# Effects of Environment and Coating Composition on CMAS – EBC Interactions

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## Abstract

Silicon carbide-based hot-section jet engine components enable increased fuel efficiency compared to state-of-theart metal-based components but require environmental barrier coatings (EBCs) to inhibit degradation from the harsh engine environment. High temperature steam (a product of fuel combustion) and molten glass (the result of dirt and ash ingested into the engine hot section) can react with, damage, and reduce EBC lifetimes. The molten glass is primarily composed of Calcium-Magnesium-Aluminosilicates (CMAS). Studying CMAS-EBC interactions is crucial for enhancing CMAS mitigation strategies and EBC lifetime models. The work presented in this dissertation explores CMAS-steam synergy on Yb-silicate degradation, investigates EBC compositional effects on molten CMAS wetting behavior, and elucidates the effect of a fifth oxide (denoted by 'X') on CMXAS glass properties.

The effects of steam on CMAS degradation mechanisms are not well-known. CMAS-EBC degradation was performed at 1300°C in an environment-controlled tube furnace for 4-, 24-, and 96-hour durations in steam (90% H<sub>2</sub>O/10% O<sub>2</sub>) compared to dry-O<sub>2</sub> (100% O<sub>2</sub>) and lab air environments. Three dense, model EBC materials were investigated: a phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, a nominal 20vol% Yb<sub>2</sub>SiO<sub>5</sub> in Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, and a nominal 25vol% Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> in Yb<sub>2</sub>SiO<sub>5</sub>. The three substrates were loaded with ~40mg of Ca33-Mg9-Al13-Si45 (single cation oxide mol%) pre-reacted CMAS. Experiments were repeated in triplicate to evaluate the effect of steam on CMAS-EBC interactions. Steam showed an increase in molten CMAS spreading compared to the dry-O<sub>2</sub> environment on both substrates. The 20Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates. In general, CMAS transport across the polished model EBC surface preferentially occurred along grain and/or phase boundaries. Steam also increased CMAS reactivity with phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> but did not affect CMAS reactivity with 20Yb2SiO5/Yb2Si2O7.

This work also assessed the effect of rare-earth disilicate (REDS) composition and processing method on CMAS wetting using a heating microscope to quantify contact angle and spreading dimensions. Substrates included freestanding atmospheric plasma spray (APS) REDS coatings (for RE = Y, La, Nd, Gd, Yb, Lu), dense phase-pure spark

plasma sintered (SPS) Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, and a dense SPS two-phase mixture of 20 vol% Yb<sub>2</sub>SiO<sub>5</sub> in Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>. CMAS (Nominally Ca33-Mg9-Al13-Si45 in single cation mol%) was loaded as a 10 mg cylindrical rod atop the specimen surface, and heated in stagnant lab air to temperatures of 1250°C. The heating microscope was used to monitor the evolution of molten CMAS contact angle, width, and height as a function of time. Post-exposure CMAS contact angle, width, and height did not show systematic trends with composition. CMAS spreading and reactivity were also examined using plan view SEM/EDS and XRD. CMAS spreading decreased with RE cation size, correlating inversely with RE-apatite phase stability. APS YbMS increased CMAS spreading compared to dense APS YbDS. Processing effects showed polished SPS Yb-silicates and unpolished APS YbDS both increased CMAS spreading relative to dense polished APS YbDS. CMAS transport was observed to spread along grain boundaries and channels provided by surface roughness or porosity. Highly connected porosity promoted CMAS infiltration over surface spreading. The reactive wetting mechanism on REDS coating materials is hypothesized to be reaction-limited with substrate wettability increasing as rare-earth apatite formation driving force decreases.

Finally, this work investigated common natural-forming (X = Na<sub>2</sub>O, FeO<sub>2</sub>, FeO<sub>2</sub>, TiO<sub>2</sub>) and coating-derived (X = Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, Lu<sub>2</sub>O<sub>3</sub>) oxide additions to CMXAS glasses - where X denotes a fifth oxide constituent and their effect on CMAS viscosity, coefficient of thermal expansion, softening temperature, and dilatometric glass transition temperature (CTE, T<sub>d</sub>, T<sub>g</sub>). CMAS viscosity, CTE, T<sub>d</sub>, and T<sub>g</sub> can indicate relative threat of CMAS attack or premature coating failure. Glass property relationships were elucidated by cation size effects and allow inferences to glass structure to be made. Iron oxide valence, group IV metal, and rare-earth metal cations – including one dual cation addition (Y<sup>3+</sup> and Yb<sup>3+</sup>) – were explored. The baseline CMAS, nominally Ca33–Mg9–Al13– Si45 (single cation mol%), was synthesized from constituent oxide powders. Natural-forming oxide additions consistently operated as network modifiers. Coating-derived oxide additions behaved as network modifiers in the molten liquid state but acted as network formers in the condensed amorphous state. Fe<sup>3+</sup> additions were shown to have the greatest effect of all additions on glass properties, exhibiting the greatest propensity for CMAS attack. Trends observed between dilatometric CMXAS glass properties allow for CMXAS properties to be inferred should one property (CTE, T<sub>a</sub>, T<sub>g</sub>) be known. FactSage viscosity calculations were most consistent with experimental data compared to equivalent Thermo-Calc calculations. Molten CMAS and CMXAS viscosity measurements were shown to correlate with net cation field strength, offering a promising alternative in property prediction for EBC lifetime methodology where thermodynamic data are not available. Coating performance should consider the effect of coating constituents on CMAS viscosity and CTE, dissolution, and precipitation behaviors.

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## 1. Introduction

Silicon carbide (SiC)-based ceramic matrix composites (CMCs) are the leading material to replace current nickel-base superalloy components in the hot sections of gas turbine engines. The high-temperature capabilities of SiC-based CMCs include thermomechanical stability, noteworthy improvements in creep resistance, and lower density than their nickel superalloy counterparts, improving engine thrust-to-weight ratio and fuel economy.<sup>1–4</sup> SiC is highly resistant to oxidation in ambient conditions due to the formation of a protective silica (SiO<sub>2</sub>) scale.<sup>5–7</sup> However, the engine combustion environment contains water vapor, which will react with silica at elevated temperatures to form gaseous silicon hydroxide (Si(OH)<sub>4</sub>),<sup>8</sup> as shown below in Equation 1.1:

$$SiO_2 + 2 H_2O(g) \rightarrow Si(OH)_4(g) \tag{1.1}$$

Environmental barrier coatings (EBCs) are used to prevent SiC-based CMCs from volatilizing. Rare-earth silicates are used as EBCs due to their good chemical compatibility with underlying SiC CMC substrate and Si bond coat.<sup>9</sup> EBC requirements include: 1) high-temperature environmental stability, 2) capability to act as an oxidant (O<sub>2</sub>, H<sub>2</sub>O) transport barrier, and 3) minimal coefficient of thermal expansion (CTE) mismatch with the underlying SiC CMC substrate and Si bond coat. Coatings with large CTE mismatches with the underlying substrate have limited lifetimes due to stress induced delamination. Ideal candidate materials also maintain high-temperature stability, and lack high-temperature polymorphs, at and below the goal operating temperature of 1500°C.<sup>9</sup> Figure 1.1a shows the seven polymorphs of rare-earth disilicates (RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>; REDS) as a function of RE ionic radius.<sup>10</sup> Figure 1.1b shows the average CTE of each REDS polymorph, with the yellow band highlighting the average CTE of SiC CMCs.<sup>11, 12</sup> Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (YbDS) is currently used as the state-of-the-art EBC material for its high temperature stability and good CTE match with SiC.



Figure 1.1: (a) High-temperature phase stability diagram of RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> polymorphs as a function of RE ionic radius where ionic radii are a function of coordination number (CN), adapted by Ridley et al.<sup>13</sup> from Turcer<sup>12</sup> and Felsche.<sup>10</sup> Reproduced with permission from John Wiley & Sons. (b) Average CTE of RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> polymorphs, adapted by Turcer<sup>12</sup> from Fernández-Carrión et al.<sup>11</sup> and reproduced with permission from John Wiley & Sons. Horizontal yellow band in (b) indicates the average CTE of SiC CMCs.

