The Influence of Calcium-Magnesium-Aluminosilicate Deposits on Internal Stresses in $\text{Yb}_2\text{Si}_2\text{O}_7$ Multilayer Environmental Barrier Coatings

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ABSTRACT

The interaction of calcium-magnesium-aluminosilicates (CMAS) with $\text{Yb}_2\text{Si}_2\text{O}_7$ -based multilayer environmental barrier coatings was studied using a combination of high-energy synchrotron X-ray techniques. Changes in the phase-specific stresses and **lattice spacings** as a function of temperature were investigated with wide-angle X-ray scattering. Small-angle X-ray scattering was used to study the interaction of CMAS with nanoporosity, while X-ray computed tomography was used to study the formation of cracks in the coating. It was found that CMAS interacts strongly with the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat, leading to changes in lattice spacing, alterations of the ambient temperature stresses, and large cracks in the CMAS that extend through the topcoat.

I. INTRODUCTION

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Due to their low density, excellent high-temperature mechanical properties, and good thermo-mechanical stability, silicon-based ceramics (i.e., SiC, Si₃N₄) are one of the most promising material systems for high temperature structural applications in gas turbine engines. [1,2] In oxidizing environments a passivating SiO₂ surface layer forms on SiC and Si₃N₄. However, this scale becomes unstable in water-containing combustion environments, resulting in the volatilization of the silica layer and component recession. [3,4] Environmental barrier coatings (EBCs) have been identified as a method of protection from such harsh turbine environments. Desirable properties for EBCs include good thermal and phase stability, low volatility in engine environments, and a coefficient of thermal expansion (CTE) that matches that of the underlying layers. Internal stresses induced by differences in CTEs between layers are the most common cause for cracking or spallation in EBCs. [5-7] Through-thickness cracks allow for water vapor to diffuse to the component, rendering the coating ineffective.

The most studied EBC system to date has been a three-layer coating system consisting of a silicon bond coat, an intermediate diffusion barrier layer of mullite (3Al₂O₃·2SiO₂), and a top layer of BSAS, (1-x)BaO-xSrO-Al₂O₃-2SiO₂, where x varies between 0 and 1. [8] The intermediate mullite layer is needed to prevent the topcoat from reacting with the Si or the substrate and to minimize oxygen diffusion through the coating, while the BSAS is the active environmental barrier layer. [2, 8] These coating systems have proven to be very long-lasting, but on exposure to calcium magnesium aluminosilicate (CMAS) deposits inevitably ingested into turbines, such as dust, sand, volcanic ash, the molten CMAS glass reacts with the BSAS topcoat and causes degradation and cracking. BSAS has also been found to react with the silica layer formed by oxidizing the underlying mullite silicon layer at high temperatures, limiting its use as

a topcoat to operating temperatures below $\sim 1300^{\circ}\text{C}$. [8, 9] Another durability issue is cracking induced by CTE mismatches between the layers of the coating system, particularly the topcoat and the mullite. [10]

Developing new EBC topcoat materials is necessary to allow higher operating temperatures and greater efficiencies. One group of candidate materials is the family of rare-earth silicates. Studies of their thermal stability and applicability for coating applications identified ytterbium monosilicate (Yb_2SiO_5) and ytterbium disilicate ($\text{Yb}_2\text{Si}_2\text{O}_7$) as promising alternatives for operating temperatures up to 1500°C . ~~$\text{Yb}_2\text{Si}_2\text{O}_7$ has~~ Both have thermochemical thermomechanical stability comparable to or better than BSAS at 1500°C in flowing 50% H_2O -balanced O_2 . [9] Subsequent studies of the two Yb-silicate systems with CMAS found minimal reactivity between $\text{Yb}_2\text{Si}_2\text{O}_7$ and CMAS, compared to Yb_2SiO_5 , which motivates the present study. [11]

In a previous study, stresses in multilayer systems of coatings with $\text{Yb}_2\text{Si}_2\text{O}_7/\text{mullite}/\text{Si}/\text{SiC}/\text{SiC}$,[#] elastic moduli and thermal expansion coefficients (CTE) of $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoats were established and internal stresses in multilayer EBCs were studied at room temperature and during *in-situ* heating and cooling experiments using high-energy X-ray diffraction. [12] During that study, in which coatings were plasma-sprayed at 1200°C , it was found that the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat is under a compressive internal stress of approximately 120 MPa in as-sprayed coatings, due to its lower CTE of $4.7 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, than that of the mullite interlayer diffusion barrier ($5.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$) and the SiC/SiC composite substrate ($5.1 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$). [10] It was also shown that the magnitude of the compressive internal stress is reduced to 80 MPa upon

[#] Although $\text{Yb}_2\text{Si}_2\text{O}_7$ has a CTE that closely matches the underlying SiC/SiC substrate, mullite is still under consideration as an interlayer due to its relative cost compared to rare-earth oxides.

cooling the coating from a thermal treatment at approximately 1200°C. This initial reduction in compressive stress was attributed to the relaxation of quenching stresses. Subsequent heat treatments showed no further changes in stresses in the topcoat. No damage such as cracking or spallation could be seen in the $\text{Yb}_2\text{Si}_2\text{O}_7$ coatings after heat-treatments at 1300°C for 96 hours.

