rare-earth monosilicates have a significantly lower thermal conductivity than their disilicate counterparts, with some approaching a conductivity of $1 \text{ W m}^{-1} \text{ K}^{-1}$, which is close to the lower limit for phonon-based thermal transport\textsuperscript{106}. While the monosilicates typically exhibit a higher resistance to steam volatilization (since their silica activity is significantly lower)\textsuperscript{75}, their CTE values are too high, as well as highly anisotropic, for use as an EBC layer material in silicon-based bond coat systems.

Felsche\textsuperscript{107} had correlated the RE-disilicate phase with temperature and RE\textsuperscript{3+} cation radius of all scandium, yttrium, and the lanthanides, Figure 4(a), while Fernández-Carrión et al.\textsuperscript{89} have reported the average bulk CTE of most of the RE-disilicate polymorphs\textsuperscript{89}, Figure 4(b). A recent measurement for the A-Sm\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} phase\textsuperscript{108}, has been added to the data in Figure 4(b). While several of the high CTE Gd- and La-disilicates have a better resistance to calcium-alumino-silicate (CMAS) attack compared to Y- and Yb disilicates (since they promote crystallization of apatite phases in molten silicates\textsuperscript{91, 93, 109}), these disilicates have a high CTE ($>8\times10^{-6} \text{ °C}^{-1}$). Figure 4(b) shows that only the $\beta$- and $\gamma$-rare earth disilicate phases have CTE values ($3.9-5.4\times10^{-6} \text{ °C}^{-1}$) that
are compatible for use in EBC systems\textsuperscript{89,110}.

The exploratory study presented here investigates the feasibility of mixing several rare-earths in a rare earth disilicate alloy and see if it is possible to create a single phase, mixed disilicate that is phase stable in the temperature range of interest, has a low thermal conductivity and a CTE sufficiently low for use as an EBC layer in a silicon bond coat-based EBC system.

### 6.2 Design of rare-earth disilicate mixtures

The majority of the larger cation radius disilicates have a CTE two to three times higher than the current EBC materials of interest, Figure 4(b). By mixing multiple rare-earth disilicates, the hy-
Figure 6.4: a) A phase stability diagram for rare earth disilicates as a function of RE$^{3+}$ ionic radius proposed by Felsche$^{107}$. The candidate phases for EBC systems are shaded in yellow. b) Average bulk CTE of rare earth disilicates grouped by phase from Fernández-Carrión et al.$^{89}$ and Ayyasamy et al.$^{108}$
pothesis explored here is that larger RE-cation disilicates can be stabilized in phases with the β- or γ-structure, whose CTE might be in the range required for a silicon bond coat-based EBC system. Some support for this has been provided by Dong et al.\textsuperscript{111}, who have shown that an equimolar mixture of Yb-, Y-, Lu-, Sc-, and Gd-disilicates formed a single β-phase disilicate. If rare-earth cations of dissimilar radii had randomly arranged themselves on the cation sublattice to form a solid solution, this could reduce the thermal conductivity of the multi-disilicate due to thermal vibrations being impeded by these larger and/or heavier cations. Larger radius solute cations will not be able to vibrate along the same mean spacing on a lattice of cations of smaller radius, reducing the energy that can be transferred\textsuperscript{78, 112}. Likewise, heavier cations on a lattice of lighter cations will transfer less momentum across. This reduces the effective thermal conductivity, enabling a layer made up of such a material to function as both an environmental and thermal barrier. Computational predictions provided in literature by Turcer et al.\textsuperscript{20} indicated that addition of another rare-earth disilicate (e.g. YDS or LuDS) to YbDS could potentially reduce the thermal conductivity of a mixture to $\sim 1$ W m$^{-1}$ K$^{-1}$.

Based upon lattice strain energy considerations, it appears unlikely that the mixing of cations of very different radii (i.e. cations located at the opposite ends of the Felsche diagram, Figure 4(a)), will result in a single-phase mixture\textsuperscript{113}. Instead, the free energy of a multi-component disilicate composed of cations of widely varying ionic radii is more likely to be minimized by decomposition into a collection of phases containing rare-earth cations of similar size\textsuperscript{108}. Evidence for this can be found from the work of Fernández-Carrión et al.\textsuperscript{113, 114} who experimentally evaluated the binary phase equilibria of $Y_2Si_2O_7$ (YDS, $Y^{3+} = 0.90$ Å) alloyed with either $Yb_2Si_2O_7$ (YbDS, $Yb^{3+} = 0.87$ Å) or $La_2Si_2O_7$ (LaDS, $La^{3+} = 1.03$ Å). In the YbDS-YDS system, Figure 6.5, where the two RE$^{3+}$ cations are of similar radius, the addition of yttrium resulted in retention of the YbDS β-phase to a Yb:Y ratio of 1:1, and this phase remained stable up to the melting temperature over much of this composition range\textsuperscript{114}. 

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One approach to the design of a multi-component rare-earth disilicate is to therefore take the phase that forms to be dictated by the average cation radius of the mixture, and use the Felsche diagram of Figure 4(a) to predict the phase that forms and the temperature range of its stability. For the Yb$_{2-x}$Y$_x$Si$_7$O$_{17}$ system with $x \leq 1$, the average cation radius lies between 0.87 and 0.885 Å, and Figure 4(a) shows that this is well within the $\beta$-phase field and stable to temperatures up to at least 1800°C. This is beneficial for EBC systems, since a single $\beta$-phase YbDS-YDS mixture would be phase stable within the range of the expected use temperatures. Furthermore, Figure 4(b) indicates that the CTE of most $\beta$-phase disilicates match well that of silicon and the SiC substrate.

Further support for this rare-earth disilicate design approach is found by examining the alloying of YDS with LaDS where the cation radius of La (0.103 Å) is substantially greater than that of Y (0.90 Å). The experimental assessment of this system by Fernández-Carrión et al.\textsuperscript{113}, Figure 6.6, found a very small $\beta$-phase field located near the Y$_2$Si$_2$O$_7$ end of the binary phase diagram, with many other phases emerging at lower Y:La ratios resulting in a complex phase diagram\textsuperscript{113}. The underlaying light grey lines in the phase diagram denote the expected phases from the Felsche dia-
gram, Figure 4(a), based on the calculated average cation radius of the YDS/LaDS ratio. The black lines and the symbols shown in Figure 6.6 denote the actual phases found by Fernández-Carrión et al.\textsuperscript{113}, which can differ substantially from the expected phases due to the presence of preferential substitution mechanisms, specifically in the G-(La,Y)\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} polymorph. In the G-(La,Y)\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} polymorph, Y preferentially occupies a “RE2” site\textsuperscript{113}. This study indicates that mixing of two rare-earth disilicates is sometimes consistent with the predictions set out by Felsche\textsuperscript{107}. However, in other cases, phase separation into two phases occurs. For example, when a relatively small concentration of LaDS (<4 mol%) was added to YDS, it was found to form the low-CTE β- and γ-phases between 1200-1500°C, although addition of more LaDS resulted in large zones on the phase diagram where phase separation occurred\textsuperscript{113}. Thus, while the addition of similar ionic radii cations to mixed rare-earth disilicates appears to result in phases that are reasonably well-predicted by the Felsche diagram, Figure 4(a), this design principle breaks down as the dispersity in cation radius increases.

\textbf{Figure 6.6:} \(\text{Y}_2\text{Si}_2\text{O}_7\)-\(\text{La}_2\text{Si}_2\text{O}_7\) phase diagram with phase boundary lines predicted using the Felsche diagram\textsuperscript{113}
Unfortunately, the absence of thermodynamic data for the rare-earth disilicates prohibits a comprehensive thermodynamic assessment of enthalpic mixing and/or entropic stabilization effects for multiple rare-earth mixed disilicates. Furthermore, the large total number of atoms to be modeled in a density functional approach, and the many cations that must be incorporated in such a calculation to converge upon a phase stability prediction, have impeded the use of this approach to predict the stability of multi-component rare-earth disilicate alloys. The study described here therefore uses an experimental approach to explore the mixing of rare-earth disilicates with varying RE-cation sizes. This is exemplified by the addition of Gd- and La-disilicates to YbDS in order to investigate the addition of a moderate and large increase in radius, respectively, according to the Felsche diagram, Figure 4(a). This experimental study reports the phase stability, the thermal conductivity, and the CTE of mixtures of rare-earth disilicates. It is noted that the benefit of using Gd- and La-disilicate as candidates is also for their apparent increased molten silicate resistance. If a mixed disilicate were obtained with low thermal conductivity and well matched CTE containing either of these cations, it might provide a route to the design of a mixed RE-disilicate with increased molten silicate resistance in the future as well, especially compared to the current YbDS EBC system whose molten silicate resistance is poor.

6.3 Experimental procedures

Table 6.1 shows the YbDS-based mixtures explored in this study, the calculated average RE-cation radius, and the phase expected to form after annealing at 1500°C as found by superimposing the average RE-cation radius onto the Felsche diagram, Figure 4(a). Two equimolar binary mixtures were first made using YbDS and either Gd$_2$Si$_2$O$_7$ (GdDS) to form (Yb$_{0.5}$Gd$_{0.5}$)$_2$Si$_2$O$_7$, or LaDS to form (Yb$_{0.5}$La$_{0.5}$)$_2$Si$_2$O$_7$. The latter was synthesized to that it could be compared with the work previously reported by Fernández-Carrión et al. A ternary system was then created by adding YDS as a third component to the binary mixtures to form (Yb$_{0.33}$Y$_{0.33}$Gd$_{0.33}$)$_2$Si$_2$O$_7$ and (Yb$_{0.33}$Y$_{0.33}$La$_{0.33}$)$_2$Si$_2$O$_7$, Table 6.1. Yttrium is relatively inexpensive compared to other rare
Table 6.1: Rare-earth components of the equiatomic rare-earth disilicate (RE1,RE2,RE3,RE4,RE5)2Si2O7 samples, together with their average cation radius and anticipated phase(s) at 1500°C based on data from Figure 4(a).