Atmospheric plasma spray (APS) is used to deposit YbDS coatings because it is cost-effective, fast, and can produce dense coatings on complex surface geometries. However, APS YbDS coatings are deposited as a heterogeneous, non-equilibrium mixture of YbDS and ytterbium monosilicate phases (Yb<sub>2</sub>SiO<sub>5</sub>; YbMS) due to silica volatilization during deposition.<sup>14</sup> An example of APS YbDS microstructure is shown in Figure 1.2. Both YbDS and YbMS have monoclinic crystal structures, but only YbMS has a highly anisotropic CTE (~6-8 x 10<sup>-6</sup> °C<sup>-1</sup>).<sup>15-17</sup> As a result, YbMS presence can lead to stress-induced cracking during thermal cycling. EBCs must also account for thermochemical degradation processes in addition to high-temperature, highvelocity steam volatility. These include, but are not limited to, calcium-magnesium-aluminosilicate (CMAS) infiltration, sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) corrosion, and bond coat oxidation via oxidant (O<sub>2</sub>, H<sub>2</sub>O) transport through the topcoat.



Figure 1.2: Cross-section back-scattered electron micrograph of APS deposited Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> coating (with Yb<sub>2</sub>SiO<sub>5</sub> secondary phase) atop a Si/SiC substrate, from Richards et al.<sup>14</sup> Reprinted with permission from Elsevier.

Of the numerous thermochemical degradation processes that limit coating lifetimes, this dissertation focuses on EBC interactions with synthetic CMAS and will also investigate steam synergy on CMAS-EBC interactions. CMAS originates from siliceous debris (i.e. sand, ash, dirt) ingestion into the engine hot-section during take-off, in-flight, and upon landing. Siliceous debris enters the engine hot section, melts to form a calcium-magnesium-aluminosilicate (CMAS) glass and adheres to engine components, resulting in coating infiltration and premature failure of the EBC.<sup>18–21</sup> Molten CMAS interactions with EBCs are detrimental for several reasons, including large CTE mismatches between YbDS and the CMAS glasses, dissolution of coating material leading to coating recession, as well as the ability for CMAS to react and form new crystalline phases, altering coating microstructures.<sup>19</sup> The magnitude and array of CMAS-EBC interactions will depend on CMAS and coating compositions. CMAS-EBC interactions will be addressed in context of Yb-silicate coating materials.

While YbDS has good thermophysical properties and chemical compatibility with SiC components, it has poor chemical resistance to steam volatility and CMAS infiltration.<sup>22–24</sup> In contrast, YbMS, the secondary phase, is desirable for its resistance to steam volatility and CMAS infiltration but the high anisotropic CTE

and large CTE mismatch make it poorly suited for applications with SiC CMCs.<sup>16, 22–25</sup> Mass spectrometry measurements done by Costa and Jacobson<sup>26</sup> demonstrated the Yb<sub>2</sub>O<sub>3</sub>-YbMS two phase region has a SiO<sub>2</sub> activity is three orders of magnitude smaller and Yb<sub>2</sub>O<sub>3</sub> activity three orders of magnitude larger than the YbMS-YbDS two phase region, illustrating why YbMS is less likely to react with steam and more likely to react with CMAS compared to YbDS.

CMAS reactivity with EBC materials is dependent on coating composition. A prominent CMAS-EBC reaction product is rare-earth oxyapatite ( $RE_{9.33}\Box_{0.33}(SiO_4)_6O_2$ ). Costa et al.<sup>27</sup> showed that CaO can increase stability of the RE-apatite structure ( $Ca_2RE_8(SiO_4)_6O_2$ ), which will increase the driving force for Yb-silcate EBC reaction in the presence of CMAS. Differences in Yb<sub>2</sub>O<sub>3</sub> activity in the Yb<sub>2</sub>O<sub>3</sub>-YbMS and YbMS-YbDS two phase regions can also explain differences in YbMS and YbDS reactivity with CMAS.<sup>23, 26</sup> Webster<sup>28</sup> also attributed CMAS reactivity to the propensity of RE-silicates to produce crystaline products that consume the melt or progress toward an equilibrium state of liquid. These are captured in Equations 1.2 and 1.3.

$$4 Yb_2Si_2O_7 + 2 CaO \rightarrow Ca_2Yb_8(SiO_4)_6O_2 + 2 SiO_2$$
(1.2)

$$4 Yb_2SiO_5 + 2 CaO + 2 SiO_2 \rightarrow Ca_2Yb_8(SiO_4)_6O_2$$
(1.3)

Equation 1.2 indicates YbDS reaction will only consume part of the melt, gradually replacing an equivalent amount of CaO with SiO<sub>2</sub> while forming apatite and progressing the CMAS melt toward an equilibrium state. Whereas Equation 1.3 indicates apatite formation from YbMS is consuming both CaO and SiO<sub>2</sub> from the melt, which should lead to an overall reduction in melt volume. However, depletion of CaO and SiO<sub>2</sub> from the CMAS glass will result in relative enrichment of MgO and Al<sub>2</sub>O<sub>3</sub> within the remaining glass. While CaO-SiO<sub>2</sub> ratio has been shown to affect apatite formation,<sup>22, 29</sup> the presence of MgO, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> are shown to produce additional reaction products, including: cyclosilicates, garnets, and disilicates.<sup>29, 30</sup> CaO-SiO<sub>2</sub> ratio (or C:S) is not only important for CMAS reactivity with EBC materials but is also shown to influence CMAS glass properties (namely molten viscosity).<sup>19, 31–33</sup> This is due to the difference in roles Ca<sup>2+</sup> and Si<sup>4+</sup> cations have in the glass network. Si<sup>4+</sup> is a network forming cation. Si<sup>4+</sup> will form bridging oxygen (BO), strengthening the glass network. Whereas Ca<sup>2+</sup> is a network modifying cation. Ca<sup>2+</sup> will form non-bridging oxygens (NBO), weakening the network.<sup>34, 35</sup> CMAS network connectivity can be inferred by C:S and is reflected by trends in CMAS glass properties. CMAS viscosity is often considered the primary glass property of importance for its relative indication of coating infiltration threat.<sup>28, 36–40</sup> However, other glass properties of interest due to the nature of the aero-engine thermal cycling include the linear coefficient of thermal expansion (CTE), softening temperature (or deformation temperature; T<sub>d</sub>), and glass transition temperature (T<sub>g</sub>). CMAS infiltration via intergranular transport, while also subjected to thermal cycling, will induce deleterious stresses at sites of CMAS attack. The threat of premature coating failure via through-coating crack formation will increase as CMAS CTE mismatch with the coating increases.<sup>41</sup> Whereas higher T<sub>d</sub> and T<sub>g</sub> are associated with earlier onset of stress accumulation on cooling, <sup>42</sup> lower T<sub>d</sub> and T<sub>g</sub> are associated with earlier onset of stress accumulation on heating.<sup>20</sup>

The goals of this dissertation are to understand: i) the synergistic effects steam has on molten CMAS spreading and infiltration of the EBC substrate; ii) the effect of EBC substrate composition and morphology on CMAS wetting behavior; and iii) how CMXAS (CMAS with a fifth oxide, denoted as X) composition impacts glass properties in the molten liquid and condensed amorphous phases. This dissertation specifically explores:

- a. CMAS exposures on model EBC materials at 1300°C in flowing steam, flowing dry-O<sub>2</sub>, and stagnant lab air environments
  - a. Model EBC materials were densified via spark plasma sintering and include phase-pure  $Yb_2Si_2O_7$  and 20 vol%  $Yb_2SiO_5$  in  $Yb_2Si_2O_7$

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- CMAS wetting studies to investigate effect of coating composition and processing method on CMAS wetting of EBC materials
- c. Fifth oxide effect on CMXAS glass properties (molten viscosity, CTE,  $T_d$ , and  $T_g$ ) in addition to comparing methods of property prediction
  - a. Property predictions tools include computational databases (Giordano, FactSage, Thermo-Calc) and numerical methods (net cation field strength)