While the performance of $\text{Yb}_2\text{Si}_2\text{O}_7$ coatings at high temperatures in air represents an important point of reference for the successful implementation of these materials as topcoats for EBCs, understanding the influence of CMAS on the thermo-mechanical performance of $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoats is critical to evaluating their potential in actual engine environments. In this study high-energy X-ray diffraction was used to measure the influence of CMAS on the ~~stress state~~ **lattice spacing, internal stresses,** and physical integrity of multilayer EBCs with $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoats.

Internal stress states of multi-layer EBC systems with $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoats were measured after controlled exposure to CMAS at elevated temperature. ~~Although the system is expected to be stress-free at temperatures above coating deposition temperature,~~ *In-situ* experiments were performed to observe the changes in **lattice spacing of** the multi-layer EBC on exposure to molten CMAS at 1350°C for up to 6 hours. Recent advances at the Advanced Photon Source (APS) at Argonne National Laboratory allowed, for the first time, for the combination of these wide-angle X-ray (WAXS) strain measurements with small angle X-ray scattering (SAXS) and X-ray computed tomography (XCT) in the same experiments to study damage evolution in the form of pores and cracks in the coating systems on several length scales. Specifically, we probe lattice spacing at the atomic level, porosity at the nanoscale, and cracks at the micro-scale.

II. EXPERIMENTAL PROCEDURES

(a) Materials and Methods

Multilayer EBCs produced via atmospheric plasma spray onto melt-infiltrated SiC/SiC ceramic matrix composites substrate were provided by Rolls-Royce. Details of the plasma spraying are discussed in previous publications. [13,14] The EBC system consists of a 150- μm thick $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat and a 350- μm thick mullite oxidation resistant ~~reaction barrier~~ layer, both sprayed onto a substrate heated to 1200°C. A 100- μm thick silicon layer, sprayed onto an unheated substrate, was used to improve bonding between the active EBC layers and the substrate. The full system, shown in Figure 1, will be referred to as a $\text{Yb}_2\text{Si}_2\text{O}_7/\text{mullite}/\text{Si}/(\text{SiC}/\text{SiC})$ multilayer EBC. The coating was deposited onto a 20 x 10 x 3 mm³ melt-infiltrated SiC/SiC composite coupon.

Samples for transmission X-ray measurements were cut into 6.3 mm wide, 1.8 mm thick sections using a diamond saw. A total of six samples were prepared. One was reserved for an *in-situ* heating experiment, while four were exposed to CMAS at temperature and studied *ex situ*. The sixth sample was left in the as-sprayed condition for reference.

The CMAS used in this study was produced by mixing CaCO_3 (Aldrich, St. Louis, MO), MgO (Alfa Aesar, Ward Hill, MA), Al_2O_3 (Praxair, Danbury, CT), and SiO_2 (Alfa Aesar) in ratios consistent with the 33CaO-9MgO-13AlO_{1.5}-45SiO₂ formula. [15,16] The powders were ball milled using water and Al_2O_3 media for 24 h. The mixture was dried and heated to 1550°C for 4 h in air in a Pt crucible to form a glass, ground with a mortar and pestle, and fired a second time at 1550°C for 4 h to ensure a homogeneous mixture. The glass was then removed from the crucible and ground to a fine powder for exposure experiments.

For studies designated as *ex-situ*, four $\text{Yb}_2\text{Si}_2\text{O}_7$ EBC samples were exposed to 35 mg/cm^2 of CMAS and then heated to 1300°C in a box furnace in air at a rate of 10°C/min and held for 1 minute, 4 hours, 24 hours, and 96 hours, respectively. All X-ray measurements (WAXS, SAXS and XCT) on *ex-situ* samples were performed after the heat treatments under ambient conditions.

For accelerated *in-situ* studies, a $\text{Yb}_2\text{Si}_2\text{O}_7$ EBC was exposed to 35 mg/cm^2 of CMAS and placed inside a resistance furnace (Linkam TS1500 Heating Stage) in an atmosphere of flowing argon at 1350°C . The sample was heated in steps of 200°C to 1200°C and in two steps of 100°C and 50°C , respectively, to 1350°C , well above the melting temperature of CMAS ($\sim 1230^\circ\text{C}$).^[14] The sample was held at 1350°C for 6 hours to observe the influence of the molten CMAS on reaction-induced lattice changes ~~and stresses~~ in the coating.