<table>
<thead>
<tr>
<th>Sample</th>
<th>RE1</th>
<th>RE2</th>
<th>RE3</th>
<th>RE4</th>
<th>RE5</th>
<th>Average RE³⁺ radius (Å)</th>
<th>Phase(s) predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A</td>
<td>Yb</td>
<td>Gd</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.90</td>
<td>γ</td>
</tr>
<tr>
<td>3A</td>
<td>Yb</td>
<td>Y</td>
<td>Gd</td>
<td>-</td>
<td>-</td>
<td>0.90</td>
<td>γ</td>
</tr>
<tr>
<td>4A</td>
<td>Yb</td>
<td>Y</td>
<td>Lu</td>
<td>Gd</td>
<td>-</td>
<td>0.89</td>
<td>γ</td>
</tr>
<tr>
<td>5A</td>
<td>Yb</td>
<td>Y</td>
<td>Lu</td>
<td>Er</td>
<td>Gd</td>
<td>0.89</td>
<td>γ</td>
</tr>
<tr>
<td>2B</td>
<td>Yb</td>
<td>La</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.95</td>
<td>F</td>
</tr>
<tr>
<td>3B</td>
<td>Yb</td>
<td>Y</td>
<td>La</td>
<td>-</td>
<td>-</td>
<td>0.93</td>
<td>δ</td>
</tr>
<tr>
<td>4B</td>
<td>Yb</td>
<td>Y</td>
<td>Lu</td>
<td>La</td>
<td>-</td>
<td>0.92</td>
<td>δ</td>
</tr>
<tr>
<td>5B</td>
<td>Yb</td>
<td>Y</td>
<td>Lu</td>
<td>Er</td>
<td>La</td>
<td>0.91</td>
<td>δ</td>
</tr>
</tbody>
</table>

earth elements, and has been of interest for use as an EBC material, but suffers from multiple phase formation during thermal spraying and subsequent annealing\(^{116}\). Lu-disilicate (Lu₂Si₂O₇, LuDS) was added as a fourth component to create equimolar quaternary mixtures, with compositions of (Yb\(_{0.25}\)Y\(_{0.25}\)Lu\(_{0.25}\)Gd\(_{0.25}\))₂Si₂O₇ and, (Yb\(_{0.25}\)Y\(_{0.25}\)Lu\(_{0.25}\)La\(_{0.25}\))₂Si₂O₇, lowering the average cation radius since the Lu-cation is the smallest radius RE-cation, aside from very expensive scandium. Two quinary mixed rare-earth disilicates were synthesized by adding Er-disilicate (Er₂Si₂O₇, ErDS) as a fifth component to the two quaternary alloys to form (Yb\(_{0.2}\)Y\(_{0.2}\)Lu\(_{0.2}\)Er\(_{0.2}\)Gd\(_{0.2}\))₂Si₂O₇ and (Yb\(_{0.2}\)Y\(_{0.2}\)Lu\(_{0.2}\)Er\(_{0.2}\)La\(_{0.2}\))₂Si₂O₇.

### 6.3.1 Materials and synthesis

The samples were made from rare-earth oxide and SiO₂ powder. The rare-earth oxides (-325 mesh, Elemental Metals, Chatham, NJ) were weighed to equimolar ratios and mixed in a 1:2 ratio with amorphous SiO₂ powder (-325 mesh, Atlantic Metals Inc., Stratford, CT) to obtain a RE₂O₃ : 2 SiO₂ ratio. The powders were then mixed using a high-energy ball mill (SPEX SamplePrep 8000D, Metuchen, NJ) for 90 minutes, using a DuPont Vertel XF liquid to promote mixing and cooling. Powders were dried in air for 1 hour in a fume hood in ambient air. The powder mixtures were cold-pressed at 40 MPa into 12.7 mm diameter pellets by packing powder in a graphite die
and compressing it using the hydraulic system of a Thermal Technologies (Santa Rose, CA, USA), Model 25-10 spark plasma sintering machine at room temperature. Samples were then annealed in an Al$_2$O$_3$ boat lined with a Pt-10Rh foil at 1500°C for 72 hours in a Sentrotech ST-1600-666 bottom-loading furnace. The Al$_2$O$_3$ sample boats were baked out for at least 24 hours at 1500°C to reduce contaminants from the boat entering the samples. Pt-10Rh foil was used as a barrier between the sample and Al$_2$O$_3$ sample boat in order to avoid formation of alumino-silicate and/or rare-earth garnet mixtures at the contact interface between the powder and boats.

### 6.3.2 Characterization methods

Annealed samples were polished using SiC grinding paper down to 1200 grit (P-4000) SiC paper. A Helios NanoLab DualBeam scanning electron microscope (FEI, Hillsboro, OR) in back-scattered electron (BSE) mode was used for surface analysis, using Z-contrast to differentiate between the different phases present. Energy dispersive spectroscopy (EDS) was used for elemental microanalysis (X-Max$^N$ 150 SDD, Oxford Instruments, Concord, MA). Porosity in the samples was measured using the ImageJ software package$^{72}$.

X-ray diffraction (XRD) measurements were performed using a PANalytical Empyrean (Malvern Panalytical, Westborough, MA), set-up with a Cu-k$_\alpha$ source and Bragg-Brentano optics combined with a reflection/transmission-spinner stage set-up for reflectance measurements. Diffraction angles (2$\theta$) 10-90° were analyzed at 0.12°/s. Samples were spun at 0.25 revolutions per second to reduce preferential orientation of grains.

The coefficient of thermal expansion was measured using a Netzsch DIL 402C dilatometer, by cutting pellets into approximately 10x3x3mm square rods, applying a 25cN constant force and heating these up to 1000°C at a rate of 5°C/min, allowing a 30-minute dwell period, follow by cooling down to room temperature at a rate of 5°C/min.
A hot disk approach using a Hot Disk TPS 3500 (Thermttest Inc., Fredericton, NB, Canada) was used to measure the thermal conductivity at ambient temperature. The hot disk uses the transient plane source (TPS) method\(^{117,118}\) to determine thermal conductivity. Two different sensors were used; one with a kapton layer and one with a mica layer over the nickel sensor. Prior to measurements, both sensors were used to measure a stainless-steel standard (13.8 \(\pm 0.5\) W \(\text{m}^{-1} \text{K}^{-1}\)) compared to literature values of approximately 14 \(\pm 0.7\) W \(\text{m}^{-1} \text{K}^{-1}\).\(^{119}\) The thermal conductivity acquired from the hot disk approach was corrected for porosity by application of the Maxwell-Eucken model\(^{120}\), approximated by \(\kappa_{\text{actual}} = \kappa_{\text{meas}}/\varphi^{(3/2)}\), where \(\varphi\) is the density as measured using ImageJ\(^{72,121}\). It is noted that the thermal conductivity was only measured at 25°C, and typically decreases as temperature is increased.

### 6.4 Results

The XRD patterns with identified phase(s) found for each sample by XRD phase analysis are shown in Figure 6.7, and listed in Table 6.2. This table also lists the porosity as found using the ImageJ software package\(^{72}\), coefficient of thermal expansion (CTE), thermal conductivity \(\kappa\) as measured by hot disk method, the thermal conductivity corrected for porosity, and the average calculated cation radius for each mixture. The CTE is plotted as a function of the average cation radius, Figure 8(a), and the thermal conductivity as a function of the average cation radius, Figure 8(b).

#### 6.4.1 Phase and elemental analysis

The samples based upon the YbDS-GdDS system, the two-component \((\text{Yb}_{0.5} \text{Gd}_{0.5})_2 \text{Si}_2 \text{O}_7\) system (2A), and ending with the five-component \((\text{Yb}_{0.2} \text{Y}_{0.2} \text{Lu}_{0.2} \text{Er}_{0.2} \text{Gd}_{0.2})_2 \text{Si}_2 \text{O}_7\) system (5A), were found to all incorporate at least the \(\gamma\)-phase. In the two- and three-component mixtures, 2A and \((\text{Yb}_{0.33} \text{Y}_{0.33} \text{Gd}_{0.33})_2 \text{Si}_2 \text{O}_7\) (3A), two phases \(\gamma+\alpha\), and \(\gamma+\delta\), respectively, were found using XRD,
Figure 6.7: XRD diagrams of a) the Yb-Gd disilicate based mixtures, and b) the Yb-La based mixtures, with compositions identified in Tables 6.1 and 6.2.
Figure 6.8: a) Thermal expansion and b) Thermal conductivity, as a function of average RE$^{3+}$ cation radius. Samples are denoted with the phase(s) found using XRD, and color bands denote the phases as indicated by the Felsche diagram, Figure 4(a).
Table 6.2: The phases found using XRD analysis, the density, CTE, thermal conductivity, and predicted by the Felsche average RE$^{3+}$ cation radius criterion of all samples analyzed in this study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average RE$^{3+}$ cation radius</th>
<th>Phase(s) predicted</th>
<th>Phase(s) observed</th>
<th>Porosity (%)</th>
<th>CTE (x10$^{-6}$ °C$^{-1}$)</th>
<th>$\kappa_{\text{meas}}$ (Wm$^{-1}$K$^{-1}$)</th>
<th>$\kappa_{\text{corr}}$ (Wm$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2A</td>
<td>0.90</td>
<td>$\gamma$</td>
<td>$\gamma + \alpha$</td>
<td>10.3</td>
<td>6.0</td>
<td>0.97 (± 0.02)</td>
<td>1.14</td>
</tr>
<tr>
<td>3A</td>
<td>0.90</td>
<td>$\gamma$</td>
<td>$\gamma + \delta$</td>
<td>16.5</td>
<td>5.7</td>
<td>0.90 (± 0.02)</td>
<td>1.18</td>
</tr>
<tr>
<td>4A</td>
<td>0.89</td>
<td>$\gamma$</td>
<td>$\gamma$</td>
<td>16.2</td>
<td>5.1</td>
<td>0.99 (± 0.02)</td>
<td>1.29</td>
</tr>
<tr>
<td>5A</td>
<td>0.89</td>
<td>$\gamma$</td>
<td>$\gamma$</td>
<td>12.9</td>
<td>3.9</td>
<td>1.49 (± 0.03)</td>
<td>1.83</td>
</tr>
<tr>
<td>2B</td>
<td>0.95</td>
<td>$F$</td>
<td>$\beta + G$</td>
<td>3.3</td>
<td>7.0</td>
<td>1.12 (± 0.03)</td>
<td>1.18</td>
</tr>
<tr>
<td>3B</td>
<td>0.93</td>
<td>$\delta$</td>
<td>$\beta + G$</td>
<td>8.5</td>
<td>6.4</td>
<td>1.06 (± 0.02)</td>
<td>1.21</td>
</tr>
<tr>
<td>4B</td>
<td>0.92</td>
<td>$\delta$</td>
<td>$\beta + G$</td>
<td>6.3</td>
<td>5.6</td>
<td>1.20 (± 0.02)</td>
<td>1.32</td>
</tr>
<tr>
<td>5B</td>
<td>0.91</td>
<td>$\delta$</td>
<td>$\beta + G$</td>
<td>4.1</td>
<td>7.1</td>
<td>1.67 (± 0.04)</td>
<td>1.78</td>
</tr>
</tbody>
</table>

Table 6.2. When more RE-cations with relatively small radii were added, the four component and (Yb$_{0.25}$Y$_{0.25}$Lu$_{0.25}$Gd$_{0.25}$)$_2$Si$_2$O$_7$ (4A), and five component (Yb$_{0.2}$Y$_{0.2}$Lu$_{0.2}$Er$_{0.2}$Gd$_{0.2}$)$_2$Si$_2$O$_7$ (5A) systems, were found to be single $\gamma$-phase systems. SEM images taken in BSE mode of the Gd-based systems, Figure 6.9, showed equal contrast across the samples, which indicates a homogeneous distribution of phases. EDS spot analysis shows a variation in RE-element concentration throughout the samples, even though no difference in contrast can be observed. In the two-component system for instance, an Yb-rich area is detected (spot A, Figure 6.9(a)), and a Gd-rich area ~75 µm further on (spot C, Figure 6.9(a)). Additionally, several unreacted SiO$_2$ particles can be seen in all samples.