## 2. CMAS – Steam Synergy Effect on Yb-silicate Degradation

# 2.1. Background

Nickel-base superalloys are being replaced with SiC-based ceramic matrix composites (CMCs) for use in gas turbine engine hot section structural materials.<sup>1, 43</sup> SiC CMCs can improve engine thrust-to-weight ratio and fuel economy due to improved high temperature thermomechanical stability, creep resistance, and lower densities compared to their nickel-base superalloy counterparts.<sup>2–4</sup> SiC is known to produce a protective silica (SiO<sub>2</sub>) scale in dry oxygen or lab air conditions,<sup>5–7</sup> but will react with water vapor at elevated temperatures to form gaseous silicon hydroxide (Si(OH)<sub>4</sub>),<sup>8</sup> as shown in Equation 2.1:

$$SiO_2 + 2 H_2O(g) \rightarrow Si(OH)_4(g) \tag{2.1}$$

As a result, environmental barrier coatings (EBC) are used to protect SiC-based CMCs from volatilizing. Current generation EBC systems utilize a silicon bond coat to prevent oxidation of the underlying SiC CMC<sup>14, 15, 44–46</sup> with an ytterbium disilicate (Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>; YbDS) topcoat. YbDS is used for its good chemical compatibility and good coefficient of thermal expansion (CTE) match with the underlying substrates (Si bond-coat and SiC CMC; ~3.5-4.5 x 10<sup>-6</sup> °C<sup>-1</sup> and ~4.5-5.5 x 10<sup>-6</sup> °C<sup>-1</sup>, respectively)<sup>47</sup> as well as high temperature structural stability.<sup>9–11</sup> EBCs are subject to numerous thermochemical degradation processes that impact coating lifetime. These include but are not limited to high temperature steam volatility and molten calcium-magnesium-aluminosilicate (CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>; CMAS) deposit degradation. Molten CMAS deposits are formed when siliceous debris is ingested by the engine during take-off, in flight, and while landing. These molten CMAS deposits adhere to engine hot-section components, reacting with and infiltrating the EBC. The CTE mismatch between solidified CMAS and the Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> EBC will yield large inplane tensile stresses which will promote through-coating cracking during thermal cycling and result in premature coating failure via delamination.<sup>18–21, 41, 48, 49</sup> Molten CMAS interactions with EBCs can also result in dissolution of coating material, leading to coating recession. Additionally, the ability for CMAS to react to form new crystalline phases and alter coating microstructures induce stresses during thermal cycling and impact coating lifetimes.<sup>19</sup>

Atmospheric plasma spray (APS) is used to cost-effectively and rapidly deposit Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, which results in a heterogeneous mixture of Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and ytterbium monosilicate (Yb<sub>2</sub>SiO<sub>5</sub>; YbMS) phases due to silica volatilization during the non-equilibrium spraying process.<sup>14</sup> Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> has good thermophysical properties and chemical compatibility with SiC components but has poor resistance to CMAS infiltration.<sup>22, 23</sup> In contrast, Yb<sub>2</sub>SiO<sub>5</sub>, the minor phase, is desirable for its resistance to CMAS infiltration but the highly anisotropic CTE (~6-8 x 10<sup>-6</sup> °C<sup>-1</sup>)<sup>15</sup> matches poorly with the Si bond-coat and SiC CMC.<sup>23</sup> Mass spectrometry measurements done by Costa and Jacobson demonstrated the Yb<sub>2</sub>O<sub>3</sub>—Yb<sub>2</sub>SiO<sub>5</sub> two phase region SiO<sub>2</sub> activity is three orders of magnitude smaller and Yb<sub>2</sub>O<sub>3</sub> activity is three orders of magnitude larger than that of the Yb<sub>2</sub>SiO<sub>5</sub>—Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> two phase region,<sup>26</sup> indicating Yb<sub>2</sub>SiO<sub>5</sub> is less likely to react with steam and more likely to form a stabilized rare-earth oxyapatite (Ca<sub>2</sub>Yb<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>).<sup>23, 27</sup> Isothermal testing of mixed Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> materials show desirable resistance to CMAS infiltration through the formation of a dense Yb-apatite layer at the CMAS interface.<sup>22</sup> As molten CMAS infiltrates the Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> matrix with relative ease, it preferentially reacts with Yb<sub>2</sub>SiO<sub>5</sub> inclusions to form a dense, inert layer of rare-earth apatite, arresting CMAS infiltration, highlighting the importance of studying mixed phase EBC materials.

The area of coating affected by CMAS attack is dependent on the ability for CMAS to spread atop the coating. CMAS spreading is governed by the molten CMAS wettability of a substrate. CMAS wetting is influenced by adhesive intermolecular interactions at the solid-liquid interface and the influence of the vapor environment on cohesive intermolecular interactions within the molten glass. Changing the

composition of the substrate, liquid, or vapor will change the adhesive and/or cohesive forces at play. Stronger adhesive forces and/or weaker cohesive forces promote more wetting and spreading. The Young equation, shown in Equation 2.2, provides the effect of interfacial energies ( $\gamma$ ) on wetting angle ( $\theta$ ).

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{2.2}$$

The subscripts on the interfacial energies correspond to the solid-vapor, solid-liquid, and liquid-vapor interfaces. Therefore, changing the vapor environment will affect the molten CMAS-vapor and EBC-vapor interfaces, affecting CMAS wetting and spreading as a result. CMAS spreading across a flat surface is a function of capillary and viscous forces in addition to time and temperature.<sup>50</sup> Where the temperature-dependence of viscosity was identified as the most important parameter influencing wetting and spreading of molten silicate debris.<sup>51</sup>

The combustion process in gas turbines forms several chemical species including, but not limited to, ~10%  $H_2O$  (g) and a varying amount of unreacted  $O_2$  (g). While unreacted  $O_2$  (g) decreases as equivalence ratio (ratio of fuel to air) increases,  $H_2O$  (g) remains relatively independent of equivalence ratio.<sup>8, 52, 53</sup> Most existing CMAS infiltration studies on  $Yb_2Si_2O_7$  are performed in lab air and those occurring in steam lack consistency to be directly comparable.<sup>54–56</sup> Harder et al. found APS  $Yb_2Si_2O_7$  coated SiC CMC with a Si bond-coat pre-loaded with CMAS (2 mg/cm<sup>2</sup>) decreased TGO growth in a steam environment but also found significant changes in coating structure despite minimal changes to coating composition.<sup>49</sup>  $H_2O$  can embed into glass structure,<sup>57, 58</sup> lower glass viscosities at low concentrations (<2 wt%),<sup>59–61</sup> and lower glass surface tension to increase its wettability.<sup>62–64</sup>

This study explores the effects of vapor environment on CMAS degradation of Yb-silicate model EBC materials. CMAS-steam synergy implications on coating interactions, expected effects of gaseous combustion products on CMAS-EBC interactions, and CMAS transport via reactive wetting are discussed.

## 2.2. Experimental

Spark plasma sintering (SPS; Thermal Technology LLC, Model SPS 25-10; Santa Rosa, CA) was used to densify several model Yb-silicate materials from starting powders (99% purity, Praxair Surface Technologies; Indianapolis, IN). Yb-silicate materials investigated in this study included: a phase-pure YbDS, 20YbMS/YbDS mixture, and a 25YbDS/YbMS mixture. 20YbMS/YbDS and 25YbDS/YbMS powders were shaken by hand for ~2 minutes to yield a course mixture of Yb-silicate powders prior to densification. The powders were added to a graphite die (Graphite Products Corp.; Madison Heights, MI) with an inner diameter of 20 mm with a layer of graphite foil (Thermal Technology LLC) lining the die interior. The YbDS and 20YbMS/YbDS powders were held under pressure at 600°C while the chamber evacuated to remove any organic binding agents that volatilized. The 25YbDS/YbMS powders did not undergo this evacuation step and were notably more porous than the other densified model EBC materials which were densified in a smaller SPS die. All powders were densified at 1550°C with an applied pressure of 65 MPa for 25 minutes. The densified pucks were annealed in a stagnant air box furnace (CM Furnaces, Model 1706; Bloomfield, NJ) at 1500°C for 24 hours (heating rate of 7.5°C/min and cooling rate of 5°C/min) to restore oxygen stoichiometry of the specimens.

X-ray diffraction (XRD; Bruker AXS LLC, D2 Phaser; Fitchburg, WI), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS; NanoScience Instruments Inc.; Phenom XL G2 SEM; Phoenix, AZ) were used in conjunction with ImageJ software<sup>65</sup> to characterize starting material phase fractions of the substrates (YbDS, YbMS, porosity). Starting material specifications are contained in Table 2.1. XRD of the unreacted substrates (Figure A1) and phase quantification via SEM (Figures A2) are contained in Appendix A. Densities were measured using the Archimedes method (Mettler Toledo, Model XSE205DU; Suwanee,

GA). Samples were cut from the SPS puck into square coupons of ~1.44 cm<sup>2</sup> or ~1 cm<sup>2</sup> and ~1 mm thick and then polished to a 4000 grit (5  $\mu$ m grit size) surface finish.