(b) Data Collection and Analysis

X-ray diffraction (XRD) was performed at beamline 1-ID at the APS. The small Bragg angles and penetration power associated with high X-ray energies (60 keV) allow for the diffraction to be performed in transmission. The beam was produced using a two crystal Laue monochromator and vertically focusing Si refractive lenses. An array of four amorphous silicon area detectors (General Electric model RT41) was placed approximately 1.2 m away from the sample to collect Wide-Angle X-ray Scattering (WAXS) data, and arranged to allow a center hole for the Small-Angle X-ray Scattering (SAXS) signal, which was collected with a ScintX 11000XR SAXS detector placed approximately 4 m from the sample. Diffraction patterns from a ceria (CeO_2) powder calibration standard (NIST) were used to establish the sample-detector distances and other relevant parameters, such as the center point of the Debye rings (beam center) and the tilt of the WAXS detectors. The setup allowed for the simultaneous collection of WAXS and SAXS

data, although the exposure time was optimized for WAXS measurements, to avoid overexposure of the GE detectors.

A beam size of $100 \times 40 \mu\text{m}^2$ (horizontal x vertical dimensions) was used for all WAXS measurements. The samples were placed in the beam with horizontally aligned layers. Samples were translated $40 \mu\text{m}$ vertically with respect to the beam for each measurement from the topcoat surface to a depth of 1.5 mm into the SiC/SiC substrate for the room temperature samples and 0.5 mm into the substrate for the *in-situ* experiment. This allowed for lattice spacings and, when warranted, stresses to be determined continuously as a function of depth throughout the entire coating. Five measurements were taken horizontally at each vertical position to achieve a diffracted volume of at least $40 \mu\text{m}^3$. The total error for each measurement was comprised of statistical peak fitting errors and standard errors from the biaxial fit of lattice parameter versus azimuth.

The methodology used to calculate strains and stresses from the Debye ring patterns was identical to that used in previous experiments. [12, 14, 16-21] Beam sizes were chosen such that a sufficient number of grains were contained within the diffracted volume to yield continuous Debye ring patterns. Each ring in the Debye pattern corresponds to a specific crystallographic lattice spacing while the azimuthal position (η) of the diffracted beam depends on the orientation of the set of diffracting planes according to Bragg's law. If non-hydrostatic stresses are present, the Debye rings distort into ellipses since the lattice spacing changes anisotropically in the material. The relationship between strain in a specific azimuthal direction and deformation of the rings is described by:

$$\varepsilon_{\eta} = \frac{r_0 - r_{\eta}}{r_0} = \frac{d_{\eta} - d_0}{d_0},$$

where r_0 and d_0 are the ring radius and interplanar spacing of the strain-free sample, respectively. [18]

Since strains are assumed to be equibiaxial, the in-plane strains ϵ_{11} and ϵ_{22} are equal and correspond to an azimuthal angle of 0° . Direction 1 and 2 here are horizontal and parallel to the coating surface while direction 3 corresponds to the vertical direction. The out-of plane strain, ϵ_{33} , corresponds to an azimuthal angle of 90° . The equibiaxial in-plane stress can be calculated using the following equation:

$$\sigma_{11} = \left(\frac{E_{hkl}}{1 + \nu_{hkl}} \right) \epsilon_{11}^{hkl} + \frac{\nu_{hkl} E_{hkl}}{(1 - 2\nu_{hkl})(1 + \nu_{hkl})} (2\epsilon_{11}^{hkl} + \epsilon_{33}^{hkl}),$$

where E_{hkl} is the elastic modulus of a specific crystallographic direction and ν_{hkl} is the Poisson's ratio for the hkl crystallographic direction. [22] The elastic moduli and Poisson's ratio for the materials components of the multi-layer coating have been summarized in Table 1.

Analysis of SAXS data from *ex-situ* heat-treated samples was performed with a combination of Irena, a SAXS analysis package, and basic curve fitting. [23] Irena was used to characterize the pore size distribution and total porosity in the as-sprayed sample, assuming spherical porosity. [24] A simple model was then used to compare the SAXS diffraction patterns from different heat treatments and explain the changes in absolute intensities that were observed.