The YbDS-LaDS based systems were all found to phase separate into the $\beta$- and G-phases, Figure 7(b). As less LaDS was mixed in, the relative intensity of the G-phase reduced, while the relative intensity of the $\beta$-phase increases. SEM images taken in BSE mode, Figure 6.10, shows stark differences in contrast between phases, with EDS spot analysis indicating darker grains are La-rich areas (spot B, Figure 6.10(a)), and lighter grains are La-deficit grains (spot C, Figure 6.10(a)). Some spots were found consisting of only a single ytterbium disilicate (spot A, Figure 6.10(a)). Increased magnification the dark grains indicated micro-cracking upon cooling, Figure 6.11.
Figure 6.9: SEM images with EDS point analysis of the Gd-based disilicate systems.
Figure 6.10: SEM images with EDS point analysis of the La-based disilicate systems
6.4.2 Coefficient of thermal expansion measurements

Coefficients of thermal expansion were measured using dilatometry for all samples, Figure 6.8(a). For both the Gd- and La-containing mixtures, the two-, three-, and four-component mixtures follow a downward trend as more components were added and the average cation radius decreased, Table 6.2, ranging between 5.1-6.0×10⁻⁶ °C⁻¹ for the Gd-based mixtures, and 5.6-7.0×10⁻⁶ °C⁻¹ for the La-based mixtures. In the five-component \( (\text{Yb}_{0.2}\text{Y}_{0.2}\text{Lu}_{0.2}\text{Er}_{0.2}\text{La}_{0.2})_2\text{Si}_2\text{O}_7\) (5A) mixture, the CTE sharply dropped from 5.1×10⁻⁶ °C⁻¹ to 3.9×10⁻⁶ °C⁻¹ as the fifth component (ErDS) was added. In contrast, the CTE of the five-component \( (\text{Yb}_{0.2}\text{Y}_{0.2}\text{Lu}_{0.2}\text{Er}_{0.2}\text{La}_{0.2})_2\text{Si}_2\text{O}_7\) (5B) mixture increased from 5.6×10⁻⁶ °C⁻¹ to 7.1×10⁻⁶ °C⁻¹ when ErDS was added to the mixture.

6.4.3 Thermal conductivity measurements

The thermal conductivity as measured using the hot disk method at room temperature is plotted against the average cation radius in Figure 8(b). For both the Gd-based and La-based mixtures, the thermal conductivity was measured <1.5 W m⁻¹ K⁻¹ up to the four-component systems. Both five component systems measured slightly higher at ~1.8 W m⁻¹ K⁻¹. The thermal conductivity shown in Figure 8(b) is the thermal conductivity corrected for porosity. The values obtained from
the hot disk measurement technique was measured to be below the amorphous limit of 1 W m\(^{-1}\) K\(^{-1}\) several times due to the presence of porosity in the samples, Table 6.2.

### 6.5 Discussion

#### 6.5.1 Implications for use in EBC systems

The primary goal of this exploratory study was to identify mixtures that could be used as hybrid T-EBC layer materials with low thermal conductivity (close to 1 W m\(^{-1}\) K\(^{-1}\)) and a CTE close to that of the SiC substrate (\(\alpha_{\text{SiC}} = 4.67 \times 10^{-6} \, ^\circ\text{C}^{-1}\)). The phenomena that dictate which crystal structure a multi-component rare-earth disilicate attains remains unclear. Felsche\(^{107}\) has argued that the radius of the RE\(^{3+}\) cation, and associated opening of the Si-O-Si bonding angle was responsible for the phases observed. Ayyasamy et al.\(^{108}\) has used density functional theory (DFT) to calculate the total energy trend of some of the individual rare-earth disilicates in order to extract insights into the polymorphism that these materials exhibit. These calculations enabled the total energy difference (\(\Delta E\)) between the lowest energy structure and other phases for a specific rare-earth disilicate at 0 degrees Kelvin to be deduced. For example, for YbDS the approach predicted that the C2/m \(\beta\)-phase has the lowest energy state, followed by the P2\(_1/c\) \(\gamma\)-phase with \(\Delta E = 3.51\) meV/atom\(^{108}\). The next lowest energy phase after that was the Pnma \(\delta\)-phase at a much higher \(\Delta E = 29.79\) meV/atom, making it much more unlikely to form.

According to the Felsche diagram, Figure 4(a), the \(\beta\)-phase of YbDS dominates across all temperatures, completely consistent with the DFT results. The diagram indicates that as the cation radius is increased slightly (from 0.87 Å for Yb to 0.90 Å for Y), the \(\gamma\)-phase becomes a preferred high temperature phase, through this too then transforms to the \(\beta\)-phase on cooling through 1200°C. DFT estimates for YDS, indicated that like YbDS, the \(\beta\)-phase was the phase with the lowest energy at 0K, followed by the \(\gamma\)-phase with \(\Delta E = 1.99\) meV/atom. The next candidate is again the \(\delta\)-phase at \(\Delta E = 10.47\) meV/atom, which is much closer to the \(\beta\)-phase compared to YbDS. When
compared with the Felsche diagram, Figure 4(a), it can be seen that at high temperature, the $\gamma$- and $\delta$-phase were both found to exist in the YDS system, though the low temperature experimentally observed was the $\alpha$-phase. The stability of high temperature phases is influenced by both the total energy of the system at 0K, and entropic contributions to the free energy. The latter are not included in DFT calculations. Thus, while DFT calculations have helped establish the lowest energy phases at 0K, they must be used with considerable caution during the design of materials intended for use at high temperature, where entropic contributions to the free energy per atom from the changes of configurational and vibrational (and other) entropy can be large compared to that of the enthalpy.

Fernández-Carrión et al.\textsuperscript{122} concluded that superimposing the average cation radius of a mixture to find the expected phase to form on the Felsche diagram, Figure 4(a), only holds when two RE-disilicates in a binary rare-earth disilicate system have a stable polymorph in common. This design approach might be improved by using the DFT calculations by Ayyasamy et al.\textsuperscript{108} to predict the “almost stable polymorphs” of phases that have a $\Delta E$ close to the lowest energy phase, and including these in the search for matching polymorphs in a pair of disilicate systems.

On the other hand, when a pair of rare-earth disilicates with a large cation radius difference (and with polymorphs with large total energy difference) are mixed, such as in the YDS-LaDS binary system studied by Fernández-Carrión et al.\textsuperscript{122}, the introduction of the La$^{3+}$ cation with a large cation radius of 0.103 Å into $\beta$/γ-phase lattices with a Y$^{3+}$ cation radius of only 0.90 Å, increases the strain energy in the system significantly. This contribution to the energy per atom, when combined with the higher configurational entropy contribution to the total energy per atom, is presumably responsible for the little La that can be dissolved in YDS. The LaDS-YDS phase diagram, Figure 6.6, visually displays this phenomenon, and indicates that less than 4 mol% LaDS can be dissolved into the YDS $\beta$- and $\gamma$-phases. In contrast, up to at least 50% YDS could be dis-
solved into the LaDS G-phase before phase separation occurs. This is consistent with the smaller RE-cation (Y\textsuperscript{3+}) being able to occupy any of the RE\textsuperscript{3+} lattice sites in the LaDS G-phase lattice, increasing the configurational entropy, and thus the total entropy in the system\textsuperscript{122}.

The La-based silicate mixtures made in this study are deemed to not be fit for use in EBC systems due to the phase separation observed in all cases, in spite of their low thermal conductivity $<2$ W m\textsuperscript{-1} K\textsuperscript{-1} for all the synthesized multi-component systems. Based on this study, and the previous work by Fernández-Carrión et al.\textsuperscript{122}, the maximum amount of La that can be mixed with either YbDS or YDS is 4 at\%, spot A in Figure 6.10(a), which reduces to zero once more components are added. The combination of phase separation, and absence of La in one of the two phases, negates the benefit a T-EBC coating might have from the addition of La.

On the other hand, the Gd-based disilicate mixtures look much more promising. The four- and five-component Gd-based mixtures fulfill the criteria for use in T-EBC systems due to their CTE being in the 3.9-5.1x10\textsuperscript{-6} °C\textsuperscript{-1} range, and their thermal conductivities being below 2 W m\textsuperscript{-1} K\textsuperscript{-1}. These systems are single phase, so no differential contraction between any high- and low-CTE phase would occur in a multi-phase material such as the La-based disilicate mixtures. As such, either the four-component (Yb\textsubscript{0.25}Y\textsubscript{0.25}Lu\textsubscript{0.25}Gd\textsubscript{0.25})\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}, or five-component (Yb\textsubscript{0.2}Y\textsubscript{0.2}Lu\textsubscript{0.2}Er\textsubscript{0.2}Gd\textsubscript{0.2})\textsubscript{2}Si\textsubscript{2}O\textsubscript{7}, would be viable candidates for use as T-EBC layer materials. It is important to note that this study has not investigated the steam volatility resistance, diffusivity of oxidizing species, and CMAS resistance properties of these compositions, which are integral parts of designing a successful EBC layer material. Furthermore, tailoring the compositions to further match the CTE, thermal conductivity, and the other properties mentioned of the mixtures more closely, is certainly possible, especially if the phenomena responsible for the crystal structures that form can be understood.
6.5.2 Phase stability in the Yb-Gd-based disilicate system

The phases that were predicted to form in \((\text{Yb}_{0.5}\text{Gd}_{0.5})_2\text{Si}_2\text{O}_7\) based on the Felsche “cation radius criterion” are noted in Tables 1 and 2. According to this, all of the compositions should form the \(\gamma\)-phase when annealed at 1500°C, since their average ionic radius is 0.89-0.90 Å. Since the radius of Gd (0.94 Å) is significantly larger than Yb (0.87 Å), it appears the Gd-cation is too large to fully dissolve in YbDS in the two-component (2A) and three-component (3A) systems, resulting in phase separation like that seen in the YDS-LaDS binary system, Figure 6.6122.

The XRD analysis for the \((\text{Yb}_{0.5}\text{Gd}_{0.5})_2\text{Si}_2\text{O}_7\) (2A) sample, Figure 7(a), indicated a two-phase system containing the \(\gamma\)- and \(\alpha\)-phases, whereas the Felsche radius criterion predicted formation of only the \(\gamma\)-phase, Table 6.2. Examination of SEM images taken in BSE imaging mode for the \((\text{Yb}_{0.5}\text{Gd}_{0.5})_2\text{Si}_2\text{O}_7\) 2A sample, Figure 6.9(a), indicated the presence of no significant BSE contrast difference throughout this sample, indicating a relatively homogeneous distribution of all elements. However, EDS spot analysis did detect regions with a difference in Yb and Gd content. The Yb-rich area, spot A in Figure 6.9(a) has a Yb:Gd atomic ratio of 58:42, resulting in a local average ionic radius of 0.90 Å. The Felsche diagram, Figure 4(a), indicates this to be the \(\gamma\)-phase at 1500°C. The B and C spots were Gd rich with a Yb:Gd atomic ratio of 34:66, resulting in an average ionic radius of 0.92 Å, and is indicated to be the \(\delta\)-phase at 1500°C. However, at \(\sim 1470^\circ\text{C}\) the phase stability diagram indicates the transition of the \(\delta\)- to the \(\alpha\)-phase, so it is likely that the \(\alpha\)-phase formed as the sample cooled down. This is consistent with the \(\alpha\)-phase detected during XRD phase analysis, Figure 7(a).

