Novel Environmental Barrier Coatings for Resistance Against Degradation by Molten

Glassy Deposits in the Presence of Water Vapor

THESIS

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By

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Abstract

Environmental barrier coatings (EBCs) are used to prevent oxidation of underlying ceramic-matrix composite (CMC) structural components in aircraft gasturbine engines. As operating temperatures increase, ingested airborne sand poses a serious threat to the stability of these coatings, because the sand adheres to the hot EBC surfaces and melts, forming calcium-magnesium-aluminosilicate (CMAS) glass. The reaction of EBCs with molten CMAS can lead to EBC delamination. Additionally, the interaction of water vapor with the CMAS-reacted EBCs can result in the formation of undesirable phases. Yb₂Si₂O₇ has been identified as a promising EBC ceramic, based on its desirable properties: phase stability up to 1600°C, low thermal expansion coefficient mismatch with common CMCs, and potential resistance against degradation by CMAS and water vapor. As-sintered Yb₂Si₂O₇ and CMAS-coated Yb₂Si₂O₇ are tested in an air environment and in a water vapor environment, at a temperature of 1300°C in both cases. The behavior of these ceramics is compared to that of reference materials. Results from oxidation and chemical stability studies and analyses are presented.

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Chapter 1: Introduction

In the push for more efficient aerospace jet engines, operating temperatures are being driven higher and higher. As a result, the structural components in the hot section of the engine, typically composed of metal superalloys, are beginning to reach their temperature limits, even with thermal barrier coatings (TBCs) providing additional high temperature capabilities. For this reason, there is a movement toward using silicon-based ceramic matrix composites (CMCs) for these structural components. When a Si-based CMC is exposed to high temperature in an environment where oxygen is present, however, it will develop a protective SiO₂ layer. In a water vapor environment, typically caused by hydrocarbons from combustion, this SiO₂ layer will volatilize and produce Si(OH)₄. As the SiO₂ layer develops and volatilizes repeatedly, the surface of the CMC component will recede, threatening the physical integrity of the part and potentially leading to failure of the component. Environmental barrier coatings (EBCs) are needed to protect the underlying Si-based CMC from the negative effects of air and moisture.

An additional challenge that develops with higher jet engine operating temperatures is the reaction of component materials with ingested silica-rich particles. This can become a more serious problem in regions of the world where airborne sand can be more readily ingested into the engines. Should this sand, or calcium-magnesiumaluminosilicate (CMAS), reach the hot section of the engine where temperatures rise above 1200°C, the CMAS will have reached a temperature above its melting region (~1160°C). Above this temperature, CMAS behaves as a glass, and instead of impinging upon the surfaces of jet engine components and then passing through the engine, it will adhere to surfaces and react with the component materials. More robust TBCs for metal superalloy components are currently being engineered to mitigate the effects of CMAS attack; however, little research has been done in the area of identifying an EBC material that can resist thermochemical reactions with CMAS.

The objective of this study is to identify an EBC material that is resistant to both CMAS glassy deposits and high temperature water vapor corrosion. A comprehensive matrix of experiments, ranging in length from 24 hours to 168 hours, was developed (Table 1). Many conditions found in a natural jet engine environment (i.e., higher pressure, air velocity) could not be simulated in the lab. Due to limitations in the laboratory set-up, the primary goal of this study was to evaluate the thermochemical interactions between $Yb_2Si_2O_7$ and CMAS in an environment of dry air or air with moisture content around the average found in the field. The behavior of the EBC materials in a water vapor environment were compared with their behavior in an air environment to better evaluate the effects of water vapor on both CMAS-coated and – uncoated samples. One indicator of a material's susceptibility to silica volatilization in water vapor is the observation of mass loss over a period of time. To help study the mass loss effects of water vapor on the EBC samples without CMAS, experiments in the water vapor environment included a SiO₂ reference sample as a comparison.