XCT measurements were also performed on *ex-situ* heat-treated samples in order to evaluate the damage evolution in the coating. In an XCT measurement, the beam is opened to produce a cross-section as large as the source will allow ($\sim 1.3\text{mm} \times 2.5\text{mm}$ at Beamline 1-ID). The sample is then rotated through 180° in steps of 0.2° while a radiograph is taken at each angular position. The 900 radiographs were then reconstructed into a 3-D image. For this experiment, the detector

was moved away from the sample in order to exploit the enhanced image contrast due to phase contrast effects. Optimizing phase contrast effects was found to make small cracks easier to see due to its magnification nature. The resolution for XCT for this experiment was found to be approximately 2.5 μm while the phase contrast effects made possible to see even submicron size features.

III. RESULTS

(a) *Ex-Situ* CMAS Exposure

The results from the ex-situ experiments, summarized in Figure 2, show the influence of exposure times at 1300°C on the room-temperature internal stresses in the three layers of the multilayer EBC as well as the average stress of the first millimeter of the SiC/SiC composite. Figure 2 shows that an unheated sample has an average compressive stress of -50 MPa at room temperature in the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat. After 4 hours at 1300°C, the average internal stress in the topcoat increased to -75 MPa, and after 96 hours the average compressive stress in the topcoat is -135 MPa. The internal tensile stresses in the mullite increase from only 10 MPa for an as-sprayed sample to 45 MPa after the 96-hour CMAS exposure. The silicon bond coat was in compression at room temperature, with the magnitude of the compressive stresses increasing slightly with longer exposure to CMAS. The average SiC/SiC composite internal stress state, shows the composite substrate to be unaffected by the changes in internal stresses in the top layers. Any changes in average SiC/SiC stress were well within the margin of error, partly due to the errors introduced by averaging stresses that were known to be sinusoidally varying with depth and partly due to the fact that stresses in the SiC are spread out over a much larger thickness, making changes in SiC stresses much smaller in magnitude. [13]

(b) *In-situ* CMAS exposure

Figure 3 shows the average stress in the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat as a function of temperature during the *in-situ* experiment. This set of samples The topcoat had an average internal compressive stress of approximately 50 MPa in the top-layer at ambient temperature. At temperatures below the melting point of CMAS ($\sim 1230^\circ\text{C}$), the magnitude of the compressive stress decreased as the topcoat neared its deposition temperature of 1200°C , as expected previously observed [23]. Once the CMAS melting temperature was reached, a small compressive stress developed, although this change was not significant at the 95% confidence level. The reasons for the relatively large errors seen in this particular experiment are two-fold. Firstly, the sample was measured as sprayed, and was thus not completely crystalline. Secondly, while understanding the stresses upon heating was certainly of interest, the behavior at temperatures above the melting point of CMAS was deemed more important to approach desired use temperatures. Accordingly, measurements during heating were completed with fewer points (three points horizontally instead of five for all other WAXS measurements), resulting in larger error bars.

It should be noted here that the volume change that occurs upon solidification of the partially amorphous, plasma-sprayed topcoat is negligible and does not significantly contribute to the change in stress seen in these samples. Archimedes' method was used to measure the density of ten samples of plasma-sprayed $\text{Yb}_2\text{Si}_2\text{O}_7$ before and after a 96-hour heat-treatment at 1300°C , and no measurable change in density was observed. [23]

Once the sample reached 1350°C , the increased crystallinity in the topcoat allowed for more detailed X-ray analysis of the topcoat. Diffraction patterns were collected in the topcoat as a

function of depth from the surface in 40 μm steps, and are here reported as changes in lattice spacing, d_0 , due to likely changes in chemistry. Figure 4 shows the changes in d_0 in the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat at 1350°C as a function of time and depth in the coating.

The influence of the interaction of $\text{Yb}_2\text{Si}_2\text{O}_7$ with the molten CMAS is apparent when looking at Figure 4. For the purposes of this graph the $\text{Yb}_2\text{Si}_2\text{O}_7$ layer, which is approximately 200 μm thick was split into three layers of equal thickness. The top layer refers to the third of the coating that is in immediate contact with the molten CMAS. The bottom layer is the third of the $\text{Yb}_2\text{Si}_2\text{O}_7$ coating that is in contact with the mullite, while the middle layer refers to the center of the coating.

After a 20-minute exposure to molten CMAS at 1350°C, the lattice parameter of the ($\bar{1}50$) reflection of $\text{Yb}_2\text{Si}_2\text{O}_7$ in the top layer was significantly lower than the lattice parameter in the center or the bottom of the coating. The difference was approximately 0.0065Å, well above the detection limit of $\sim 0.001\text{\AA}$. As the temperature was held at 1350°C for 6 hours, the lattice parameter decreased measurably in the middle and bottom of the coating (by $\sim 0.0037\text{\AA}$ and $0.0047\text{\AA}$, respectively), while decreasing only slightly in the top layer ($\sim 0.0028\text{\AA}$).