The addition of an equimolar amount of \(\text{Y}_2\text{Si}_2\text{O}_7\) to form \((\text{Yb}_{0.33}\text{Y}_{0.33}\text{Gd}_{0.33})_2\text{Si}_2\text{O}_7\) (3A) did not change the average cation radius, Table 6.2, although XRD phase analysis indicated this resulted in the formation of the \(\gamma\)- and \(\delta\)-phases, Figure 7(a). Again, only the \(\gamma\)-phase should have formed according to the Felsche diagram, Figure 4(a), although this time the \(\delta\)-phase had also
formed during annealing at 1500°C. EDS analysis indicates that the amount of Y detected remains constant throughout the sample at between 34-40 at%. A Yb-rich (38 at%) region was detected at spot A in Figure 6.9(b), where the concentration of Gd was relatively low (27 at%), resulting in an average ionic radius of 0.89 Å, which corresponds to the \( \gamma \)-phase. On the other hand, the Gd-rich regions (spots B and C in Figure 6.9(b)) shows a decrease in Yb-content, with average ionic radii of 0.91 Å, which corresponds to the \( \delta \)-phase at 1500°C. Upon cooling, this composition goes through the \( \gamma \)-phase between 1450→1370°C, and the \( \alpha \)-phase region below 1370°C. Since no \( \alpha \)-phase was detected in this sample, it appears that the formation of the \( \alpha \)-phase would be too sluggish ≤1370°C.

XRD analysis of the four-component \((\text{Yb}_{0.25}\text{Y}_{0.25}\text{Lu}_{0.25}\text{Gd}_{0.25})_2\text{Si}_2\text{O}_7\) sample 4A, Figure 6.9(c), indicated the formation of a single \( \gamma \)-phase material. This time, the average cation radius of 0.89 Å followed the prediction according to the Felsche diagram, Figure 4(a) and Table 6.2. EDS analysis, Figure 6.9(c), indicates a mostly homogeneous distribution of the RE-cations throughout the sample, with both EDS spot measurements having an average ionic radius of 0.89 Å. The addition of Er as the fifth and final component to form \((\text{Yb}_{0.2}\text{Y}_{0.2}\text{Lu}_{0.2}\text{Er}_{0.2}\text{Gd}_{0.2})_2\text{Si}_2\text{O}_7\) also resulted in the formation of a single \( \gamma \)-phase. EDS analysis indicated a larger variation in composition, revealing Yb-rich grains (spot A in Figure 6.9(d)) with an average ionic radius of 0.89 Å, and Er-rich grains (spot B in Figure 6.9(d)) with an average ionic radius of 0.90 Å.

Ayyasamy et al.\(^{108}\) have shown the total energy difference for the \( \alpha \)-, \( \delta \)-, and \( \gamma \)-phases in GdDS are all about 1.4-2.0 meV/atom higher than the lowest energy \( \beta \)-phase at 0 K. It therefore appears plausible for GdDS to stabilize in any of these phases upon cooling from 1500°C. However, the stability diagram of Felsche\(^{107}\), Figure 4(a), indicates that GdDS only forms the \( \delta \)-phase (≥1380°C) and then transforms to the \( \alpha \)-phase on cooling below 1380°C, and so is not expected to attain either the \( \gamma \)- or \( \beta \)-phase. On the other hand, Dong et al.\(^{111}\) were able to form a single \( \beta \)-phase using an
equimolar five-component \((\text{Yb}_{0.2}\text{Y}_{0.2}\text{Lu}_{0.2}\text{Sc}_{0.2}\text{Gd}_{0.2})_2\text{Si}_2\text{O}_7\), indicating that a Gd-based disilicate, combined with other RE-disilicates that are energetically favorable to form the \(\beta\)-phase, are indeed able to form the \(\beta\)-phase by mixing.

The \(\gamma\)-phase in the binary 2A system contained \(\sim 42\) at\% Gd according to EDS analysis. However, in the three- and four-components systems, samples 3A and 4A respectively, the Gd content in the \(\gamma\)-phase did not exceed \(\sim 26\) at\%, making it appear that there is maximum solubility limit of GdDS in the multi-component \(\gamma\)-phase. Since this solubility limit of \(\sim 26\) at\% does not appear in the binary system, it appears that this solubility limit is dependent on the other rare-earth elements present in the sample.

6.5.3 Thermal property variations in the Yb-Gd-based disilicate system

The CTE of the two-, three-, and four-component A-series of samples showed a steady decrease as less Gd was present in the mixture, Figure 8(a), and when the fifth component was added the CTE decreased from \(5.1 \times 10^{-6} \, ^o\text{C}^{-1}\) to \(3.9 \times 10^{-6} \, ^o\text{C}^{-1}\). It is noted that porosity has no influence on the CTE\(^{123}\). This shows that a single-phase Gd-based disilicate can be created with the amount of GdDS limited by the solubility in the \(\gamma\)-phase at about \(\sim 26\) mol\% GdDS.

Thermal conductivity measurements of the Gd-based disilicate systems revealed that once two-or-more components are mixed together, thermal conductivity reduces significantly compared to individual rare-earth disilicates to below 2 W m\(^{-1}\) K\(^{-1}\) when measured at 25\(^\circ\)C. The lowest thermal conductivities found is for the phase separated binary system at 1.14 W m\(^{-1}\) K\(^{-1}\), Table 6.2, consistent with phase separation forming grain boundaries that increases phonon scattering opportunities. As more components are added and single-phase mixtures formed, the thermal conductivity increased slightly to 1.29 W m\(^{-1}\) K\(^{-1}\) for the four-component system, and 1.83 W m\(^{-1}\) K\(^{-1}\) for the five-component system. This increase in thermal conductivity for the five-component
system is consistent with a reduction in larger cation radius Gd in the system, and the absence of phase boundaries, reducing the probability of phonon scattering opportunities.

6.5.4 Phase stability in the Yb-La-based disilicate system

The La-based disilicate samples incorporate LaDS with increasing number of components, starting with the binary YbDS-LaDS system to form \( \text{Yb}_{0.5}\text{La}_{0.5}\text{Si}_2\text{O}_7 \). The expected phases, noted in Tables 1 and 2, shift from the F-phase in the two-component system, to the \( \delta \)-phase. SEM imaging in BSE mode revealed phase separation by showing a clear BSE contrast between grains, Figure 6.10(a). EDS analysis of these grains indicated that some small precipitates formed of pure YbDS (spot A in Figure 6.10(a)). Grains with darker contrast, indicating a lower average Z-concentration (spot B in Figure 6.10(a)), have a high amount of La with a La:Yb atomic ratio of 72:28, resulting in an average ionic radius of 0.98 Å, corresponding with the G-phase at 1500°C. The grains with lighter contrast (spot C in Figure 6.10(a)), and a higher average Z-concentration, have a low amount of La and a high amount of Yb in a 4:96, resulting in an average ionic radius of 0.87 Å, corresponding with the \( \beta \)-phase. XRD phase analysis indicated phase separation of this mixture into the aforementioned \( \beta \)- and G-phases with low thermal conductivity (1.18 W m\(^{-1}\) K\(^{-1}\)), and a relatively high CTE of 7.0\( \times \)10\(^{-6}\) °C\(^{-1}\).

The binary YDS-LaDS system explored by Fernández-Carrión et al.\(^{122} \) showed that \( \sim 4 \) at% La could be dissolved in YDS, similar to the maximum amount of La found in YbDS in the two-component system, Figure 6.10(a). Even though the Yb\(^{3+} \) cation radius (0.87 Å) is smaller than that of the Y\(^{3+} \) cation (0.90 Å), this does not seem to have a significant impact on the solubility limit of La in YbDS. Like the Yb-Gd system, the average ionic radius for separate phases follows the cation radius criterion on the Felsche diagram, Figure 4(a).

The predicted \( \delta \)-phase did not form as more components were added, and instead the \( \beta \)- and
G-phases are maintained, Figure 7(b). In the three-, four-, and five-component systems, the lighter grains are found to contain no La at all, while the darker grains contain mostly La (≥ 56 at%), Figure 6.10. The La-rich grains of the four- and five-component systems contain only 4 at% Lu, while the other RE-cations (Yb, Y, and Er) were present in higher concentrations (11-17 at%). The average cation radius in the lighter grains was 0.88 Å in all samples, consistent with the β-phase on the Felsche diagram, while the average cation radius in the darker grains was 0.97 Å in all samples, consistent with the G-phase. These grains showed micro-cracking, consistent with the grain having a high CTE that contracted more compared to the light grains.

6.5.5 Thermal properties of the Yb-La-based disilicate system

With increasing number of components, a systematic decrease in CTE was observed while both β- and G-phases were maintained, with the CTE of the four-component (Yb$_{0.25}$Y$_{0.25}$Lu$_{0.25}$La$_{0.25}$)$_2$Si$_2$O$_7$ mixture reaching 5.6x10$^{-6}$ °C$^{-1}$. When Er was added as a fifth component to form (Yb$_{0.2}$Y$_{0.2}$Lu$_{0.2}$Er$_{0.2}$La$_{0.2}$)$_2$Si$_2$O$_7$, the CTE increased to 7.1x10$^{-6}$ °C$^{-1}$. In addition to the rise in CTE, the thermal conductivity increased from 1.32 W m$^{-1}$ K$^{-1}$ in the four-component system, to 1.78 W m$^{-1}$ K$^{-1}$ in the five-component system. It has to be noted that even though the lowest-measured CTE of the four-component (Yb$_{0.25}$Y$_{0.25}$Lu$_{0.25}$La$_{0.25}$)$_2$Si$_2$O$_7$ is 5.6x10$^{-6}$ °C$^{-1}$, this CTE is measured using a bulk measurement method. Both phases will have a large variation in individual CTE between them, with the β-phase more likely being on the order of ~4x10$^{-6}$ °C$^{-1}$, and the G-phase in the 6.4-11.2x10$^{-6}$ °C$^{-1}$ range. This also does not account for directional anisotropy in the CTE. Hence, during cooling, differential contraction results in formation of cracks, Figure 6.10(d), that will eventually lead to catastrophic failure of the material should the material be subjected to thermal cycling.
6.5.6 Solubility limit of larger RE$^{3+}$ cations in smaller multi-component phases

In the YbDS-GdDS system 42 mol% was able to dissolve in the $\gamma$-phase, and in the YbDS-LaDS system 4 mol% LaDS was able to dissolve in the $\beta$-phase. Based on the findings by Fernández-Carrión et al.$^{122}$ for the YDS-LaDS system, this phenomenon was argued to be the result of large strain energies being generated between the different size RE$^{3+}$ cations, significantly increasing the internal energy of the system and decreasing the potential for mixing. Since no single $\gamma$-phase was obtained in the binary YbDS-GdDS system, the argument for a maximum solubility before a maximum internal energy is achieved is extended to this binary system, resulting in a maximum solubility limit of $\sim$42 mol% GdDS in YbDS before a miscibility gap forms.