	FRC with CMAS	FRC without CMAS	SiO. roforonco compla
	EDC WILL CMAS	EBC without CIVIAS	SIO ₂ reference sample
24h	Air / Water Vapor	Air / Water Vapor	Water Vapor
72h	Air / Water Vapor	Water Vapor	Water Vapor
120h	Air / Water Vapor	Water Vapor	Water Vapor
168h	Air / Water Vapor	Air / Water Vapor	Water Vapor

Table 1: Environment-specific experiments, performed at 1300°C, for EBC materials and reference materials

In order to meet the primary objective of this study, these basic studies on CMAS molten-deposit attack on EBCs with and without the influence of high temperature water vapor corrosion must be performed. Several rare-earth silicates have been identified as potential EBC ceramics, based on their desirable properties: phase stability, low thermal expansion coefficient (CTE) mismatch with common CMCs such as SiC and Si₃N₄, and promising resistance against degradation by CMAS and water vapor. The following chapter provides a more in-depth look at the primary EBC materials that have been previously or are currently being studied.

Chapter 2: Environmental Barrier Coating Selection

2.1: Background

In the process of identifying a promising EBC material choice, options were weighted against a series of ideal material characteristics: phase stability through 1300°C; low CTE mismatch with SiC and Si_3N_4 , common CMCs proposed for hot section jet engine components; chemical compatibility with SiC and Si_3N_4 ; relatively low silica activity; and low material cost. The material must be dense to help prevent exposure of the underlying substrate to water vapor.

2.2: Barium-Strontium-Alumino-Silicate (BSAS)

EBCs are a multilayered coating system, used to prevent oxidation of underlying ceramic-matrix composite (CMC) structural components in aircraft gas-turbine engines. A conventional layered system includes an initial layer of dense Si on the CMC, providing a close CTE match. This is followed by a layer that consists of a mixture of mullite and $Ba_{(1-x)}Sr_xAl_2Si_2O_8$ (BSAS),to help prevent oxidation. Often, the dense topcoat consists of BSAS to help increase oxidation resistance and slow SiO₂ volatilization. A cross-sectional SEM image of a representative layering structure is presented in Figure 1.



Figure 1: Cross-sectional SEM image of common EBC layering system containing $\ensuremath{\mathsf{BSAS}}^1$

This BSAS layered system works well, to a degree. It is challenged by increasing jet engine operating temperatures and environmental demands. Of particular interest is the reaction between BSAS and CMAS when these operating temperatures provide an environment conducive to creating glassy CMAS deposits on the hot section components. CMAS reacts with the BSAS and penetrates the coating. This reaction product increases SiO₂ volatility of the EBC system. Backscattered electron (BSE) images of this reaction can be seen in Figure 2.



Figure 2: BSE images of reaction between BSAS and CMAS at 1300°C after (a) 1 hour and (b) 4 $\rm hours^2$

Since the robustness of the conventional BSAS layered system is questionable at higher temperatures and in the presence of CMAS, other possible EBC materials were investigated for this study.

2.3: Rare-earth Silicates

Rare earth silicates are a group of materials that have many of the qualities that are necessary for an ideal EBC. In particular, monosilicates and disilicates containing yttrium, ytterbium, or lutetium are of the greatest interest. Many of these materials exhibit phase stability through 1300°C and low CTE mismatch with SiC and Si₃N₄, as shown in Table 2. Additionally, their silica activity is relatively low, they show chemical compatibility with SiC and Si₃N₄, and have a relatively low material cost.

SiC	Si ₃ N ₄	Y ₂ SiO ₅	Yb ₂ SiO ₅	$Y_2Si_2O_7$	Yb ₂ Si ₂ O ₇
4.5-5.5	3-4	5-6	3.5-4.5	3-4	4-5

Table 2: Reported coefficients of thermal expansion (x 10^{-6} °C^{-1}) of potential RE-silicates EBCs and underlying CMCs³

Lu₂Si₂O₇ exhibits a CTE of 3.7 x $10^{-6\circ}$ C⁻¹, which minimizes the risk of delamination or cracking due to CTE mismatch with SiC. Lu₂Si₂O₇ also exhibits an improvement in thermal expansion upon another somewhat common EBC system comprised of BSAS (CTE: 4 to 5 x $10^{-6\circ}$ C⁻¹) with yttria-stabilized zirconia (CTE: 10 to $11 \times 10^{-6\circ}$ C⁻¹) topcoat.