Mat	erial	Yb₂Si₂O⁊ Content (vol%)	Yb₂SiO₅ Content (vol%)	Porosity Content (vol%)	Density (g/cm³)	Relative Density (%)*	Coupon Size [cm²]
Phase-	Nominal	100	0	0	6.15		~1 44
pure YbDS	Measured	94-98	0	2-6	5.80-6.05	94-98	1.44
20 YbMS/	Nominal	80	20	0	6.38		~1.00
YbDS	Measured	78.4-80.5	19.5-21.6	<1	6.05-6.24	95-99	1.00
25 YbDS/	Nominal	25	75	0	7.00		~1.00
YbMS	Measured	24-37.3	62-73.5	1.5-3.5	5.47-5.60	78-80	1.00

Table 2.1: Model EBC substrate starting material specifications

\* = using 7.279 g-cm<sup>-3</sup> as YbMS density from ICDD PDF #00-040-0386.

A nominal CMAS composition of 33 Ca – 9 Mg – 13 Al – 45 Si (single cation mol%) was used to mirror the debris composition of engine deposits. <sup>36, 66</sup> The CMAS constituent powders underwent mixing via dry ball milling with zirconia milling media ( $\geq$ 95% purity, Glen Mills; Clifton, NJ) for ~24 hours prior to molten glass synthesis at 1500°C for 4 hours in a Pt5Au crucible ensure homogeneity. The use of pre-reacted CMAS avoids constituent oxides melting incongruently and forming a heterogeneous solution (which affects CMAS reactivity and molten properties) before formation of a homogenous molten glass. The homogeneous molten CMAS glass was quenched in water, dried, and powdered via mortar and pestle. Approximately 40 mg of CMAS glass powder was pressed into a 0.25″ diameter green body and sintered at ~1200°C for 4 hours. Composition of the glass was measured by EDS and determined to be 33.7 Ca – 9 Mg – 13.7 Al – 43.6 Si (in single cation mol%), yielding a 0.75 CaO-SiO<sub>2</sub> ratio. EDS results on the CMAS used are reported by Webster and Opila.<sup>31</sup>

Phase-pure YbDS samples were cut to ~1.44 cm<sup>2</sup> x ~1 mm coupons to preserve unreacted edges at the selected times. 20YbMS/YbDS and 25YbDS/YbMS samples were cut to ~1 cm<sup>2</sup> x ~1 mm coupons to compare to previous studies performed by Webster and Opila in lab air.<sup>22</sup> The loading values of ~28 or 40 mg CMAS/cm<sup>2</sup>, respectively, are greater than those observed in service but allow for evaluation of thermochemical interactions. For reference, in-service safe levels of ingested debris are established at 0.2 mg-m<sup>-3</sup> and aircraft are allowed to operate in conditions up to 2 mg-m<sup>-3</sup>.<sup>67–69</sup>

The Yb-silicate coupon and CMAS pellet were loaded into an environment-controlled horizontal tube furnace (CM Furnaces, Model 1730-12 HTF; Bloomfield, NJ) with a 1.375" inner diameter, 1.65" outer diameter alumina tube (99.8% pure, McDanel Advanced Ceramic Technologies; Beaver Falls, PA). Coupon loading and unloading was done at 1300°C to isolate environmental effects on CMAS-EBC thermochemical interactions and avoid reactions occurring during an extended heating and/or cooling process. Exposures for 4-, 24-, and 96-hour durations were conducted. Figure 2.1 shows the furnace setup utilized for steam testing, where the schematic was adapted from previous work by Opila.<sup>70</sup> The system operated at a flow rate of 1000 sccm with a gas velocity of ~1.6 cm/s for both steam (90 vol-% H<sub>2</sub>O/10 vol-% O<sub>2</sub>) and dry-O<sub>2</sub> (100 vol-% O<sub>2</sub>) environments. Comparable studies were conducted in stagnant lab air.



Figure 2.1: Schematic of custom horizontal tube furnace setup for CMAS exposure in controlled environment, adapted from Opila.<sup>70</sup> and reproduced with permission from John Wiley & Sons.

A 90 vol-%  $H_2O/10$  vol-%  $O_2$  was used to approximate exposure to water vapor partial pressures of ~0.9 atm for a ~10 atm gas turbine engine.<sup>8, 52, 53</sup> A peristaltic pump (Ismatec, SA Reglo Analog MS 2/12; Glattburg, Switzerland) fed deionized 18.2 M $\Omega$  liquid water into a 1 mm inner diameter, 3 mm outer diameter fused quartz capillary (Quartz Scientific; Fairport Harbor, OH) which saturated a fused quartz wool plug (Quartz Scientific) that was held at ~400°C to allow water vaporization to occur. The high temperature steam was then carried by flowing oxygen across the sample, condensed in the outlet tubing after exiting the system, and collected in a 1 L graduated cylinder. The fused quartz capillary inlet and the peristaltic pump were only used in steam exposures.

Plan view XRD was conducted on post-exposure specimens to identify the crystalline phases of the reaction products. Post-exposure specimens were imaged using SEM first in plan view and then in cross-section. A thin layer of gold/palladium was deposited (Technics, Hummer Sputter Coater; Hayward, CA) on the post-exposure samples prior to microscopy to provide a conductive surface. Back-scattered electron (BSE) mode was used to identify phase contrast. Macroscale stitched micrographs used an image

stitching feature integrated with the Phenom XL G2 software package. CMAS spreading and infiltration were quantified post-exposure in plan view and in cross-section, respectively. CMAS spreading was quantified by removing the background and thresholding the remaining area. Apatite ring size was approximated from the size of an oval or ellipse traced over the perimeter of the apatite ring or edge of CMAS residual CMAS pool where apatite formation has begun in the absence of a dense apatite ring. This process is shown in Figure 2.2. Specimens were cut in cross-section to quantify CMAS infiltration. Infiltration was measured across the CMAS – EBC interface and taken as the deepest point at which glass was discerned using BSE SEM and EDS. The CMAS-EBC interface was determined by connecting a line between the two unreacted edges. Infiltration measurements were made every 500 µm across this line. High magnification SEM/EDS were acquired using the Quanta 650/Aztec X-MaxN 150. Appendix A organizes the raw data and derived statistics on CMAS spreading and infiltration into Tables A1-A3.



Figure 2.2: (a) Macroscopic stitched plan view BSE micrograph of Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> coupon after 4-hour CMAS exposure at 1300°C in flowing steam. (b) Example of background removal for CMAS spreading quantification, red circle denotes apatite ring area approximation.

## 2.3. Results

Phase-pure YbDS and 20YbMS/YbDS substrates were exposed to CMAS in flowing dry O<sub>2</sub> and flowing steam environments for each time length (4-, 24-, and 96-hour durations). CMAS exposures were performed on at least three separate samples under each condition (environment and time) for both substrates. Phase pure YbDS was also exposed to CMAS in stagnant lab air at least three times for each time length, while 20YbMS/YbDS was not repeatedly exposed to CMAS in stagnant air for all time lengths. CMAS exposure on 25YbDS/YbMS was only performed in stagnant lab air (not ever in steam), nor repeated in triplicate, and is not informative of CMAS-steam synergy effects. Therefore, results on CMAS spreading mechanism and are organized in Appendix A. Qualitative and quantitative results on CMAS spreading as well as preliminary results on CMAS infiltration of phase-pure YbDS and 20YbMS/YbDS are covered in the following sections. Feature quantification showed a parabolic dependence with time and is thus plotted as a function of the square root of time [h<sup>0.5</sup>].

## 2.3.1. CMAS Spreading

Plan view CMAS-EBC interactions in dry-O<sub>2</sub> and steam environments were repeated in triplicate for the phase-pure YbDS and 20YbMS/YbDS model EBC materials for all time lengths. Plan view CMAS-EBC interactions in stagnant lab air were only repeated on phase-pure YbDS for all time lengths. Features of interest included the residual CMAS glass pool, the formation of an apatite ring, and the presence of a swollen CMAS infiltrate region beyond the apatite ring. These features are identified in Figure 2.3 for the

phase-pure YbDS substrate and were quantified to evaluate the effect of environment on CMAS surface transport.