The same principle is also likely to occur for the mixing of multiple RE-cations with similar radius, such as Yb$^{3+}$ (0.87 Å) and Y$^{3+}$ (0.90Å). When these are mixed together, a strain energy is generated between these in the RE-disilicate unit cell due to the difference in RE$^{3+}$ cation sizes. Since their radii are very similar, and both RE-disilicates have stable polymorphs in common (i.e. the $\beta$- and $\gamma$-phases), the strain penalty to the internal energy appears to be much less significant compared to the other binaries. However, when a larger radius RE$^{3+}$ cation, such as Gd$^{3+}$ (0.94 Å) or La$^{3+}$ (1.03 Å) is added to this binary to form a ternary compound, a significant drop in solubility of both GdDS and LaDS in the YbDS-YDS system is apparent. As such, it is likely that the strain generated in this system due to mixing of YbDS and YDS, adds a penalty that is significant enough penalty to lower the additional strain that can be added by GdDS or LaDS addition to the $\gamma$-phase. This is evident from the drop in the solubility limit of GdDS in the 3A and 4A systems from 42 mol% to 26 mol%, and LaDS in the 3B, 4B, and 5B systems from 4 mol% to 0 mol%.

As was argued by Fernández-Carrión et al.$^{122}$, mixing of the smaller radii cations in the larger RE-disilicate $\alpha$-, $\delta$-, and G-phases, is likely to be driven by entropic contributions, even though these smaller radii RE-disilicates are not necessarily stable in these polymorphs. Even though
several multi-component rare-earth disilicate systems were found to be candidates for use in EBC systems, the extent of how and why these phases form with specific solubility limits is still not fully understood. In order to be able to predict which compositions are able to form single-phase materials, it is necessary to investigate what the solubility limit of each RE-cation is in each polymorph. Additionally, it will be necessary to understand what the impact of strain energy is on mixing, and what the entropic contributions (configurational, vibrational, electronic, etc) are on the mixing of these multi-component systems.

6.6 Conclusions

Annealing of various multi-component rare-earth disilicate mixtures, consisting of at least two, up to a maximum of five components, consisting of at least an equimolar amount of Yb$_2$Si$_2$O$_7$ (YbDS), and Gd$_2$Si$_2$O$_7$ (GdDS) or La$_2$Si$_2$O$_7$ (LaDS), has shown that the coefficient of thermal expansion (CTE) and thermal conductivity of these materials can be tailored to meet requirements for use in environmental barrier coating (EBC) systems, while also lowering the thermal conductivity closer to 1 W m$^{-1}$ K$^{-1}$ in order to make a hybrid thermal and environmental barrier coating (T-EBC) system. Additional components added to account for the three-, four-, and five-component systems, are Y$_2$Si$_2$O$_7$ (YDS), Lu$_2$Si$_2$O$_7$ (LuDS), and Er$_2$Si$_2$O$_7$ (ErDS). It was found that:

1. The four- and five-component Yb-Gd-based disilicate systems created had a thermal conductivity not higher than 1.8 W m$^{-1}$ K$^{-1}$.

2. The CTE of the four-component (Yb$_{0.25}$Y$_{0.25}$Lu$_{0.25}$Gd$_{0.25}$)$_2$Si$_2$O$_7$ mixture was 5.1x10$^{-6}$ °C$^{-1}$, at the upper design range for EBC materials, and the CTE of the five-component (Yb$_{0.2}$Y$_{0.2}$Lu$_{0.2}$Er$_{0.2}$Gd$_{0.2}$)$_2$Si$_2$O$_7$ mixture was much lower at 3.9x10$^{-6}$ °C$^{-1}$.

3. All Yb-La-based systems showed phase separation, forming both the low CTE $\beta$-phase, and the higher CTE G-phase, resulting in differential contraction throughout the samples and subsequent microcracking.
4. Mixing of the larger RE$^{3+}$ cations with smaller radii cations created solubility limits of the larger RE$^{3+}$ cations that decreased as more components were added to both Yb-Gd-based and Yb-La-based systems. The solubility of GdDS in YbDS was found to decrease from 42 mol% to 26 mol% as YDS was added as a third component. Likewise, the solubility of LaDS in YbDS decreased from 4 mol% to 0 mol% as YDS was added as a third component.

In order to be able to predict which compositions are able to form single-phase materials, it is evident that the solubility limit of each RE-cation needs to be explored further for each rare-earth disilicate polymorph. Additionally, it will be necessary to understand what the impact of strain energy and entropic contributions (configurational, vibrational, electronic, etc) are on the mixing of these multi-component systems.
7 Discussion

This dissertation has explored concepts for reducing the growth of a $\beta$-cristobalite SiO$_2$ TGO on a silicon bond coat in a silicon-YbDS EBC system, in order to potentially suppress coating delamination and extend the coating life time. The growth of the SiO$_2$ TGO has previously been shown to lead to the cracking and eventual failure of the silicon-YbDS EBC system. The two concepts that were explored in this dissertation in order to provide answers to this problem are:

1. The addition of a sacrificial material to the silicon bond coat to transform the SiO$_2$ TGO into a thermomechanically compatible material.

2. Application of thermal management methods to reduce the temperature of the silicon bond coat surface in order to exponentially lower its rate of oxidation.

7.1 Concept 1: Transformation of the $\beta$-cristobalite SiO$_2$ TGO in a thermomechanically compatible material

When SiO$_2$ is in contact with either ZrO$_2$ or HfO$_2$, a solid-state reaction occurs to form zirconium or hafnium orthosilicate ($\text{ZrSiO}_4$; zircon, with a CTE of $5.1 \times 10^{-6} \, ^\circ\text{C}^{-1}$, and $\text{HfSiO}_4$; hafnon, with a CTE of $3.6 \times 10^{-6} \, ^\circ\text{C}^{-1}$, respectively). Both materials are thermochemically and thermomechanically compatible with the silicon-YbDS EBC system ($4.0-4.67 \times 10^{-6} \, ^\circ\text{C}^{-1}$). Since ZrO$_2$ undergoes a phase transformation at $\sim 1200^\circ\text{C}$, HfO$_2$ is the better candidate for use in a coating system as it does not undergo a phase transformation until well above the intended use temperature of EBC systems. Additionally, it has a CTE of $6.1 \times 10^{-6} \, ^\circ\text{C}^{-1}$, relatively similar to the silicon-YbDS coating system. However, literature has not reported on either the kinetics or reaction mechanism of hafnon formation, although some insight can be gained from the reaction mechanism of zircon formation$^{42}$. Literature has been reported on mixed silicon and HfO$_2$ bond coats tested previously$^{24}$, although these showed extensive oxidation of the silicon during thermal exposure as oxidizing...
species percolated rapidly through the HfO$_2$ in the bond coat.

In order to better understand the reaction kinetics and mechanisms by which SiO$_2$ reacts with HfO$_2$ to form hafnon, and in order to allow for intelligent design of an EBC system that effectively reduces the SiO$_2$ TGO thickness, three projects were undertaken. The first, described in Chapter 2, investigated the mixing of cristobalite SiO$_2$ and HfO$_2$ powders, their partial consolidation using spark plasma sintering (SPS), and annealing at temperatures between 1250°C-1400°C. This was then followed by mixing and consolidation of spheroidal silicon particles with HfO$_2$ in Chapter 3, and oxidation of these particles between 1250°C and 1316°C. The results from these chapters were then used to design a novel duplex silicon-HfO$_2$ bond coat in Chapter 4, which was successfully shown to reduce the SiO$_2$ TGO thickness by formation of a hafnon TGO.

7.1.1 The cristobalite SiO$_2$ + HfO$_2$ powder composite system

In order to investigate how the hafnon formation reaction proceeds in the temperature range of interest for the use of EBC systems, the kinetics and reaction mechanisms of the reaction between cristobalite and HfO$_2$ powders were investigated by annealing powder composite systems between 1250°C-1400°C. A mixture of cristobalite and HfO$_2$ was partially consolidated using SPS, resulting in a powder composite with a 35-40% volume fraction of porosity. Annealing of these samples resulted in the formation of hafnon, which inherited the microstructure of the porous HfO$_2$ particles. As the reaction progressed, the densification of hafnon layers was observed. This is consistent with what literature reported on the formation of zircon (ZrSiO$_4$)$_4^{42}$, where it was argued that the silicate forms via the interstitial diffusion of Si$^{4+}$ from SiO$_2$ through zircon and subsequently reacts with ZrO$_2$ at the zircon-ZrO$_2$ interface. In order to maintain electroneutrality, O$^{2−}$ would have be supplied from the SiO$_2$ as well. The addition of Si$^{4+}$ and O$^{2−}$ at the silicate/oxide interface increases the local volume, thus resulting in the densification of pores as volumetric expansion occurs.
X-ray diffraction (XRD) with calibration corrected Rietveld refinement was done on the partially consolidated cristobalite-HfO$_2$ powder composites annealed between 1250°C-1400°C for 1-20 hours. The molar fraction obtained from Rietveld refinement revealed an initial regime of linear growth of the hafnon layer with increasing growth rate as temperature increased. This is consistent with a large HfO$_2$ surface area available for reaction with Si$^{4+}$ and O$^{2-}$. As temperature increased, the rate of hafnon formation increased as well. Once sufficient hafnon had formed, further growth required diffusion of Si$^{4+}$ through the hafnon layer, resulting in a regime of parabolic reaction kinetics. The time at which the linear regime switched to parabolic kinetics decreased as temperature increased. The small HfO$_2$ grain diameter (∼0.5 µm) and porosity in the HfO$_2$ allowed for fast diffusion of Si$^{4+}$ and O$^{2-}$ along grain boundaries once hafnon had formed.

This project indicated that hafnon has the capacity to form at a faster rate than SiO$_2$ is seen to form in EBC systems. Since hafnon inherits the HfO$_2$ microstructure, the design of an EBC system would require HfO$_2$ to be placed between the incoming flux of oxidizing species and the silicon bond coat.