(c) Small-Angle X-Ray Scattering

SAXS was used to study the interaction between CMAS and $\text{Yb}_2\text{Si}_2\text{O}_7$ near the CMAS/ $\text{Yb}_2\text{Si}_2\text{O}_7$ interface. SAXS data were collected simultaneously with WAXS data with an area detector. The data from the 2-D detector were then integrated over 360° to maximize signal and allow for quantitative analysis.

SAXS plots of scattered intensity vs. the scattering vector $q (= 4\pi \sin\theta/\lambda)$ from four different *ex-situ* experiments (unheated, 4 hours, 24 hours and 96 hours at 1300°C), taken from the top 20 μm of the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat are summarized in Figure 5(a). The scattered intensity is highest for the as-sprayed sample. As the molten CMAS begins to interact with the topcoat, the scattered intensity decreases significantly. The total porosity within the probed porosity size range was found to be 8%, with an average pore size of 36 nm and a median diameter of 30 nm.

The absolute intensity data was then used to perform quantitative analysis of SAXS data. A simple model was developed to explain the decrease in scattered intensity as a function of exposure time to liquid CMAS by partial filling of nanopores by liquid CMAS. This model relies on a few simplifying assumptions outlined below:

- (1) The porosity in the coating is spherical.
- (2) Before being exposed to CMAS, the porosity in the coating was filled with air.
- (3) Upon exposure to CMAS, some of the porosity gets filled with CMAS. Pores are either filled with CMAS or air, never both.
- (4) The average density of the pores upon infiltration with CMAS can be treated as one composite value. If half the pores are infiltrated with air and half with CMAS:

$$\rho_{pores_average} = \frac{\rho_{air} + \rho_{CMAS}}{2}$$

- (5) Upon heating the sample to 1300°C, the diameter of the pore, as well as the total porosity and the distribution of pore sizes remain unchanged.

Regions for SAXS analysis were chosen such that the top 20 μm of the $\text{Yb}_2\text{Si}_2\text{O}_7$ coating were probed for all four conditions of interest (unheated, 4 hours, 24 hours, and 96 hours at 1300°C). As can be seen in Figure 5(a), the intensity of the SAXS patterns changed noticeably (a 40% decrease in intensity from the as-sprayed sample to the sample heated for 96 hours at 1300°C) when samples were exposed to molten CMAS. However, the shape of the scattered intensities as a function of diffraction angle remains practically unchanged. The changes that are taking place induce a downward shift in scattered intensity, not a shift in scattering vector. This observation is especially important for the assumption that the distribution of pore diameters does not change with CMAS exposures. A uniform downward shift in scattered intensity, I , validates this assumption. If the pore size distribution remains unchanged, the infiltration of the pores by CMAS can be estimated using the equation governing the scattering intensity in the Guinier and Porod region:

$$I_q \cong n(\Delta\rho)^2 V^2 \exp \left[-4\pi^2 \left(\frac{2\theta}{\lambda} \right)^2 R_{gs}^2 \right]$$

$$I_q = \frac{(\Delta\rho)^2}{8\pi^3} \frac{\sum_a w_a \pi a_a^2}{q^4} = \frac{(\Delta\rho)^2}{8\pi^3} \frac{S_T}{q^4}$$

where $\Delta\rho$ is the difference in electron density between the phases, V is the volume per scatterer, R_{gs} is the Guinier radius of the particle, $\sum_a$ is the integral over all scatterers, w_a is the frequency of a particular scattering area, a_a , q is the scattering vector, λ is the wavelength, and S_T is the total

surface area in the irradiated sample. These equations show the scattered intensity scales as the square of the difference in electron density between the two phases.

When air, which has a density ≈ 0 , is replaced by CMAS, which has a density of 2.7g/cm^3 , the difference in electron density decreases (the density of $\text{Yb}_2\text{Si}_2\text{O}_7$ is 6.15g/cm^3), leading to a decrease in scattered intensity. The difference in density (expressed as g cm^{-3}) between the $\text{Yb}_2\text{Si}_2\text{O}_7$ and the porosity can be calculated as:

$$\Delta\rho = 6.15 - 3.45x$$

where x is the fraction of porosity that has been infiltrated by CMAS. Given that a decrease in the difference in electron density causes a proportional downward shift in scattered intensity, x can be used as a fitting parameter. Figure 5(b)6 shows the fits that can be achieved by varying x to optimize the difference in electron density.

Table 2 summarizes the values for the fraction of filled porosity and $\Delta\rho$ that were used for the scattered intensities shown in Figure 5(b)6. It shows that the percentage of pores filled increases as a function of heating time at 1300°C , as was expected. This interpretation of the SAXS suggests that 67 % of the porosity in the range from 10 to 200 nm in the top 20 μm gets filled by CMAS glass during a 96-hour heat treatment at 1300°C .