In Figure 3, Felsche has documented rare earth disilicate phase stability with respect to the ionic radius of the rare earth element, over the temperature range of 800°C to 1800°C. The rare earth elements are listed on the horizontal axis at the top of the chart at locations corresponding to their ionic radii. The lines separating the phase regions indicate where a phase change occurs. (Phases shown in Figure 3: A: tetragonal; B and F: trigonal; C and D: monoclinic; E: orthorhombic; G: pseudo-orthorhombic.) Both Lusilicates and Yb-silicates exhibit monoclinic phase stability up to 1600°C. Due to the significantly higher cost of Lu, Yb was investigated more closely.



Figure 3: Rare earth disilicate phase stability as a function of ionic radius⁴

As seen in the Yb₂O₃-SiO₂ phase diagram (Figure 4), Yb₂SiO₅ and Yb₂Si₂O₇ are both line compounds, showing phase stability up to 1950°C (Yb₂SiO₅) and 1850°C (Yb₂Si₂O₇). Rare earth monosilicates (RE₂SiO₅) exhibit greater chemical stability with H₂O than rare earth disilicates (RE₂Si₂O₇). In a water vapor environment, the SiO₂ in the disilicate will volatilize and produce Si(OH)₄, potentially leading to the eventual transformation of the disilicate to a monosilicate. The monosilicate is more chemically stable, so SiO₂ within the EBC is less likely to volatilize.



Figure 4: Yb_2O_3 - SiO_2 phase diagram with monosilicate and disilicate line compounds indicated⁵

2.4: Proposed EBC System

The story changes completely when CMAS is considered. When CMAS interacts with the monosilicate, the silica from the CMAS enriches the monosilicate, eventually transforming it into a disilicate. An unpredictable phase change based on environmental factors would be detrimental to the integrity of the component. However, when CMAS comes into contact with the disilicate, the disilicate is already saturated with silica, and the system remains chemically stable with no phase changes. Therefore, RE₂Si₂O₇ shows greater chemical stability with CMAS than RE₂SiO₅. Also, there is little CTE mismatch

between $Yb_2Si_2O_7$ and the proposed CMCs, as compared to the CTE mismatch between Yb_2SiO_5 and the CMCs. $Yb_2Si_2O_7$ has been identified as a promising EBC material and pursued.

Chapter 3: Experimental Procedure

3.1: Yb₂Si₂O₇ Preparation

The environmental barrier coatings used in this study were made via reaction sintering. A stoichiometric molar ratio of Yb₂O₃(99.99% purity, MTI Corporation, Richmond, CA) and SiO₂ (reagent grade, Supelco Analytical, Bellefonte, PA) (Yb₂O₃:SiO₂ = 1:2) powders wereball milled in ethanol for 48 hours. The resulting slurry was then dried on a hot plate while continuously stirred. Using a hydraulic press, the powder was pressed into 0.5-inch diameter pellets at a pressure of 2500 lbs. Using cold isostatic pressing (CIP), the green body was subjected to a pressure of 205 MPa. The resulting pellet was then sintered in a platinum crucible at 1650°C for 24 hours, resulting in at least 97% theoretical density ($\rho = 6.13$ g/cm³), as measured using Archimedes' principle. X-ray diffraction (XRD) was performed on each pellet to confirmat least 90% estimated phase purity, using an X-ray diffractometer (XDS 2000, Scintag Inc., Cupertino, CA). A representative XRD scan is shown in Figure 5, with primary Yb₂Si₂O₇ peaks indicated by triangles, and a dashed-line circle around the region where the primary Yb₂SiO₅ peaks would appear if the monosilicate were present. Unmarked peaks include minor Yb₂Si₂O₇ peaks, unreacted SiO₂, and XRD background.