7.1.2 The silicon + HfO$_2$ powder composite system

The effect of parallel silicon oxidation and hafnon formation was investigated by mixing spheroidal silicon particles with HfO$_2$ powder, partially consolidating the powder mixture using SPS, and subsequently annealing the powder composite at 1250°C, 1280°C, and 1316°C. At temperatures below 1200°C the oxidation of silicon results in the formation of a vitreous SiO$_2$ phase, which at temperatures above 1200°C devitrifies to form β-cristobalite. The rate of silicon oxidation at temperatures below 1200°C to form vitreous SiO$_2$ is well-described by the Deal and Grove model$^{37}$, but does not model the formation of the crystalline SiO$_2$ phase above 1200°C. In order to model the rate of silicon oxidation when a crystalline SiO$_2$ layer had formed, spheroidal silicon particles were oxi-
dized at 1250°C, 1280°C, and 1316°C in laboratory air under atmospheric conditions ($p_{O_2} = 0.21$ atm). The measured thickness of this crystalline SiO$_2$ was found to be thinner than the thickness of a vitreous SiO$_2$ extrapolated from the Deal and Grove model, wherefore it was assumed no devitrification would occur. This indicated that a crystalline SiO$_2$ layer is more protective compared to a vitreous SiO$_2$ layer, consistent with a lower oxygen diffusivity of the crystalline phase compared to the vitreous state$^{39}$.

Oxidation of the silicon + HfO$_2$ powder composite system initially exhibited growth of the SiO$_2$ layer at a similar growth rate to that of an unprotected silicon particle. This growth continued until the SiO$_2$ layer reached a thickness of $\sim$200 nm, where after a transient period occurred where SiO$_2$ growth either ceased or temporarily decreased. SEM imaging revealed pore spaces between HfO$_2$ being filled with the expanding SiO$_2$ layer during this incubation period. It appears that hafnon would thus not form until the SiO$_2$ layer was in sufficient contact with the HfO$_2$ particles. Once hafnon formation started, both SiO$_2$ and hafnon exhibited parabolic reaction kinetics, and neither of the layers formed during annealing revealed a linear regime such as previously found for the cristobalite + HfO$_2$ system described in Chapter 2.

The thickness of the SiO$_2$ layer formed in the silicon + HfO$_2$ powder composite system was found to be at least half that of the crystalline SiO$_2$ layer formed on unprotected spheroidal silicon particles, indicating that modification of the silicon bond coat with HfO$_2$ is a viable candidate for reduction of the SiO$_2$ TGO thickness. This would reduce the chance of delamination of the coating system, and increase the potential lifetime of the coating system.

7.1.3 Application of a silicon-HfO$_2$ duplex bond coat in the silicon/YbDS EBC system

The results from Chapters 2 and 3 indicated that $\beta$-cristobalite could be successfully transformed into hafnon at a sufficiently rapid rate when annealed in atmospheric conditions ($p_{O_2} = 0.21$ atm).
Hafnon was indicated to form at the hafnon-HfO$_2$ interface, requiring the sacrificial HfO$_2$ layer to be situated between the incoming oxidizing species and the silicon bond coat. Research by Anton et al.$^{45}$ and Zhu et al.$^{124}$ indicated that mixed silicon + HfO$_2$ composite bond coats showed excessive oxidation of the silicon as oxidizing species percolated rapidly through the relatively oxygen transparent HfO$_2$. This resulted in the design of a duplex silicon + HfO$_2$ bond coat system, where a $\sim$3 $\mu$m thick HfO$_2$ was to be deposited on a silicon bond coat using coaxial plasma directed vapor deposition (CP-DVD). During deposition, the edges of the silicon bond coat were masked so HfO$_2$ was only deposited on the center of the sample and oxidizing species could not penetrate deep into the sample along the HfO$_2$ layer. After deposition of the HfO$_2$ layer, a YbDS EBC layer was deposited on the complete sample using APS.

Oxidation of a silicon + HfO$_2$ duplex bond coat (without environmental barrier) in lab air at 1316°C revealed that hafnon formation occurred parallel to the coating surface along the SiO$_2$/HfO$_2$ interface, and perpendicular to the coating surface along HfO$_2$ grain boundaries. Steam cycling of a duplex silicon + HfO$_2$ bond coat with YbDS EBC layer at 1316°C revealed the formation of hafnon in the same fashion. During the annealing process, HfO$_2$ layer was also found to react with YbMS from the YbDS EBC layer, forming a cubic fluorite (F$_{SS}$) Yb$_2$O$_3$-stabilized HfO$_2$ layer with a high CTE (12.3x10$^{-6}$ °C$^{-1}$). Additionally, the HfO$_2$ was also found to extensively sinter, opening up vertical pores in the HfO$_2$ layer as time progressed. The vertical pores were eventually filled up by SiO$_2$ and transformed to hafnon.

Since the edges of the samples were masked during CP-DVD deposition of the HfO$_2$ layer, the SiO$_2$ thickness could be determined in locations with and without HfO$_2$ present. In locations where no HfO$_2$ was deposited, the SiO$_2$ thickness of the conventional silicon/YbDS system could be determined as well. The TGO layer thickness in the silicon/HfO$_2$/YbDS EBC system was found to be roughly half of the TGO formed in the silicon/YbDS EBC system. No channel cracking was
observed throughout the coating system up to 1000 1-hour steam cycles. This project successfully demonstrated that application of a duplex silicon-HfO$_2$ bond coat can be used to significantly reduce the cristobalite SiO$_2$ thickness in silicon/YbDS EBC systems.

7.2 Concept 2: Thermal management methods for reduction of the bond coat surface temperature

Aside from directly changing the chemistry at the silicon/YbDS interface as done for the first concept, an alternative is to apply thermal management concepts in order to create a thermal gradient between the coating surface and the internally cooled substrate. As the temperature decreases across the YbDS EBC layer and at the silicon bond coat surface, the oxygen diffusivity along the YbDS layer and the oxidation rate of the silicon bond coat decrease exponentially. Testing of EBC systems in academic settings is primarily done by exposing the complete coating system to the same temperature in a basic research furnace. This differs from EBC systems used in modern gas turbine engines, where SiC-based components are internally cooled using air from the engine’s compressor, creating a thermal gradient that lowers the temperature across the coating system with respect to the coating surface. The YbDS EBC layer has a relatively low thermal conductivity ($4.5-8$ W m$^{-1}$ K$^{-1}$) compared to the silicon bond coat ($>50$ W m$^{-1}$ K$^{-1}$), and thus serves as a thermal barrier as well as an environmental barrier, if a temperature gradient is present. However, during exposure to a high temperature (1316°C) steam environment the surface of the YbDS layer will react with water vapor to form volatile Si(OH)$_4$ gas and a porous YbMS layer that cracks upon cooling. During thermal cycling this has shown to lead to local spallation of the YbMS, reducing the effective thickness of the EBC layer. Protecting the surface of the YbDS EBC layer is thus also critical in order to ensure the longevity of the EBC system.

Two methods were explored in order to potentially reduce the temperature at the silicon bond coat when a SiC substrate would be internally cooled. The first method explores the deposition
of a TBC layer with a low thermal conductivity to the YbDS EBC layer in Chapter 5, focusing on the thermomechanical compatibility of such a TBC layer with the silicon/YbDS system during deposition and during thermal cycling in a steam environment. The second method explored the synthesis of multi-component rare-earth disilicates, with the goal to reduce the thermal conductivity closer to 1 W m\(^{-1}\) K\(^{-1}\), while keeping the CTE in the range of thermomechanical compatibility for EBC systems. This is described in Chapter 6.

7.2.1 Deposition and steam cycling of a monoclinic HfO\(_2\) TBC layer

Research by Poerschke et al.\(^{86,95}\) indicated that application of a Yb-hafnate TBC layer to a YbDS EBC layer resulted in a solid-state reaction between the two materials to form a YbMS intermediate layer. Since YbMS has a CTE of 7.2x10\(^{-6}\) °C\(^{-1}\), and the Yb-hafnates have CTE on the order of 9-11x10\(^{-6}\) °C\(^{-1}\), thermal cycling would result in premature cracking and delamination of this coating system\(^{29,30}\). In contrast, monoclinic HfO\(_2\) has a CTE of 6.1x10\(^{-6}\) °C\(^{-1}\) and a thermal conductivity of ≤2 W m\(^{-1}\) K\(^{-1}\), making it a suitable candidate for deposition as a thermal barrier coating (TBC) layer. Designing the deposition of this material as a TBC layer was two-fold. Firstly, application of a TBC layer could lower the temperature throughout the silicon/YbDS EBC system if the SiC-based substrate was to be internally cooled. This reduces the diffusivity of oxidizing species through the YbDS EBC layer, and lowers the oxidation rate of the silicon bond coat. Secondly, this layer would create a direct barrier between the high temperature steam environment and the YbDS EBC layer, reducing its steam volatility, and thus extending the expected life time of the coating system.

The silicon/YbDS EBC system was fabricated using atmospheric plasma spray (APS) by deposition of powders onto a heated SiC substrate held at 1200°C. Monoclinic HfO\(_2\) powder was deposited directly onto the hot silicon/YbDS EBC system held at 1200°C, and imaging of the resulting coating revealed clustered porosity in the TBC layer as a result of deposition onto the hot
coating system. Deposition at high temperature was necessary in order to let the m-HfO₂ powder sufficiently bond with the YbDS layer, although this resulted in immediate channel cracking of the TBC layer after deposition due to stress concentrations forming at the extremities of the clustered porosity. Densification during coating deposition also increased the effective Young’s modulus of the TBC layer, which linearly increases the ERR and stresses in the coating layer. Channel cracking continued across the EBC-TBC interface, and cracks were deflected and/or bifurcated into the compressed YbDS EBC layer. When thermally cycled in a high-temperature (1316°C) steam environment, the TBC layer spalled off within several thermal cycles. Predictions of the ERR at the interfaces of the silicon/YbDS/HfO₂ system confirms that a large stored elastic strain energy is generated at all coating interfaces, reaching \( \sim 100 \text{ J/m}^2 \) at the YbDS/HfO₂ interface for the 150 µm thick TBC layer deposited using APS. Flaws with sharp crack tips, such as the bifurcated cracks close to the EBC/TBC interface, are then energetically favorable to propagate in order to relieve stresses, which is what led to the rapid delamination observed in these samples.

In order to reduce the propensity for cracking, a columnar PVD-type HfO₂ TBC layer was deposited using EB-DVD instead. The gaps between columns have a smaller crack tip opening angle compared to the sharp flaws seen in the APS-deposited TBC, lowering the stress field around the blunt crack tips, and lowering the propensity for crack propagation. When subjected to a high temperature (1316°C) steam environment, imaging revealed the formation of a thin cubic fluorite (F₁₀) layer along the EBC-TBC interface as the m-HfO₂ TBC reacted with YbMS present in the YbDS EBC layer. This layer had a composition of 16 mol% Yb₂O₃-stabilized HfO₂ with a high CTE of 12.3x10⁻⁶ °C⁻¹. Consequently, a YbDS layer free of YbMS formed on the other side of the YbDS-F₁₀ interface. One of the samples was isothermally annealed for 500 hours (without thermal cycling), and imaging revealed the formation of a \( \sim 3 \text{ µm} \) thick F₁₀ reaction layer that partially delaminated at the YbDS-F₁₀ interface. Significant sintering of the columnar m-HfO₂ TBC was also observed. The TBC was segmented at regular intervals, where edges lifted up from
the YbDS-F_{SS} interface as delamination occurred. Cracks that extended from the edges of these segments coalesced, resulting in ejection of these segments from the coating system.