Figure 2.3: Plan view BSE micrographs of phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> after CMAS exposure at 1300°C. Exposures were conducted in (a,b) stagnant lab air, (d,e) flowing dry O<sub>2</sub>, and (g,h) flowing steam for (a,d,g) 4- and (b,e,h) 24- hours. 4-hour exposures yielded a residual glass wetting perimeter. Higher magnification plan view micrographs of 24-hour exposures in (c) stagnant lab air, (f) flowing dry O<sub>2</sub>, and (i) flowing steam show the boundary between the apatite ring and swollen CMAS infiltrate region.
CMAS spreading was defined by the residual CMAS glass pool area or swollen CMAS infiltrate regions. All plan view micrographs are organized in Appendix A and contained in Figures A3 and A4. CMAS spreading was qualitatively evaluated by observing the wetting perimeter of CMAS spreading perimeters, ratio of residual CMAS compared to surface apatite formation, as well as the density of apatite within and surrounding the apatite ring feature. The steam environment was shown to increase irregularity in the CMAS wetting perimeter on phase-pure YbDS substrates after 4-hours (Figures 2.3 and A3), which increased CMAS spreading compared to dry O<sub>2</sub> and lab air environments (Figure 2.4a). However, the steam environment increased CMAS wetting perimeter regularity on 20YbMS/YbDS substrates (Figure A8) and limited residual CMAS spreading (Figure 2.4b).

The flowing steam environment increased CMAS spreading on phase pure YbDS but decreased CMAS spreading rate relative to the other environments explored (Figure 2.4a). Spreading area measurements after 96-hours on both substrates were largely constrained by coupon size. CMAS spreading on 20YbMS/YbDS did not show dependence on environment. This is largely due to the inconsistency of CMAS interactions on 24-hour exposures in flowing O<sub>2</sub> (Figure A7) and lack of statistics for exposures in stagnant lab air environments (Figure 2.4b). The addition of 20YbMS decreased CMAS spreading in flowing steam environments but increased spreading rate compared to phase-pure YbDS.



Figure 2.4: CMAS spreading area measurements normalized per mg of CMAS loaded after exposures varying in length and environment on (a) phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and (b) mixed 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates at 1300°C. Lines are included only as a visual tool.

Apatite ring areas increased in flowing steam and dry O<sub>2</sub> environments, with apatite ring areas growing faster in steam environments on both substrates (Figure 2.5). Coupon size often constrained apatite ring area approximations in 96-hour exposures for both substrates. The steam environment generally increased surface apatite density within the apatite ring and promoted apatite formation beyond the apatite ring feature on phase-pure YbDS. Whereas an excess of residual CMAS covered 20YbMS/YbDS coupon surfaces with a comparably limited amount of surface apatite formation. Similar to CMAS spreading measurements, 20YbMS/YbDS did not see a systematic effect of environment or time on apatite ring size.



Figure 2.5: Apatite ring area approximations normalized per mg of CMAS loaded after exposures varying in length and environment on (a) phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and (b) mixed 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates at 1300°C. Lines are included only as a visual tool.

CMAS transport across the EBC substrate surface was observed to preferentially follow grain and, when applicable, phase boundaries (Figures 2.6 and 2.7). The presence of YbMS inclusions increases surface apatite formation at the CMAS wetting perimeter due to the increased YbMS reactivity with Ca-rich CMAS relative to YbDS. CMAS transport via the mechanism of reactive wetting will be addressed in the discussion.



Figure 2.6: High-mag plan view BSE micrographs of CMAS spreading perimeter on phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates in stagnant lab air. Micrographs captured after CMAS exposure for (a) 4-hours (10,000x), (b) 24-hours (1,000x), and (c,d) 96-hours (5,000x and 1,000x, respectively) at 1300°C. Large grain in (c) shown to impede residual CMAS spreading. All other micrographs show CMAS preferentially spreads via Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> grain boundaries.



Figure 2.7: High-mag plan view BSE micrographs of CMAS spreading perimeter on mixed material (ac,e,f) 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and (d) 25 Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>/Yb<sub>2</sub>SiO<sub>5</sub> substrates. Micrographs captured after CMAS exposure for (a-c) 4-hours in stagnant lab air (500x, 2,000x, and 3,000x, respectively), (d) 24-hours in stagnant lab air (3,000x), and (e-f) 24-hours in flowing dry O<sub>2</sub> (500x and 2,000x, respectively). CMAS spreading via Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> grain boundaries is shown in (b) with larger grains shown to impede residual CMAS spreading in (f). Preferential CMAS interactions with Yb<sub>2</sub>SiO<sub>5</sub> inclusions are shown in (c,d,f). Contrast of phases from light to dark contrast is as follows: YbMS, YbDS, CMAS.

#### 2.3.2. CMAS Infiltration

This section provides infiltration results that contribute to understanding the effect of high temperature steam on CMAS-EBC interactions and CMAS transport mechanisms. While specimens were exposed in steam and dry-O<sub>2</sub> environments and repeated in triplicate for both EBC materials, infiltration was not quantified for all specimen exposures. CMAS infiltration features were qualitatively consistent across environments but differed between substrates. Phase-pure YbDS yielded apatite formation in the uppermost region of the cross-section, bubble-pore formation at the CMAS-EBC interface, and formation of blister cracks in the underlying substrate. Yb-silicate mixed materials yielded lenticularly shaped residual CMAS glass pools, some recession of the 20YbMS/YbDS substrate, and a Yb-apatite reaction product layer at the CMAS-EBC interface. These features are identified in Figures 2.8 and 2.9 for phase-pure YbDS and 20YbMS/YbDS, respectively. Cross-section micrographs contributing to single trials of CMAS infiltration measurements are contained in Figures 2.10 and 2.11. CMAS infiltration on 25YbDS/YbMS in stagnant lab air at 1300°C was measured (contained in Appendix A) but does not contribute to the interpretation of CMAS-steam results. CMAS infiltration of 25YbDS/YbMS is addressed in the discussion in context of CMAS transport mechanisms.



Figure 2.8: Cross-section BSE micrographs of phase-pure  $Yb_2Si_2O_7$  after CMAS exposure in flowing  $H_2O$  at 1300°C.



Figure 2.9: Cross-section BSE micrographs of 20 vol%  $Yb_2SiO_5$  in  $Yb_2Si_2O_7$  after CMAS exposure in flowing  $H_2O$  at 1300°C.

Comparing the plan view SEM phase contrast of swollen CMAS infiltrate regions in Figure 2.3, the lighter contrast of CMAS swollen infiltrate region in Figure 2.3h corresponds with less CMAS at the surface due to greater infiltration of the substrate. This is confirmed when comparing 24-hour lab air and steam exposure cross-sections (Figure 2.10). CMAS reaction mechanisms varied between substrates, with phase-pure YbDS precipitating apatite within the CMAS melt and 20YbMS/YbDS forming apatite at the CMAS-EBC interface (Figure 2.12). Infiltration measurements across single trials of phase-pure YbDS exposed to CMAS in each environment revealed steam increased the infiltration depth by ~800 µm and ~1050 µm compared to dry-O<sub>2</sub> and lab air, respectively, after 24-hours (Figure 2.13a). CMAS completely infiltrated the phase-pure YbDS samples after 96-hour exposures in all environments and infiltration depth could not be accurately determined as a result. Statistics on the sample thickness were collected and marked in Figure 2.13a, where an arrow indicates the infiltration depth is likely greater than this measured value.

CMAS infiltration on single trials of 20YbMS/YbDS was reduced by an order of magnitude compared to phase-pure YbDS. Environment had little effect on CMAS infiltration of mixed materials, except for the 96hour CMAS exposure in steam increasing infiltration compared to dry O<sub>2</sub>. CMAS reaction layers were shown to increase with time with steam increasing reaction layer thickness.



Figure 2.10: Stitched cross-section BSE micrographs of phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates after CMAS exposure at 1300°C for (top row) 4-, (middle row) 24-, and (bottom row) 96-hour durations. CMAS exposures were performed in (left column) stagnant lab air, (middle column) flowing dry-O<sub>2</sub>, and (right column) flowing steam environments. Preliminary infiltration measurements reported in this work are from these substrates.