Figure 5: Representative XRD pattern of EBC pellet with acceptable phase purity for testing

3.2: CMAS Preparation

In order to maintain a consistent sand composition for experiments, simulated CMAS glass frit, based on a representative sand composition (Table 3), was used. The composition of the simulated CMAS was determined from actual sand deposits found in the field, provided by Naval Air Systems Command, Patuxent River, MD, for a previous study.⁶

Composition	SiO ₂	CaO	MgO	Al ₂ O ₃	Na ₂ O	K ₂ O	Fe _x O _y
mol%	50.0	38.0	5.0	4.0	1.0	1.0	1.0 (Fe ₂ O ₃)
wt%	49.7	35.3	3.3	6.7	1.0	1.6	2.4 (FeO)

Table 3: Composition of the sand used to prepare the simulated CMAS glass

Procedures for preparation of the simulated CMAS glass frit were established by Aygun⁶ and are as follows. Reagent grade powders of the oxides represented in Table 3 (Fisher Scientific, Pittsburgh, PA) were mixed and melted twice: first in a platinum crucible in a box furnace (Thermolyne, Dubuque, IA) in air for 4 hours at 1550°C, and then the resulting glass was crushed and remelted as before in order to ensure homogeneity. The glass resulting from this second melting was crushed and sieved using #500 mesh.⁶ The composition of the CMAS is comparable to those used in other studies.

3.3: Testing Preparation

All Yb₂Si₂O₇ EBC pellets to be tested were polished to a 1 μ m finish using standard metallographic techniques to produce a flat surface with a mirror finish. Specimens being tested for CMAS/EBC interaction were prepared using the following procedure.CMAS-frit paste was uniformly applied to the top surface of an Yb₂Si₂O₇ EBC pellet, such that a uniform CMAS concentration per unit EBC area of 35 mg/cm² was maintained on the top surface of the sample. Specimens being tested without CMAS did not require further preparation. SiO_2 reference samples were prepared by cutting specimens comparable in size to the EBC samples from a SiO_2 slide. The dimensions of each sample were measured using calipers and each sample, including applied CMAS if applicable, was weighed prior to testing.

3.4: Air Environment Testing

For each air environment test, an $Yb_2Si_2O_7$ specimen with CMAS on the top surface and an $Yb_2Si_2O_7$ specimen without CMAS were laid flat in a platinum crucible. They were then heat-treated isothermally at 1300°C for 24, 72, 120, or 168 hours in air using a thermal cycling furnace (CM Furnaces Inc., Bloomfield, NJ).

3.5: Water Vapor Environment Testing

Each water vapor environment test was conducted in a controlled-environment fused quartz tube furnace (SentroTech, Berea, OH), basing the tube material choice on the experimental set-up of Opila, et al.⁷ For each test, three specimens were placed in a fused quartz combustion boat. These specimens included a SiO₂ reference sample, an Yb₂Si₂O₇ sample without CMAS applied, and an Yb₂Si₂O₇ sample with a uniform layer of CMAS on its top surface. These samples were placed in the combustion boat in this order and inserted into the tube furnace so that the air-water flow would reach the Yb₂Si₂O₇ sample last, in order to reduce the possibility of airborne CMAS contaminating the other samples. The samples were tested simultaneously in order to compare each material's response when exposed to the same conditions. These specimens were heattreated isothermally at 1300°C for 24, 72, 120, or 168 hours in 50% air – 50% water vapor (8 L/min volumetric flow) in the aforementioned controlled-environment fused quartz tube furnace. The water vapor exiting the tube furnace was cooled via a radiator system and collected to ensure consistent air-water flow.

3.6: Characterization Methods

Following each test, each sample was measured using calipers and weighed. Using this data, dimensional changes in the pellets could be detected, as well as any mass gain or loss.

XRD patterns of the top surface of EBCs with and without CMAS applied were obtained using an X-ray diffractometer.