Two samples were thermally cycled in the same high temperature steam environment as the isothermally annealed sample, and visual inspection of the coating surface during the cold cycle of the thermal cycling process (\(\sim 110^\circ\text{C}\)) indicated that spallation visibly started in one sample after 103 1-hour cycles. A second sample did not show spallation until 750 1-hour cycles. The F_{SS} reaction layer in these samples was significantly thinner (\(\sim 1 \, \mu\text{m}\)), and imaging revealed that the modes of cracking observed in these samples was different from that seen in the isothermally annealed sample. In addition to delamination observed at the F_{SS}-TBC interface, channel cracking of the F_{SS} reaction layer and delamination at the porous F_{SS}-TBC interface was also observed. The channel cracking of the F_{SS} reaction layer led to very thin, bifurcated cracks extending into the YbDS EBC layer, which propagated during thermal cycling as a result of large stored strain energy in the coating. Eventually, bifurcated cracks coalesced into bigger cracks, and in synergy with delamination along the YbDS-F_{SS} and F_{SS}-TBC interfaces, this resulted in delamination of large segments of the TBC layer.

Prediction of the ERR of this coating system indicated that the high CTE of the F_{SS} reaction layer would increase the ERR most severely at the YbDS-F_{SS} interface (\(\sim 65 \, \text{J/m}^2\)), followed by the F_{SS}-TBC interface (\(\sim 55 \, \text{J/m}^2\)), making crack propagation and delamination in this coating system energetically favorable. Even though deposition of the m-HfO_{2} TBC layer using EB-DVD appears to result in a thermomechanically stable coating system, the formation and densification of the F_{SS} reaction layer is a detrimental thermochemical mechanism that prevents the usability of m-HfO_{2} as a TBC layer for use on a YbDS EBC layer. More research on improved T-EBC design is required in order to successfully apply a TBC system to the current silicon-YbDS EBC systems.
7.2.2 Multi-component rare-earth disilicates: An approach to tunable properties of environmental barrier coatings

Instead of application of a TBC layer, a different thermal management concept is to reduce the thermal conductivity of the EBC layer itself, which is on the order of 4.5-8 W m$^{-1}$ K$^{-1}$ for YbDS, further towards to the "amorphous limit" of $\sim$1 W m$^{-1}$ K$^{-1}$. This would lead to a significant reduction in temperature at the silicon bond coat surface if the SiC substrate was to be internally cooled. Computational predictions provided in literature by Turcer et al. indicated that addition of another rare-earth disilicate (e.g. YDS or LuDS) to YbDS could potentially reduce the thermal conductivity of a mixture to $\sim$1 W m$^{-1}$ K$^{-1}$. A caveat for creating a rare-earth disilicate mixture is that it has to be thermomechanically compatible with the silicon bond coat and SiC substrate, i.e. have a CTE of $\sim$3.5-5.5 $\times$ 10$^{-6}$ °C$^{-1}$, in order to prevent cracking and failure during thermal cycling. Research presented in literature has argued that other properties of EBC systems, such as steam volatility, molten silicate resistance, and diffusivity of oxidizing species, may be improved as a result of mixing multiple rare-earth disilicates.

As mentioned, the goal of this project was to explore the synthesis of a single-phase, mixed rare-earth disilicate, with a thermal conductivity as close to 1 W m$^{-1}$ K$^{-1}$ as possible, and with a CTE close to that of the silicon bond coat and SiC substrate. A single-phase material is beneficial as it will not undergo differential contraction or expansion of multiple phases during heating and cooling. It was chosen to synthesize multi-component Yb-Gd-based disilicate and Yb-La-based disilicate systems in order to explore the effect of mixing multiple rare-earth disilicates with small RE$^{3+}$ radii (e.g. Yb, Y, Lu) with a moderately sized RE$^{3+}$ cation (Gd = 0.94 Å), and with the largest RE$^{3+}$ cation (La = 1.03 Å).

Research by Fernández-Carrión et al. on the mixing of binary rare-earth disilicate systems, such as YbDS-YDS, and YDS-LaDS, had already been established previously. For
instance, an equimolar mixture of YbDS-YDS system revealed the $\beta$-phase can be stabilized until it reaches the melting point, in contrast to pure YDS that undergoes three phase transformations ($\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \delta$) before melting. It was argued that mixing of two rare-earth disilicates with similar RE$^{3+}$ cation radii adhered to a "cation radius criterion", where the expected phase could be predicted by calculation of the average cation radius of the mixture, and superimposing this average radius on the "Felsche diagram". This was found to hold true for rare-earth disilicate phases that have at least one stable polymorph in common (i.e. a small variation in total energy difference between the phases), such as is the case for YbDS and YDS. When rare-earth disilicates with a large variation in cation radius and total energy difference were mixed together, such as in a YDS-LaDS binary system, the amount of LaDS that could be dissolved into YDS was not more than 4 mol%, which was attributed to La$^{3+}$ generating a large strain energy when dissolved in the YDS lattice, significantly increasing the internal energy in the system. On the other hand, about 50 mol% YDS could be dissolved in LaDS as substitution of smaller RE$^{3+}$ radii cations on a large radius La$^{3+}$ site would not generate such strain energy. Instead, the entropic contribution to mixing (e.g. configurational, vibrational, and electronic) increases solid solubility and stabilization of the mixture in a single phase. Research by Fernández-Carrión et al. also revealed that the CTE of rare-earth disilicates correlates approximately with the size of the RE$^{3+}$ cation, where the smaller $\beta$-phase disilicates (i.e. Lu, Yb, and Er) have CTE $\sim 4 \times 10^{-6}$ °C$^{-1}$, while the larger A-phase disilicates (i.e. Pr, Sm, and La) have CTE $\sim 12-14 \times 10^{-6}$ °C$^{-1}$. If a low CTE mixture would be required, a maximum of only 4 mol% LaDS could be retained in the low CTE YDS $\gamma$-phase before phase separation occurs, limiting the benefit of adding such a large radius cation to an EBC layer material.

Up to three additional rare-earth disilicates were added to the binary YbDS-GdDS and YbDS-LaDS systems. Based on the "cation radius criterion", addition of these additional phases would lower the average ionic radius of the mixtures with the potential to stabilize it in a different phase with lower CTE. Fernández-Carrión et al. had shown that $\beta$- and $\gamma$-phase rare-earth disilicates...
are the only phases with a CTE in the range of interest for use in EBC systems. The Yb-Gd-based disilicate mixtures were predicted to all stabilize in the $\gamma$-phase, while the Yb-La-based disilicate mixtures were predicted to stabilize in the F-phase for the binary (Yb$_{0.5}$La$_{0.5}$)$_2$Si$_2$O$_7$ mixture, and in the $\delta$-phase for the three-, four-, and five-component mixtures, and would likely not be candidates for use in EBC systems.

XRD analysis indicated that the two-component (Yb$_{0.5}$Gd$_{0.5}$)$_2$Si$_2$O$_7$ mixture phase separated into the $\gamma$- and $\alpha$-phases, and the three-component (Yb$_{0.33}$Y$_{0.33}$Gd$_{0.33}$)$_2$Si$_2$O$_7$ mixture phase separated into the $\gamma$- and $\delta$-phases. EDS analysis indicated that as the third component (YDS) was added, the solubility of GdDS in the $\gamma$-phase significantly dropped from $\sim$42 mol% to $\sim$26 mol% GdDS. Once the fourth component (LuDS) was added to form (Yb$_{0.25}$Y$_{0.25}$Gd$_{0.25}$)$_2$Si$_2$O$_7$, a single $\gamma$-phase was detected. Addition of the fifth component (ErDS) also resulted in the formation of a single $\gamma$-phase. The CTE of the four- and five-component mixtures was found to be 5.1x10$^{-6}$ °C$^{-1}$ and 3.9x10$^{-6}$ °C$^{-1}$, respectively, within the desired CTE range. The thermal conductivity of these samples was also found to be 1.29 W m$^{-1}$ K$^{-1}$ and 1.83 W m$^{-1}$ K$^{-1}$, respectively. The slight increase in thermal conductivity for the five-component system appears to be consistent with a decrease in concentration of the relatively larger Gd$^{3+}$ cation, decreasing the potential for phonon scattering and thus increasing thermal conductivity.

XRD analysis of the Yb-La-based disilicate system revealed that all samples phase separated into the $\beta$- and G-phases. In the binary YbDS-LaDS system, only 4 mol% of LaDS was able to dissolve into the YbDS-based $\beta$-phase. As more components were added, this reduced to 0 mol% in the three-, four-, and five-component samples. Meanwhile, the components with smaller radii were able to dissolve in the LaDS-based G-phase lattice, similar to what was observed for the YDS-LaDS binary system by Fernández-Carrión et al.$^{113}$ The CTE was shown to decrease from 7.0x10$^{-6}$ °C$^{-1}$ in the binary system, to 5.6x10$^{-6}$ °C$^{-1}$ in the quaternary system, and increasing to 7.1x10$^{-6}$ °C$^{-1}$ in the quinary system. The thermal conductivity remained $\leq$2 W m$^{-1}$ K$^{-1}$ for all
samples in the Yb-La-based disilicate system, which appears to be consistent with phase separation into multiple phases.

The argument regarding the contribution of strain energy and entropy on mixing provided in literature by Fernández-Carrión et al.\textsuperscript{113,114} appears to hold for the multi-component rare-earth disilicate systems as well. Dissolution of LaDS in YbDS is limited to $\sim\! 4$ mol%, and addition of more components reduces this number to 0 mol%, consistent with a strain energy contribution from the mixing YbDS (0.87 Å) and YDS (0.90 Å) and/or Lu (0.86 Å) and Er (0.89 Å), which is significant enough to reject the dissolution of LaDS into this system. This phenomenon appears to extend to the Yb-Gd-based disilicate systems as well, as indicated by a decrease in solubility of GdDS in the YbDS-based $\gamma$-phase from $\sim\! 42$ mol% in the two-component system, to $\sim\! 26$ mol% in the three- and four-component systems. In order to ensure no phase separation occurs, the concentration of GdDS added to such a mixture should thus be kept below this apparent solubility limit, as demonstrated with the four- and five-component systems.