Figure 2.11: Stitched cross-section BSE micrographs of mixed materials substrates after CMAS exposure at 1300°C for (top row) 4-, (middle row) 24-, and (bottom row) 96-hour durations. CMAS exposures were performed in (left column) flowing dry-O<sub>2</sub> on 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and (right column) flowing steam on 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>. Preliminary infiltration measurements reported in this work are from these substrates.



Figure 2.12: Cross-section BSE micrographs of Yb-apatite reaction products after CMAS exposure on (a,b) phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> at 1300°C in steam for 4-hours (50x and 200x respectively) and (b) 20Yb<sub>2</sub>SiO<sub>5</sub>/ Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> at 1300°C in steam for 96-hours (25x).



Figure 2.13: CMAS infiltration measurements after exposures varying in length and environment on (a) phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and (b) mixed 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates at 1300°C. (c) Reaction layer thicknesses of apatite formation on 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>. Phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrate thickness limited CMAS infiltration during 96-hour exposures and is likely larger than measured. NOTE: the change in y-axis scale from (a) to (b). Lines are included only as a visual tool.

#### 2.4. Discussion

High temperature steam was shown to affect molten CMAS-EBC interactions by increasing spreading (Figures 2.3 and 2.4a), infiltration after 24-hours exposure at 1300°C (Figure 2.14a), and reactivity (Figures 2.3 and 2.5a) to increase surface apatite on phase-pure YbDS substrates. The steam environment allowed water vapor to saturate and adsorb to the molten CMAS and EBC surfaces. Water vapor is known to chemisorb to silicate glass,<sup>71</sup> embed hydroxyl (OH<sup>-</sup>) species into the glass structure,<sup>57, 58</sup> lower glass viscosities at low concentrations (<2 wt%),<sup>59–61</sup> and lower glass surface tension to increase its wettability.<sup>62–64</sup> Figure 2.14 uses the Giordano viscosity model<sup>72</sup> to show the effect of H<sub>2</sub>O additions to CMAS viscosity. A similar method to Webster & Opila<sup>31</sup> was implemented in which the 0.73 ratio between Ca<sup>2+</sup> and Si<sup>4+</sup> was maintained. H<sub>2</sub>O was added in amounts of HO<sub>0.5</sub> (single cation mole %) between 2.5 and 25%. The addition of 2.5 mole% HO<sub>0.5</sub> relative to the baseline showed the greatest magnitude of change, greater than any magnitude of change between subsequent additions. Therefore, even small additions of H<sub>2</sub>O (≤2.5 mole% HO<sub>0.5</sub> or ~0.41 wt% H<sub>2</sub>O) to the CMAS glass structure have large impacts on CMAS viscosity. It should be noted that other viscosity models using a thermodynamic approach, like FactSage<sup>73</sup> or Thermo-Calc,<sup>74</sup> have better accuracies but often lack H<sub>2</sub>O or OH<sup>-</sup> as possible constituents.



Figure 2.14: Effect of water content on calculated CMAS viscosity, generated using Giordano viscosity model.<sup>72</sup> Lines are included only as a visual tool.

While water vapor is only one of several jet fuel combustion products found in the engine environment, as shown in Figure 2.15, it is the only major polar vapor species.<sup>52, 53</sup> Parikh<sup>62</sup> showed glass surface tension decreased with dipole moment of vapor species, where non-polar vapor species had little effect on glass surface tension. This study showed that CMAS spreading in non-polar vapor environments (dry O<sub>2</sub> and lab air) behaved similarly to one another. Therefore, the other non-polar vapor species found in the engine combustion environment are expected to have negligible effects on CMAS surface tension and, as a result, negligible effects on CMAS spreading, viscosity, and reactivity. The primary difference in features between dry O<sub>2</sub> and lab air environments is the density of apatite within the apatite ring.



Figure 2.15: Effect of equivalence ratio (fuel to air ratio) on engine combustion vapor species. Work originally produced by Jacobson.<sup>52, 53</sup> Reproduced with permission from John Wiley & Sons.

CMAS spreading on EBC materials follows a reactive wetting mechanism, where transport gradually transitions from spreading atop the coating surface to downward infiltration. This work shows that CMAS surface transport primarily occurs via capillary action along grain boundaries (Figures 2.6 and 2.7). Larger grains were observed to pin CMAS spreading. Increasing coating material reactivity by supplanting YbDS with YbMS was shown to decrease CMAS spreading (Figure 2.4), preferentially reacting with YbMS (Figure 2.7), and mitigate CMAS infiltration by approximately an order of magnitude (Figure 2.11). Whereas increasing porosity, in the case of 25YbDS/YbMS, shifts the driving force for CMAS transport to favor infiltration downwards instead of spreading radially (Figure A14). It is expected that CMAS interactions on 25YbDS/YbMS samples of equivalent density to 20YbMS/YbDS would decrease infiltration and reaction layer thickness.

Water vapor adsorption on ceramic surfaces can increase atomic diffusion as seen in microcrystal precipitation during sintering of MgO powders<sup>75</sup> and accelerate hydroxyapatite grain growth.<sup>76</sup> It is hypothesized that both of these processes occur as a result of a reduction in interfacial energy ( $\gamma_{SV}$ ), which decreased the energy barrier to nucleation.<sup>77, 78</sup> It is also possible for any H<sub>2</sub>O and/or OH<sup>-</sup> diffusion into the glass and subsequent disruption of the network structure is decreasing Yb<sup>3+</sup> saturation limits, accelerating apatite formation as a result. In both hypotheses H<sub>2</sub>O acts as a catalyst, reducing the energy barrier for apatite formation. This could explain the increased apatite ring size and area of surface apatite coverage after CMAS exposure on phase-pure YbDS in water vaper (Figures 2.3 and 2.5a). However, water vapor did not increase CMAS reactivity on 20YbMS/YbDS, possibly due to the difference in substrate reactivity, apatite formation mechanism, or a combination of both. Stokes et al.<sup>29</sup> and Zhao et al.<sup>79</sup> showed YbDS formed Yb-apatite through a dissolution and re-precipitation mechanism. Therefore, Yb-apatite formation on phase-pure YbDS is dependent on Yb<sup>3+</sup> dissolution into the CMAS glass and then reprecipitation either homogeneously in the CMAS glass or at the CMAS-vapor interface (Figures 2.12a and 2.12b). Whereas, apatite formation on 20YbMS/YbDS in steam predominantly occurs at the CMAS-EBC interface. Webster & Opila<sup>22</sup> and Zhao et al.<sup>79</sup> showed dense Yb-apatite formation as a result of CMAS reaction with YbMS. Surface apatite was only found in 20YbMS/YbDS after CMAS infiltrated beyond the reaction front, dislodging Yb-apatite grains, and allowing Yb-apatite reaction product to float to the surface (Figure 2.12c). This is fundamentally different from CMAS interactions on phase-pure YbDS, where surface apatite production occurs at the CMAS-vapor interface and not the CMAS-EBC interface.

CMAS infiltration of phase-pure YbDS exhibited several thermomechanical risks to EBC performance (Figure 2.10). The 4-hour samples produced delamination cracks underneath the residual CMAS pool, while all longer-time (≥24-hour samples) displayed blister cracking to various degrees. CMAS-EBC interactions in stagnant lab air were qualitatively consistent with prior work done by Webster and Opila<sup>22</sup>

for phase-pure YbDS and 20YbMS/YbDS substrates. Wiesner et al.<sup>80</sup> and Turcer et al.<sup>81</sup> also observed blister cracking in YbDS. Turcer et al. attributed it to a dilatation gradient of CMAS proliferating at the YbDS grain boundaries due to the lack of reaction product formation. This study supports the work by Turcer et al. as well as Webster and Opila<sup>22</sup> that incorporating a more reactive constituent (YbMS in the case of this work) into the EBC design can mitigate blister crack formation (Figure 2.11). Blister cracking in hafnia/hafnon composite substrates was also observed by Ericks et al.<sup>82</sup> indicating that the phenomenon is not unique to YbDS.