As-pressed EBC specimens, heat-treated EBC specimens without CMAS, and CMAS-interacted EBC specimens were mounted in epoxy and ground approximately 5 mm in depth to produce cross-sections. The mounted cross-sections were polished to a 1 µm finish using routine metallographic techniques and observed in a scanning electron microscope (SEM; Sirion, FEI, Hillsboro, OR) equipped with an energy dispersive spectrometer (EDS; EDAX, Mahwah, NJ). EDS was used to create elemental composition maps of representative CMAS-EBC reaction areas.

Transmission electron microscopy (TEM) specimens of CMAS-interacted EBCs were prepared using a focused ion beam (FIB; Helios 600, FEI, Hillsboro, OR). These specimens were observed in a Tecnai TEM (Tecnai F20, FEI, Hillsboro, OR; 200 kV) equipped with an EDS.

Chapter 4: Results

4.1: Air Environment Testing

Figure 6 shows a cross-sectional BSE image of an as-sintered Yb₂Si₂O₇ EBC pellet adjacent to cross-sectional BSE images of Yb₂Si₂O₇ pellets that have been exposed to a 1300°C air environment for 24 and 168 hours, respectively. Over time, little change in microstructure was observed.



Figure 6: Cross-sectional BSE images of $Yb_2Si_2O_7$ pellets: (1-r) as-sintered, after 24h in air environment, after 168h in air environment

In Figures 7 through 10, a BSE image of a sample cross-section from each air environment test is displayed alongside EDS maps of calcium, ytterbium, and silicon. Due to EDS peak overlap of magnesium and aluminum with ytterbium and silicon, the presence of calcium is the strongest qualitative indicator of CMAS penetration into the EBC. Many of the ytterbium maps indicate the presence of Yb in the reaction layer, showing that the EBC is in fact reacting with the CMAS, and the presence of CMAS in the EBC is not limited to grain boundary penetration. In the BSE image in Figure 7, the darker gray region in the upper half of the image is primarily residual CMAS sitting on top of the EBC, and the lighter-colored grains of reaction product can be seen not only in the reaction layer, but scattered in the CMAS layer as well. As time progresses, the EBC and amorphous CMAS continue to react, forming a crystalline reaction layer that helps to prevent bulk CMAS penetration into EBC grain boundaries.



Figure 7: (clockwise from upper left) BSE image, and EDS maps of Ca, Si, and Yb in specimen exposed to air environment at 1300°C for 24 hours



Figure 8: (clockwise from upper left) BSE image, and EDS maps of Ca, Si, and Yb in specimen exposed to air environment at 1300°C for 72 hours



Figure 9: (clockwise from upper left) BSE image, and EDS maps of Ca, Si, and Yb in specimen exposed to air environment at 1300°C for 120 hours



Figure 10: (clockwise from upper left) BSE image, and EDS maps of Ca, Si, and Yb in specimen exposed to air environment at 1300°C for 168 hours

Figure 11 shows a time-based progression of BSE EBC cross-sectional images following air environment testing in the presence of CMAS. These cross-sectional images offer a more comprehensive view of the extent of the EBC-CMAS reaction. The visual clarity of the resulting reaction microstructure is not as great as after testing in water vapor environment, shown in Section 4.2.



Figure 11: BSE images of EBC cross-sections of reaction zones after 24h, 72h, 120h, and 168h at 1300°C in airenvironment

Table 4 shows the calculation of the change in mass (mg) with respect to the original top surface area of the sample (cm²) for each sample in each air environment test. Each measurement shows the change in mass that occurs from t = 0. Yb₂Si₂O₇ samples without CMAS were not tested, as the microstructure of the 24 hour and 168 hour samples were similar and showed negligible variation from the as-sintered microstructure; therefore, it was determined that this sample condition did not warrant further testing in air environment. Values of detected mass change less than 1 x 10⁻⁵ mg/cm² are reported as zero.