(d) X-ray Computed Tomography

Reconstructed three-dimensional XCT datasets consist of 900 slices with $1\text{ }\mu\text{m}^3$ voxel size, have a physical resolution of about 2.5 μm . Selected cross sections of the samples are presented in

Figures 6 and 7, and illustrate the contrast and resolution of these measurements. Figure 6(a) shows an XCT reconstruction of a cross-section of a sample that had been exposed to CMAS at 1300°C for 1 minute. The most obvious feature of this image is the large through-crack that has originated at the CMAS surface and extended all the way from the CMAS/Yb₂Si₂O₇ interface through the topcoat. The crack extends across the entire sample in the plane parallel to the surface, and is between 10–20 µm wide. The resolution is also sufficient to resolve smaller cracks in the mullite. These cracks are less than 3 µm in width and at least 200 µm long. The contrast between the three phases most pertinent for this analysis, the CMAS glass, the Yb₂Si₂O₇ topcoat and the mullite interlayer diffusion barrier, is adequate for interfaces to be clearly visible.

The XCT image in Figure 6(b) further illustrates the size and extent of the cracking in the same sample by showing a plane parallel to the EBC surface cutting through the CMAS glass. The light-colored phase on the right-hand side is Yb₂Si₂O₇. The large horizontal crack from right to left through the image is the same one that could be seen in the cross-sectional image in Figure 7(a). Additional cracks can be seen branching from this large crack, leading to an extensive network of cracks. Figure 6(c), an image parallel to the EBC surface cutting through the Yb₂Si₂O₇ topcoat, proves that these cracks were not only present in the CMAS (Figure 7(b)), but extended through the active EBC material. Beside the porosity the faint lines of smaller, thin cracks in the Yb₂Si₂O₇ topcoat can also be seen in this image, while the large crack can be easily observed.

When heating a sample for 96 hours rather than just one minute at 1300°C, the behavior of the progression of the CMAS/Yb₂Si₂O₇ reaction at the interface was found to be much more

pronounced. Figure 7(a) shows an XCT cross-section of one of these samples. The CMAS layer, which had been very thick after the 1-minute heat treatment, is diminished because of the reaction with the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat material. There is evidence of some large crystallites, such as the one on the left-hand side of the image that extends from the $\text{Yb}_2\text{Si}_2\text{O}_7$ –CMAS interface to the surface. Also apparent in this image is a large crack that originated at the CMAS surface and extended through the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat to the $\text{Yb}_2\text{Si}_2\text{O}_7$ /mullite interface. Extensive cracking in the mullite bondcoat also is observed. More evidence of the formation of large crystallites can be seen in Figure 8(b), where a plane parallel to the EBC surface cutting through the CMAS is shown. Large crystallites, noted by different contrast, have formed close to the CMAS/ $\text{Yb}_2\text{Si}_2\text{O}_7$ interface. These diopside ($\text{CaMgSi}_2\text{O}_6$) crystals, confirmed via EDS analysis, were crystallization products of CMAS and have previously been observed in high-temperature CMAS interactions. [25, 26] Some of these crystallites were as large as 300 μm in length. A large crack in the bottom-left corner of the image can also be seen. This crack is much more obvious when looking at a slice through the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat, as seen in Figure 7(b). In addition to the large crack, there are smaller cracks branching off. Another important detail observed in the XCT images is the density at the top of the $\text{Yb}_2\text{Si}_2\text{O}_7$ layer. In the sample that has been exposed to CMAS for 96 hours, the top of the $\text{Yb}_2\text{Si}_2\text{O}_7$ appears to be denser than the rest of the $\text{Yb}_2\text{Si}_2\text{O}_7$ layer. While the thickness of this denser layer varies depending on the position in the sample, it has been estimated to be approximately 30 μm thick.

IV. DISCUSSION

(a) X-Ray Diffraction Measurements

The increase in compressive stresses with increased exposure to molten CMAS found after the ex-situ heat treatments was very similar in magnitude to those observed in past synchrotron

stress studies performed on multilayer EBCs with BSAS topcoats exposed to CMAS. [16] The increase in observed internal stresses, in both cases, can be attributed to the higher CTE of CMAS with respect to the topcoat. Confounding this picture, however, are results from the *in-situ* exposure of the multilayer EBC to molten CMAS at 1350°C. The presence of CMAS at 1350°C significantly decreased the lattice parameter of $\text{Yb}_2\text{Si}_2\text{O}_7$, by a small (0.06%), but significant amount, providing strong evidence of a reaction between the $\text{Yb}_2\text{Si}_2\text{O}_7$ and the CMAS even after short exposure times. (Figure 4)