The large CMAS loading used in this study (~28 and 40 mg CMAS/cm<sup>2</sup>) was useful for investigating thermochemical interactions but resulted in CMAS overflow at longer times ( $\geq$ 24 hours). Low CMAS loads have also been shown to have thermomechanical consequences to multilayer EBC systems.<sup>49</sup> Thus, future CMAS-EBC interaction studies should utilize lower CMAS loading ( $\leq$ 5 mg/cm<sup>2</sup>) as a more reliable way of evaluating both thermochemical degradation mechanisms and thermomechanical integrity of the EBC under conditions more relevant to in-service CMAS ingestion levels (<2 mg-m<sup>-3</sup>).<sup>67–69</sup>

Lastly, this work illuminates the deleterious influence of high temperature steam on molten CMAS-EBC interactions through a systematic comparison of environments and substrate materials. The presence of high temperature water vapor increased spreading, reactivity, and infiltration on phase-pure YbDS as well as increased infiltration and reaction layer thickness on 20YbMS/YbDS. The acceleration of these phenomena is likely due to water vapor decreasing CMAS viscosity, surface tension, and energy barriers to nucleation.

#### 2.5. Conclusions

The following conclusions can be drawn from this work:

- Steam effects on CMAS-EBC interactions are likely governed by changes to three mechanisms: viscosity, interfacial energies, and substrate reactivity.
  - a. Increased CMAS spreading due to steam influences is likely due to reductions in CMAS viscosity and surface tension. These decreases in CMAS viscosity and surface tension also likely result in increased infiltration.
  - b. Increased surface apatite presence on phase-pure YbDS samples is likely due to decreases in interfacial energy increasing the driving force to nucleation.
- Increasing substrate reactivity through the addition of 20 vol% YbMS to YbDS decreased CMAS spreading area for all times in steam as well as mitigated coating recession and blister crack formation.
- Steam did not significantly increase CMAS infiltration of 20YbMS/YbDS relative to the dry O<sub>2</sub> environment but increased the area of 20YbMS/YbDS coating material affected without increasing infiltration depth.

### 3. Effect of EBC Composition on Molten Calcium-Magnesium-Aluminosilicate Wetting Behavior

#### 3.1. Background

Silicon carbide (SiC)-based ceramic matrix composites (CMCs) are the leading material to replace current nickel-base superalloy components in the hot sections of gas turbine engines. The high-temperature capabilities of SiC-based CMCs include thermomechanical stability, noteworthy improvements in creep resistance, and lower density than their nickel superalloy counterparts, improving engine thrust-to-weight ratio and fuel economy.<sup>1–4</sup> SiC is highly resistant to oxidation in air and dry oxygen due to the formation of a protective silica (SiO<sub>2</sub>) scale.<sup>5–7</sup> However, the engine combustion environment contains water vapor, which will react with silica at elevated temperatures to form gaseous silicon hydroxide (Si(OH)<sub>4</sub>),<sup>8</sup> as shown below in Equation 3.1:

$$SiO_2 + 2 H_2O(g) \rightarrow Si(OH)_4(g)$$
(3.1)

Environmental barrier coatings (EBC) are used to prevent SiC-based CMCs from volatilizing. Rare-earth silicates are used as EBCs due to their good chemical compatibility with underlying SiC substrate and Si bond coat, ability to exhibit improved high-temperature environmental stability, and minimal coefficient of thermal expansion (CTE) mismatch with the underlying substrate.<sup>9–11</sup>

State-of-the-art EBC technologies utilize a silicon bond coat to prevent oxidation of the underlying SiC CMC and a silicate-based ceramic topcoat.<sup>14, 15, 44–46</sup> Select rare-earth disilicates (RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>; REDS), where RE are the lanthanides, Sc, or Y, are under investigation as topcoats for their good coefficient of thermal expansion (CTE) match with the SiC CMC (~4.5-5.5 x  $10^{-6}$  °C<sup>-1</sup>)<sup>47</sup> and Si bond coat (~3.5-4.5 x  $10^{-6}$  °C<sup>-1</sup>).<sup>47</sup>

Coatings with large CTE mismatches with the underlying substrate have limited lifetimes due to stress induced delamination. Ideal candidate materials also maintain high-temperature stability, and lack hightemperature polymorphs, at and below the goal operating temperature of 1500°C.<sup>9</sup> At these operating temperatures siliceous debris (i.e. sand, ash, dirt) ingested by the engine during take-off, in-flight, and upon landing. Siliceous debris are composed of calcium-magnesium-aluminosilicates (CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) or CMAS. Siliceous debris enters the engine hot section, melts to form a CMAS glass and adheres to engine components, resulting in coating infiltration and premature failure of the EBC.<sup>18–21</sup> Molten CMAS interactions with EBCs can be detrimental for several reasons, including: 1) large CTE mismatches between the EBC and CMAS glass; 2) dissolution of coating material leading to coating recession; 3) CMAS reactivity leading to formation of new crystalline phases and altering coating microstructures.<sup>19</sup> EBCs must resist molten CMAS deposit degradation.

An important phenomenon in CMAS – EBC interactions is molten CMAS wetting behavior. Wetting results when a liquid meets and maintains contact with a solid surface. The wettability of a liquid on a solid surface is controlled by the adhesive intermolecular interactions of the solid-liquid interface and cohesive intermolecular interactions within the liquid. Stronger adhesive forces and weaker cohesive forces result in more wetting. The degree of wetting is governed by the equilibrium contact angle which is dependent on interfacial energies. The Young equation, shown in Equation 3.2, provides the relationship between contact angle ( $\theta$ ) and interfacial energies ( $\gamma_{ij}$ ), where the subscripts correspond to the solid-vapor, solid-liquid, and liquid-vapor interfaces.

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{3.2}$$

Complete wetting occurs at a contact angle of 0°, partial wetting occurs at contact angles <90°, partial non-wetting occurs at contact angles >90°, and non-wetting occurs at contact angles of 180°. As a drop is

placed on a solid surface, it will spread until an equilibrium contact diameter is achieved. The drop diameter on a horizontal solid surface is a function of capillary, gravitational, and viscous forces in addition to time. CMAS composition affects the intermolecular forces of the glass melt and thus the liquid-vapor as well as the solid-liquid interfacial energies.

The substrate also contributes to wetting behavior, where contact angles are influenced by surface roughness, heterogeneity, and reactivity.<sup>50</sup> Surface roughness, which is inevitable in as-sprayed coatings, provides additional interfacial area for the spreading liquid to occupy and increases total solid-liquid interfacial energy as a result. Apel-Paz and Marmur showed how surface roughness affected spreading, increasing spreading beyond the droplet radius through capillary flow into the surface features.<sup>83</sup> On the other hand, extremely rough surfaces can reduce spreading by producing a metastable contact angle due to a physical barrier or lead to entrapment of vapor beneath the spreading liquid resulting in a composite surface. Heterogeneity, which is unavoidable in polycrystalline and multi-phase substrates, can affect contact angle measurement by allowing liquid to preferentially pin to regions that yield lower contact angles.

Coating reactivity, which can be tailored to mitigate CMAS attack through CMAS-phobic (non-reactive) or CMAS-philic (reactive) design approaches, plays a key role in CMAS wetting behavior. CMAS reactivity with REDS to form a stable rare-earth apatite ( $Ca_2RE_8Si_6O_{26}$ ) varies systematically with RE cation size.<sup>27, 84</sup> Nd – one of the largest RE cations – has the largest rare-earth apatite stability and Yb – one of the smallest – has the smallest rare-earth apatite stability.<sup>85, 86</sup> It is hypothesized that substrate reactivity will correlate with CMAS droplet adhesive forces, where increasing rare-earth cation stability in the apatite structure is expected to decrease CMAS wettability.

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Reactive wetting is controlled by diffusion and chemical reactions at the interface. The two rate-limiting mechanisms of reactive wetting are (i) reaction-limited and (ii) transport-limited spreading.<sup>50</sup> Where in (i) the reaction kinetics at the solid-liquid-gas phase interface control the rate of liquid transport across the substrate surface (assuming diffusion within the droplet is rapid).<sup>87</sup> While in (ii) the reaction rate is rapid relative to local diffusion and wetting is limited by liquid transport to the solid-liquid-gas phase interface. Coating design should consider the reactive wetting mechanism depending on CMAS reactivity.