	Yb ₂ Si ₂ O ₇ without CMAS	Yb ₂ Si ₂ O ₇ with CMAS
24h	- 0.0556	- 1.615
72h	N/A	- 0.00124
120h	N/A	- 0.00104
168h	0	- 2.928

Table 4: Mass change data ($\Delta mg/cm^2$) for air environment testing

4.2: Water Vapor Environment Testing

Figure 12 shows a cross-sectional BSE image of an as-sintered Yb₂Si₂O₇ EBC pellet adjacent to a cross-sectional BSE image of an Yb₂Si₂O₇ pellet that has been exposed to a 1300°C air environment for 24 hours. Figure 13 shows the cross-sectional BSE image of an as-sintered Yb₂Si₂O₇ EBC pellet next to the cross-sectional BSE image of an Yb₂Si₂O₇ pellet that has been exposed to a 1300°C air environment for 168 hours. In both cases, little change in microstructure was observed over time.



Figure 12: Cross-sectional BSE images of $Yb_2Si_2O_7$ pellets as-sintered (left) and after 24h in water vapor environment (right)



Figure 13: Cross-sectional BSE images of $Yb_2Si_2O_7$ pellets as-sintered (left) and after 168h in water vapor environment (right)

In Figures 14 through 17, a BSE image of a sample cross-section from each water vapor environment test is displayed alongside EDS maps of calcium, ytterbium, and silicon. As above, the presence of calcium is the strongest qualitative indicator of CMAS penetration into the EBC. In the BSE images in Figures 14 through 16, the darker gray region in the upper half of the image is primarily residual CMAS sitting on top of the EBC, where the microstructure of the reaction product can be clearly seen. As time progresses, the EBC and amorphous CMAS continue to react, forming a crystalline reaction layer that helps to prevent bulk CMAS penetration into EBC grain boundaries. Also, the CMAS and water vapor continue to react as time progresses, creating complex reaction products which are discussed further in Chapter 5.



Figure 14: (clockwise from upper left) BSE image, and EDS maps of Ca, Si, and Yb in specimen exposed to water vapor environment at 1300°C for 24 hours



Figure 15: (clockwise from upper left) BSE image, and EDS maps of Ca, Si, and Yb of specimen exposed to water vapor environment at 1300°C for 72 hours



Figure 16: (clockwise from upper left) BSE image, and EDS maps of Ca, Si, and Yb of specimen exposed to water vapor environment at 1300°C for 120 hours



Figure 17: (clockwise from upper left) BSE image, and EDS maps of Ca, Si, and Yb of specimen exposed to water vapor environment at 1300°C for 168 hours

Figure 18 shows a sequential progression of EBC cross-sections following water vapor environment testing in the presence of CMAS. These cross-sectional images offer a more comprehensive view of the extent of the EBC-CMAS reaction, in addition to the character of the resulting reaction microstructure.



Figure 18: BSE images of EBC cross-sections of reaction zones after 24h, 72h, 120h, and 168h at 1300°C inwater vapor environment

Table 5 shows the calculation of the change in mass (mg) with respect to the original top surface area of the sample (cm²) for each sample in each water vapor environment test. Each measurement shows the change in mass that occurs from t = 0. Values of detected mass change less than 1 x 10⁻⁵ mg/cm² are reported as zero.

	SiO ₂	Yb ₂ Si ₂ O ₇ without CMAS	Yb ₂ Si ₂ O ₇ with CMAS
24h	- 0.138	0	- 2.453
72h	- 0.175	0	+ 0.361
120h	- 0.523	0	+0.00156
168h	- 0.427	- 0.681	$+ 1.629 \text{ x } 10^{-4}$

Table 5: Mass change data ($\Delta mg/cm^2$) for water vapor environment testing

TEM results from a related study on the interaction of $Yb_2Si_2O_7$ and CMAS in a water vapor environment at 1250°C can be found in Figures 20 and 21 in the Appendix.