It is well documented that CMAS has the ability to degrade a wide variety of environmental and thermal barrier coatings via the removal of large cations, such as Y^{3+} , Zr^{4+} and Gd^{3+} . [27-29] It follows that the probable source of the change in lattice parameter in the present study was the removal of Yb ions from the $\text{Yb}_2\text{Si}_2\text{O}_7$, with their replacement by Ca ions, which differ in size by only ~ 5%, plus creation of a lattice defect. Rare-earth-alkali ion exchanges have been noted in other mineralogical systems.[30, 31] Since the change in lattice parameter is not more than 0.06%, it is hypothesized that no more than a few atomic percent calcium can be accepted by the ytterbium disilicate structure in solid solution, as has been observed in other line compounds.[32, 33] In this experiment we were able to show that this degradation lattice parameter change can be tracked via *in-situ* synchrotron X-ray diffraction.

Upon initial exposure the CMAS removes Yb exchange reaction occurs primarily from the very top of the coating. As the sample is held at 1350°C the CMAS continues removing Yb ions exchange continues from the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat, leading to further decreases in the d-spacing. As the glass penetrates further into the topcoat, and the system responds by trying to equilibrate the

via the migration of Yb ions, a decrease in d-spacing advances throughout the entire coating. The reaction between CMAS and $\text{Yb}_2\text{Si}_2\text{O}_7$ plays an important role that can only be understood when combining *ex-situ* and *in-situ* experiments.

As a check that the *in-situ* observations in the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat are chemically derived, rather than measurement artifacts, stresses-d-spacings in mullite and silicon layers were also evaluated, and plotted in Figure 8. A small increase in internal tensile stresses in the mullite layer was observed. The d-spacing of the mullite (240) peak shows no statistically significant change in d-spacing at any position in the mullite, either adjacent to the $\text{Yb}_2\text{Si}_2\text{O}_7$ or to the silicon. The silicon (311) peak also shows no measurable change at all over the duration on the *in-situ* experiment. However, near zero and invariant stresses in silicon were detected. This was expected, given that 1350°C is very close to the melting temperature of silicon. The silicon could respond to external stresses by creep, making a non-zero internal stresses in this layer at high temperature unlikely.

(b) Damage Evolution

X-ray computed tomography experiments showed the influence of CMAS on the structural integrity of the coatings. Large cracks, originating at the CMAS surface and penetrating both the CMAS surface and the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat, formed during cooling upon CMAS solidification. These cracks originated at the CMAS surface, meaning that After the CMAS has cooled below its glass transition temperature and the Si-layer has ceased to creep, thermal mismatches between the CMAS ($\text{CTE} \approx 6 \times 10^{-6} \text{ }^\circ\text{C}^{-1} - 8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) [29, 30], the $\text{Yb}_2\text{Si}_2\text{O}_7$ ($\text{CTE} \approx 4.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), and the remaining multilayers and coating substrate induce sufficiently large tensile stresses in the

glass to lead to the formation of cracks. There is also visual evidence of partial crystallization of the CMAS. The volume fraction of crystallized material, however, is too small to pick up with WAXS. When combining the evidence from these two data sets it becomes clear how great a challenge the presence of CMAS can be to the efficacy of an $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat.

The issues introduced by the presence of the glass were found to be two-fold. The first challenge is the difference in thermal expansion between the CMAS and the EBC multilayer. Upon solidification of the CMAS, the higher CTE of the CMAS causes a build-up of large tensile stresses in the glass. ~~This difference in CTE has been shown lead to large increases in compressive stresses in the topcoat and, upon cooling.~~ These stresses result in large cracks that originate from the glass surface and extend through the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat. While this is a serious issue for designing EBC topcoats, the tests presented in this work likely portray an exaggeration of the issues caused by differential thermal expansion. While large amounts of CMAS have been found in actual turbines, the deposition in an actual turbine environment would be much more gradual. Any CMAS that deposits on a turbine would likely react with the EBC material before a concentration as large as 35 mg/cm^2 accumulates.

Secondly, SAXS analysis highlighted how strongly CMAS interacted with the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat. The nanoscale porosity at the very top of the coating, found to be approximately 8 vol%, was quickly infiltrated with liquid CMAS, leading to a decrease in scattered intensity. The overall porosity was found to be comparable across different pore size ranges (between 10-100 nm and between 10-100 μm), as thresholded XCT images revealed approximately 8% micron-sized porosity across the entire topcoat. After the 96-hour heat-treatment, thresholding of XCT

images of the top 40 μm of the coating revealed a decrease in microporosity to between 1-2 vol%. This decrease in microporosity is comparable in magnitude to the decrease observed via SAXS for the nanoporosity in the same layer. This suggests that the CMAS infiltrates both porosity size scales during this thermal treatment.