In order to be able to predict which compositions are able to form single-phase materials, it is evident that the solubility limit of each RE-cation needs to be explored further for each rare-earth disilicate polymorph. Additionally, it will be necessary to understand what the impact of strain energy and entropic contributions (configurational, vibrational, electronic, etc) are on the mixing of these multi-component systems.
8 Conclusions

The concepts explored in this dissertation were (1) to find a sacrificial material to transform the β-cristobalite SiO$_2$ thermally grown oxide (TGO) into a thermo-mechanically compatible material, and (2) to find thermal management methods that can reduce the temperature of the silicon bond coat surface in order to lower its rate of oxidation. Concept 1 was accomplished in three sequential steps, where first the hafnium silicate (HfSiO$_4$; hafnon) formation kinetics and reaction mechanism were investigated by annealing of a cristobalite + HfO$_2$ powder composite system. This was succeeded by an investigation on the dynamic formation of hafnon in a silicon + HfO$_2$ powder composite system. Finally, a silicon-HfO$_2$ duplex bond coat was designed for the silicon/Yb$_2$Si$_2$O$_7$ (YbDS) environmental barrier coating (EBC) system and exposed to a high temperature steam environment. Concept 2 was accomplished using two separate methods, where the first encompassed deposition of a monoclinic (m-)HfO$_2$ thermal barrier coating (TBC) layer on top of the silicon/YbDS EBC system, and the second explores the synthesis of a multi-component rare-earth disilicate system in order to tailor the thermal conductivity and coefficient of thermal expansion (CTE) for use as a combined thermal and environmental barrier coating (T-EBC) system.

The primary results gathered in this dissertation were addressed in Chapter 7, and will be concluded in the aforementioned order. Recommendations for future work will be given after the conclusions.

8.1 Concept 1: Transformation of the β-cristobalite SiO$_2$ TGO in a thermo-mechanically compatible material

Investigation of the cristobalite + HfO$_2$ and silicon + HfO$_2$ powder composite systems in sequential order indicated that hafnon forms at a rate that is sufficiently rapid to consume at least half of a SiO$_2$ thermally grown oxide (TGO) that forms. It was concluded that:
• The rate of hafnon formation shows diffusion limited kinetics, consistent with diffusion of Si\(^{4+}\) through the hafnon layer.

• Porosity and grain boundaries have a significant effect on the microstructural evolution of the hafnon formation reaction, as Si\(^{4+}\) appears to diffuse preferentially along free surfaces and grain boundaries.

• Oxidation of silicon obstructed by HfO\(_2\) results in SiO\(_2\) growth in pore spaces in between HfO\(_2\) particles.

• The effective SiO\(_2\) thickness is reduced by at least half as a result of hafnon formation in atmospheric conditions, warranting the development of a silicon + HfO\(_2\) composite bond coat.

The design and testing of a duplex silicon + HfO\(_2\) bond coat system covered with a YbDS EBC layer in a high temperature steam environment found that:

• Reaction of Yb\(_2\)SiO\(_5\) (YbMS) present in the YbDS EBC layer with the m-HfO\(_2\) layer, results in the formation of a cubic fluorite (F\(_{SS}\)) reaction layer and a YbMS-free YbDS EBC layer close to the F\(_{SS}\)-YbDS interface.

• The m-HfO\(_2\) layer densifies as hafnon and F\(_{SS}\) form over the course of 1000 1-hour steam cycles.

• The thickness of the SiO\(_2\) TGO was halved compared to the conventional silicon bond coat TGO thickness, and was significantly reduced compared to previous research\(^{31}\).

• No channel cracking was evident in the cristobalite TGO throughout the samples up to 1000 1-hour steam cycles.

• Even though a significant increase in CTE occurred due to formation of the F\(_{SS}\) phase, the stored elastic strain energy was significantly reduced by the formation of hafnon.
Overall, it has been shown that the formation of hafnon, specifically by application of a duplex silicon + HfO$_2$ bond coat, is deemed very beneficial and can significantly reduce the thickness of the detrimental $\beta$-cristobalite SiO$_2$ TGO during thermal cycling in a high temperature (1316°C) steam environment. This has the potential to significantly increase the longevity of silicon/YbDS EBC systems.

8.2 Concept 2: Thermal management methods for reduction of the bond coat surface temperature

The first method explored in this concept investigated the deposition of a m-HfO$_2$ thermal barrier coating (TBC) layer on a silicon/YbDS EBC system using both atmospheric plasma spray (APS) and electron beam-directed vapor deposition (EB-DVD). It was concluded that:

- Deposition of a m-HfO$_2$ TBC layer with clustered porosity on a silicon/YbDS EBC system using APS, resulted in channel cracking of the TBC layer due to large stored strain energy in the coating system, leading to rapid spallation within several thermal cycles.
- Deposition of a columnar, porous, and crack-free m-HfO$_2$ TBC layer was successful using EB-DVD, and unsuccessful using APS.
- Reaction between the YbDS EBC layer and the m-HfO$_2$ TBC layer resulted in the formation of a cubic fluorite (F$_{SS}$), 16 mol% Yb$_2$O$_3$-stabilized HfO$_2$ layer with a CTE of 12.3x10$^{-6}$ °C$^{-1}$, and a YbMS-free layer in the YbDS EBC.
- Large stored elastic strain energy throughout the coating system resulted in several modes of cracking along the F$_{SS}$ layer, including channel cracking and bifurcation into the YbDS EBC layer, delamination along the YbDS-F$_{SS}$ and F$_{SS}$-TBC interfaces, and shearing off of the TBC from the F$_{SS}$ reaction layer due to differential contraction between both layers.
In order to successfully make use of a HfO\textsubscript{2}-based TBC, reaction between the YbDS and m-HfO\textsubscript{2} should be actively avoided.

The second method explored the synthesis of multi-component rare-earth disilicates in order to find a mixture with a low thermal conductivity and a CTE close to that of other EBC materials. Yb-Gd-based disilicate and Yb-La-based disilicate systems consisting of at least two and up to five components were considered. The binary systems consisted of at least Yb\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} (YbDS), and either Gd\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} (GdDS) or La\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} (LaDS). By examination of the Yb-Gd-based disilicate system it was concluded that:

- Mixing of the larger Gd\textsuperscript{3+} and La\textsuperscript{3+} cations with smaller radii cations (i.e. Lu, Yb, Er, and Y) appeared to establish solubility limits of the larger RE\textsuperscript{3+} cations that decreased as more components were added to both Yb-Gd-based disilicate and Yb-La-based disilicate systems.

- The solubility of GdDS in YbDS decreased from 42 mol\% in the two-component system, to 26 mol\% in the three-, four, and five-component systems.

- The solubility of LaDS in YbDS decreased from 4 mol\% in the two-component system, to 0 mol\% in the three-, four, and five-component systems.

- The thermal conductivity of all systems remained <2 W m\textsuperscript{-1} K\textsuperscript{-1} at room temperature.

- The CTE of the four-component (Yb\textsubscript{0.25}Y\textsubscript{0.25}Lu\textsubscript{0.25}Gd\textsubscript{0.25})\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} mixture was 5.1x10\textsuperscript{-6} \degree C\textsuperscript{-1} and the CTE of the five-component (Yb\textsubscript{0.2}Y\textsubscript{0.2}Lu\textsubscript{0.2}Er\textsubscript{0.2}Gd\textsubscript{0.2})\textsubscript{2}Si\textsubscript{2}O\textsubscript{7} mixture was lower at 3.9x10\textsuperscript{-6} \degree C\textsuperscript{-1}.

- All Yb-La-based systems consistently showed phase separation, forming the low CTE β-phase and the higher CTE G-phase. Differential contraction throughout the samples during cooling resulted in micro-cracking.
More detailed research is necessary to investigate the influence of strain energy and entropic contributions to mixing of these multi-component rare-earth disilicate systems. Additionally, the steam volatility resistance, diffusivity of oxidizing species, and resistance against molten silicate interaction need to be tested in order to determine the feasibility for use of these systems as EBC layer materials.

8.3 Recommendations for future work

The reaction of the m-HfO$_2$ and YbDS layers shown in chapters 4 and 5 were found to result in the formation of a Yb$_2$O$_3$-stabilized HfO$_2$ phase with a CTE two-to-three times higher compared to the silicon/YbDS EBC system. Due to the thermo-chemical incompatibility of the EBC and TBC layers leading to thermo-mechanical failure, a barrier between the YbDS EBC layer and m-HfO$_2$ TBC layer should be explored. This can be done by deposition of a hafnon intermediate layer between the YbDS EBC layer and the HfO$_2$ TBC. Several preliminary attempts were made to deposit a thin hafnon layer using CP-DVD by co-evaporation of HfO$_2$ and SiO$_2$. SiO$_2$ was found to behave quite erratically during deposition, often cracking and shattering during deposition, resulting in very difficult control of the deposition rate of SiO$_2$. Due to the brittle nature of SiO$_2$ and the formation of SiO$_2$ phases that easily crack (e.g. cristobalite), it is advised to attempt the deposition of silicon while flowing O$_2$ during deposition in order to form SiO$_2$. Since silicon does not fracture easily during deposition, it would give much better evaporation control during deposition. The same could be done for HfO$_2$, where a pure hafnium rod could be used to form HfO$_2$ during oxidation. HfO$_2$ source rods do not break as easily compared to SiO$_2$, although it does happen with enough frequency to influence the deposition rate and change the local composition of the coating.

Instead from deposition of a thin hafnon layer between YbDS and a HfO$_2$ TBC, deposition of a complete hafnon EBC layer could be attempted possible as well. Since hafnon and HfO$_2$ are thermo-chemically stable together, the adverse reaction between YbDS and HfO$_2$ could be avoided.
The promising CTE and thermal conductivity of the (Yb$_{0.25}$Y$_{0.25}$Lu$_{0.25}$Gd$_{0.25}$)$_2$Si$_2$O$_7$ and (Yb$_{0.2}$Y$_{0.2}$Er$_{0.2}$Gd$_{0.2}$)$_2$Si$_2$O$_7$ multi-component disilicates should be explored further. First, it could be useful to investigate the influence of lowering the amount of GdDS in the four-component system while maintaining the equimolar ratios of the small radii cation disilicates. This could potentially lower the CTE to 4.5x10$^{-6}$ °C$^{-1}$, while keeping the thermal conductivity closer to 1 W m$^{-1}$ K$^{-1}$. A potential composition could for instance be (Yb$_{0.26}$Y$_{0.26}$Lu$_{0.26}$Gd$_{0.22}$)$_2$Si$_2$O$_7$. If this would be successful, a thermal spray powder could be synthesized and deposited as an EBC layer.

The influence of composition and temperature on the solubility limit of the larger radius cation should be investigated as well. For instance, if the composition of the (Yb$_{0.33}$Y$_{0.33}$Gd$_{0.33}$)$_2$Si$_2$O$_7$ would be altered to include more YbDS than YDS to create (Yb$_{0.44}$Y$_{0.22}$Gd$_{0.33}$)$_2$Si$_2$O$_7$, how would this influence the solubility limit? In addition to this, what happens to the solubility of GdDS in the three-component (Yb$_{0.33}$Y$_{0.33}$Gd$_{0.33}$)$_2$Si$_2$O$_7$ system when it is annealed at 1450°C or 1550°C. This could then also be done for other systems, replacing GdDS with SmDS for instance, in order to see if the solubility limit is dependent on the RE$^{3+}$ cation radius.
# Appendices

## A Material properties of EBC candidate materials

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