Chapter 5: Discussion

As can be seen in Figures 7 through 11 and 14 through 18, a thermochemical reaction occurs in both air environments and water vapor environments at 1300°C. In this study, evaluation of the reaction zone is limited to the cross-section of the area where each sample was sectioned after testing. In the water vapor environment, it appears that an apatite-like reaction phase forms, as evidenced by the needle-like microstructure visible in Figure 16. TEM results indicate that this reaction phase is composed of Yb-Ca-Si-Fe, a compound of which little is known.

TEM results (Figures 20 and 21) from a 24 hour water vapor environment test at 1250°C show the presence of crystalline CMAS near the surface of the EBC-CMAS sample. There is an Yb-Ca-Si-Fe reaction phase below that, situated amid amorphous CMAS glass. At the base of the evaluated region is the Yb₂Si₂O₇ EBC material. Further studies involving this unusual Yb-Ca-Si-Fe compound is necessary in order to gain a better understanding of the reaction phase and its properties.

Mass loss measurements are not a significantly reliable method of determining the degree to which the EBC material and/or CMAS is reacting with its environment. There are a variety of situations that can contribute to an inaccurate measure of mass loss or

gain. In the air environment, insufficient drying of the glass frit-ethanol mixture prior to the initial weighing of the sample could lead to a falsely high mass loss measurement, as the ethanol that was weighed during the initial measurement would fully dry during the experiment. Within the water vapor testing environment, there is the potential for volatilization of SiO₂ of the fused quartz tube and fused quartz combustion boats, as well as the development of a film on the surface of the specimen which has been in contact with the combustion boat. The stainless steel end caps of the tube furnace also have the potential to corrode when exposed to water vapor over a period of time, leading to the possibility of material foreign to the study depositing on the specimens as the air flow passes over them. There also is the possibility of the creation of reaction products that result in a mass loss or gain, which can be confirmed via TEM analysis. In either environment, there can be variability in the measurement of the specimen dimensions, although any errors by this method would have a negligible effect on the mass loss calculation when compared with changes in the raw mass measurement. Since the duration of these experiments reached a maximum length of 168 hours at 1300°C, any true mass loss of the uncoated EBC material is expected to be less than 0.263 mg/cm^2 as reported by Maier, when evaluated without regard to microstructural development.⁸

One proposed mechanism suggests that the CMAS that has deposited on the EBC can act as a kind of sacrificial layer. This would mean that the SiO_2 in the CMAS selectively volatilizes, rather than the SiO_2 in the $Yb_2Si_2O_7$, thereby retaining as much of the EBC integrity as possible and protecting the underlying CMC substrate much more

effectively. Further studies are necessary to determine the validity of this mechanism theory.

Another theory as to what is happening to the CMAS-coated EBCs in a water vapor environmentis that as the SiO₂ in the CMAS preferentially volatilizes, it shifts the CMAS composition from amorphous Pseudo-wollastonite to crystalline Gehlenite. In the ternary phase diagram of major components of CMAS shown in Figure 19, a dashed red oval shows the region of common CMAS compositions from the field. The phase shift due to depletion of SiO₂ in this CMAS composition is indicated by a red arrow. Pseudo-wollastonite is difficult to crystallize; conversely, Gehlenite crystallizes readily. Amorphous CMAS more easily penetrates the EBC via grain boundary attack. However, with this shift to a crystalline phase, the now-crystalline CMAS does not pose a significant threat to the integrity of the EBC, as it crystallizes on the surface of the EBC and does not penetrate the EBC along the grain boundaries.



Figure 19: Ternary phase diagram for primary components of CMAS, with common CMAS composition region indicated by dashed red oval⁹

Chapter 6: Conclusions

In both air and water vapor environments, it appears that the formation of the reaction product may slow the penetration of CMAS along the grain boundaries of the EBC. In a water vapor environment, it appears that SiO₂ in the CMAS will preferentially volatilize, causing the CMAS composition to shift from an amorphous phase to a crystalline phase. This phase shift helps to protect the Yb₂Si₂O₇EBC from SiO₂ volatilization and grain boundary CMAS penetration. The complexity of the reactions taking place in the Yb₂Si₂O₇-CMAS system and the possible contamination present in the laboratory set-up negate the significance of the mass change measurements as a definitive indication of the efficacy of the EBCs when exposed to air or water vapor environments. Additionally, the mass gain that occurred in some of the samples may be due to the formation of reaction products from the EBC, CMAS, and water vapor. Further analysis is necessary to confirm the validity of these theories.