IV. SUMMARY AND IMPLICATIONS

Synchrotron X-ray studies on the interaction between $\text{Yb}_2\text{Si}_2\text{O}_7$ /mullite/Si/(SiC/SiC) multilayer EBCs and CMAS were performed. WAXS measurements showed that molten CMAS lead to decreases in lattice parameters in the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat of these systems, likely via the removal exchange of Yb ions from the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat with Ca ions in the CMAS.

Compressive stresses in the topcoat were found to form upon cooling to room temperature after CMAS exposure. The XCT reconstructions showed that thermal mismatch stresses developed upon solidification of CMAS led to through-cracks in the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat. These through-cracks originated at the surface of the glass upon solidification.

SAXS also suggested that CMAS infiltrated the porosity towards the surface of the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat. Approximately 67% of all pores between 10-200 nm were shown to have been infiltrated by CMAS after a 96-hour heat treatment at 1300°C.

The strong reaction and infiltration between CMAS and the porous $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat represents a significant problem when considering using $\text{Yb}_2\text{Si}_2\text{O}_7$ as a potential topcoat material for next-generation EBC systems. The combination of the relatively low volatility of $\text{Yb}_2\text{Si}_2\text{O}_7$, its

excellent mechanical properties and its strong interaction with CMAS suggest that the best role for $\text{Yb}_2\text{Si}_2\text{O}_7$ may be to serve as an EBC that is protected by an oxide thermal barrier coating.

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LIST OF FIGURE CAPTIONS

Figure 1. SEM image of a $\text{Yb}_2\text{Si}_2\text{O}_7/\text{mullite}/\text{Si}/\text{SiC}$ multilayer EBC

Figure 2. Average *ex-situ* equibiaxial stress in the layers of the multilayer EBCs as a function of heat treatment at 1300°C. The samples had been loaded with 35 mg/cm² of CMAS prior to heating. The horizontal lines with the corresponding color represent the stresses in an as-sprayed sample.

Figure 3. Average equibiaxial internal stress in an $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat as a function of temperature during heating. The sample had been exposed to 35mg/cm² of CMAS prior to heating.

Figure 4. Lattice spacing of the $(\bar{1}50)(211)$ reflection in a $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat as a function of position and time at 1350°C. The sample was exposed to 35 mg/cm² of CMAS prior to heating.

Figure 5. (a) Scattered X-ray intensity vs. scattering vector, q , of the top 20 μm of the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat as a function of exposure time to CMAS at 1300°C, and (b) after fitting based on the percentage of porosity filled by CMAS.

~~**Figure 6.** Scattered X-ray intensity vs. scattering vector, q , of the top 20 μm of the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat as a function of exposure time to CMAS at 1300°C after fitting based on the percentage of porosity filled by CMAS.~~

Figure 6. XCT reconstructed images of a $\text{Yb}_2\text{Si}_2\text{O}_7/\text{mullite}/\text{Si}/(\text{SiC}/\text{SiC})$ multilayer EBC after a 1-minute heat treatment at 1300°C. a) Cross-section of the multi-layer EBC sample. Cracks in the mullite diffusion-barrier interlayer are highlighted by white arrows. b) Reconstructed image parallel to the EBC surface through the CMAS glass. Inset is a cross-section highlighting the approximate y-position of the cut. c) Reconstructed image parallel to the EBC surface through the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat. Inset is a cross-section highlighting the approximate y-position of the cut.

Figure 7. XCT reconstructed images of a $\text{Yb}_2\text{Si}_2\text{O}_7/\text{mullite}/\text{Si}/(\text{SiC}/\text{SiC})$ multilayer EBC after a 96-hour heat treatment at 1300°C . a) Cross-section of the multi-layer EBC sample. Cracks in the mullite diffusion barrier layer are highlighted by white arrows. b) Reconstructed image parallel to the EBC surface through the CMAS glass. Inset is a cross-section highlighting the approximate y-position of the cut. c) Reconstructed image parallel to the EBC surface through the $\text{Yb}_2\text{Si}_2\text{O}_7$ topcoat. Inset is a cross-section highlighting the approximate y-position of the cut.

Figure 8. Average *in-situ* equibiaxial stress Lattice spacings of the (240) reflection in the mullite diffusion barrier interlayer as a function of position and the (311) reflection of the silicon bondcoat, all as a function of time held at 1350°C . The sample had been loaded with $35\text{mg}/\text{cm}^2$ of CMAS prior to heating.

Figure 1

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Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Graphical abstract