By following the matrix of experiments outlined earlier, substantial groundwork has been laid in the evaluation of $Yb_2Si_2O_7$ as a potential EBC material in both water vapor and air environments, as well as with and without the presence of CMAS. Further investigation into the behavior of Yb_2SiO_5 as a potential EBC material would be beneficial to determine the soundness of the argument as to whether or not rare earth disilicates perform better than rare earth monosilicates in the two environments tested. Also of worth would be the future development of a layering system for $Yb_2Si_2O_7$ on SiC or Si_3N_4 and the assessment of the mechanical robustness of the system, as well as the mechanical properties of the EBC alone.

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Appendix: Hot-pressed Yb₂Si₂O₇

A.1: Experimental Procedure

The environmental barrier coatings used in this study were made via hot pressing. $Yb_2O_3(99.99\% \text{ purity}, MTI Corporation, Richmond, CA)$ and SiO_2 (99.9% fumed silica, Cabot Corporation, Billerica, MA) powders were mixed in a 1:2 molar ratio and hot-pressed at 55 MPa and 1600°C for 3 hours, resulting in 98% theoretical density.

Simulated CMAS glass frit was prepared as described in Section 3.2 above. CMAS/EBC interaction experiments were performed using the following procedure.CMAS-frit paste was uniformly applied to the top surface of Yb₂Si₂O₇ EBCs, such that a constant CMAS concentration per unit EBC area of 5 mg/cm² was maintained in all of the experiments. These specimens were laid flat in a platinum crucible for air environment testing or in a fused quartz combustion boat for water vapor environment testing, with the CMAS-coated EBC top surface facing up.

For air environment testing, $Yb_2Si_2O_7$ specimens were heat-treated isothermally at 1250°C for 24h or 120h in air using a thermal cycling furnace (CM Furnaces Inc., Bloomfield, NJ). For each water vapor environment test, three specimens (a SiO₂ reference sample, a Yb₂Si₂O₇ sample without CMAS applied, and a Yb₂Si₂O₇ sample with a uniform 5 mg/cm² CMAS layer on its top surface) were tested simultaneously in

order to compare each material's response when exposed to the same conditions. These specimens were heat-treated isothermally at 1250°C for 24h, 48h, 72h, or 120h in 50% air – 50% water vapor (8 L/min volumetric flow) using a controlled-environment fused quartz tube furnace.

Material characterization was performed in a manner similar to that outlined in Section 3.6 above.

A.2: Results

Figure 20 shows TEM results from a 24 hour water vapor environment test on hot-pressed $Yb_2Si_2O_7$ with 5 mg/cm² of CMAS evenly distributed across its top surface. The region from where the TEM foil was extracted is indicated by the rectangle on the SEM image on the right side of the figure.Figure 21 shows the indexed TEM pattern from the crystalline CMAS region in Figure 20. This pattern indicates that the crystalline CMAS phase is Gehlenite. (TEM work courtesy of Andy Gledhill and Julie Drexler.)



Figure 20: TEM results from $Yb_2Si_2O_7$ sample exposed to water vapor environment for 24 hours at $1250^\circ C$



Figure 21: Indexed TEM pattern from crystallized CMAS region indicating Gehlenite

A.3: Discussion

The results from Figures 20 and 21 are discussed in Chapter 5. This study, although promising, was terminated. The process of reaction sintering in the hot press caused the EBC pellets to retain residual stresses. During testing at 1250°C, these stresses relaxed and caused buckling of the pellet to occur. This buckling led to the opening of pathways in the EBC pellet for CMAS to flow, thereby interfering with the surface reaction study being performed.