Research investigating CMAS wetting behavior is primarily limited to 7 wt% yttria stabilized zirconia (7YSZ) as the substrate material. Studies investigated CMAS wetting as a function of 7YSZ processing and surface roughness, typically showing more wetting on rougher surfaces and less wetting on denser substrates.<sup>88–95</sup> Experiments evaluating equilibrium wetting and spreading phenomena of molten volcanic ash on an alumina substrate identified the temperature-dependence of viscosity as the most important parameter influencing the deposition propensity (wetting and spreading) of molten debris.<sup>51</sup>

This study explores the effects of EBC composition and morphology on CMAS wetting. EBC substrates of interest include phase-pure YbDS and mixed 20YbMS/YbDS model materials as well as freestanding sprayed REDS coatings, where RE = Y, La, Nd, Gd, Yb, Lu. RE size effects on coating reactivity and reactive wetting mechanism, effects of surface roughness and porosity on CMAS transport, and the relationship between CMAS wetting and infiltration is discussed. Lastly, several implications to coating performance are addressed/discussed.

#### 3.2. Experimental

Spark plasma sintering (SPS; Thermal Technology LLC, Model SPS 25-10; Santa Rosa, CA) was used to densify phase-pure YbDS and mixed YbMS/YbDS materials from starting powders (99% purity, Praxair Surface Technologies; Indianapolis, IN). Mixed YbDS/20YbMS powders were shaken by hand for ~2 minutes, while phase-pure YbDS were added directly to a graphite die (Graphite Products Corp.; Madison Heights, MI) with an inner diameter of 20 mm that was lined with a layer of graphite foil (Thermal Technology LLC). Both powders underwent densification at 1550°C while under a pressure of 65 MPa for 25 minutes.<sup>28</sup> SPS samples were annealed in a stagnant air box furnace (CM Furnaces, Model 1706; Bloomfield, NJ) to restore oxygen stoichiometry of the specimens and were heated to 1500°C for 24h, following a heating rate of 7.5°C/min and cooling rate of 5°C/min. SPS substrates were sectioned to ~1 cm<sup>2</sup> and ~1 mm thick coupons.

Freestanding atmosphere plasma sprayed (APS) REDS coatings (where RE = Y, La, Nd, Gd, Yb, Lu) were provided by Rolls-Royce and received in the crystallized heat-treated state. APS REDS substrates measured ~1.69 cm<sup>2</sup> and ~2.5 mm thick and were polished to the same 4000 grit (5µm grit size) surface finish as the SPS densified substrates. Two dense APS YbDS from two different spray batches were explored. One APS YbDS came with the group of freestanding APS REDS materials. While the other came as a nominally dense equivalent (denoted as Blend A) in a series of porous freestanding APS YbDS substrates (with porosity content increasing alphabetically for Blends C and F).

X-ray diffraction (XRD; Bruker AXS LLC, D2 Phaser; Fitchburg, WI), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS; NanoScience Instruments Inc.; Phenom XL G2 SEM; Phoenix, AZ) were used in conjunction with ImageJ software<sup>65</sup> to characterize starting material phase fractions of SPS

substrates (YbDS, YbMS, porosity). XRD of all substrates (Figure B1) and phase identification (Figures B2-B8) are contained in Appendix B. Reference patterns and their corresponding ICDD reference number are listed in Table B1. Density measurements were performed using the Archimedes method (Mettler Toledo, Model XSE205DU; Suwanee, GA).

A nominal CMAS composition of 33 Ca – 9 Mg – 13 Al – 45 Si (single cation mol%) was used due to likeness in debris analyzed from engine deposits.<sup>36</sup> CMAS constituent powders were mixed via ball milling using zirconia milling media ( $\geq$ 95% purity, Glen Mills; Clifton, NJ) for ~24 hours before being pre-reacted in a Pt5Au crucible for 4 hours at 1500°C to form a homogenous glass melt. Glass rods were drawn from the silicate melt as they air-cooled through its workable temperature. Composition of the glass was measured by EDS from three measurements on one piece of glass and determined to be 30.1 Ca – 9.3 Mg – 13.6 Al – 47.0 Si (in single cation mol%). EDS of CMAS is contained in Figure B9 and Table B2 in Appendix B.

CMAS glass rods were sectioned into ~10 mg cylinders with diameters ranging from 1.8 mm to 2.6 mm and placed onto the polished EBC surface before being loaded into the heating microscope furnace (Linseis, L74/HS/1700; Selb, Germany) at room temperature. The CMAS – EBC sample pairing was heated from room temperature in stagnant lab air to 1000°C at a rate of 10°C/min, then to 1150°C at a rate of 5°C/min, then to 1250°C at a rate of 2.5°C/min to reduce thermal lag. Specimens were held at temperature for 2 hours (three samples) or 4 hours (one sample) where a close-capture device (CCD) camera tracked the evolution of the CMAS glass cylinder's silhouette – measuring contact angle, height, and width – as it melted and spread across the EBC material surface. An example of CCD footage at the points of interest is displayed in Figure 3.1. Measurements on each sample (depicted in Figure 3.1a) yielded two contact angles (purple arc), one width (yellow horizontal line), and one height (orange vertical line) for each point of interest in the run. Thus, contact angle, height, and width measurements were acquired for four samples, each 1150°C, 1250°C at 0h, and 1250°C at 2h – except in select cases where outliers in wetting measurements were removed (denoted by red text). Appendix B organizes raw data and derived statistics on polished substrates in Tables B4 and B5, respectively, and unpolished substrates in Table B6.



Figure 3.1: Side-view CCD images of CMAS wetting on SPS 20YbMS/YbDS at (a) ~1150°C, (b) ~1250°C at 0h, (c) ~1250°C at 2h, and (d) ~1250°C at 4h. CMAS contact angle (purple arc), width (yellow horizontal line), and height (orange vertical line) measurements are denoted in (a).

XRD and SEM/EDS were conducted on post-exposure specimens to evaluate reaction products. Postexposure specimens were imaged using SEM first in plan view. SEM samples were coated (Technics, Hummer Sputter Coater; Hayward, CA) with a thin layer of gold/palladium prior to characterization to provide a conductive surface. Micrographs were taken in back-scattered electron (BSE) mode to identify phase contrast. Macroscale stitched micrographs were obtained using the Phenom XL G2 equipped with an image stitching feature. Stitched BSE SEM micrographs of unreacted substrate corners (post-exposure) were collected to quantify substrate plan view porosity. Plan view porosity was quantified from three locations with an example of porosity quantification shown in Figure B10. Individual porosity measurements are listed in Table B3. CMAS spreading was quantified post-exposure in plan view. Spreading area was normalized by the mass of CMAS loaded. CMAS spreading measurements on polished substrates are listed in Table B7. Grain size measurements were conducted on an unreacted area of SPS Yb-silicate substrates using a modified linear intercept method, derived from ASTM E112-13.<sup>96</sup> Average grain size – summarized for the SPS Yb-silicate materials in Table 3.1 – was determined from the intersection and intercepts of grains with a mask of six lines (three in each horizontal and vertical directions). Yb-silicate substrate microstructure for SPS and APS materials in plan view is displayed in Figure 3.2. All APS YbDS substrates displayed similar morphologies. Grain size of SPS substrates was generally courser than the APS counterparts. Grain size was not measured for APS substrates due to the inhomogeneity of the phases producing much smaller grain sizes, mostly ~1 µm or less in diameter.



Figure 3.2: Back-scatter electron micrographs showing microstructures of Yb-silicate materials substrates in plan-view. Substrates include (a) SPS YbDS, (b) SPS 20YbMS/YbDS, (c) APS YbDS – C, (d) APS YbMS, and (e) APS (Y+Yb)DS. (f) Grain sizes were quantified using this mask of three horizontal and three vertical lines atop the SPS micrographs. APS results in some non-equilibrium phases, as shown in (c,d), where light contrast corresponds to Yb<sub>2</sub>SiO<sub>5</sub> and dark contrast corresponds to Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> in (b,c,d). Light contrast corresponds to Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and dark contrast corresponds to Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> in (e). Black regions are porosity.

SubstrateAve. Total Grain Size (μm)Ave. Grain Size, by phase (μm)SPS YbDS5.05.0 (YbDS)SPS 20YbMS/YbDS3.03.3 (YbDS), 2.4 (YbMS)

Table 3.1: Average grain size for SPS Yb-silicate substrates

#### 3.3. Results

Wetting measurements are plotted versus average RE cation size. Average RE cation size was determined from the coordination number (CN) of the RE sites associated with the dominant REDS structure. Work by Felsche<sup>10</sup> informed RE cation coordination and work by Shannon informed RE cation size.<sup>97</sup> The dominant REDS structure was identified through XRD of heat-treated APS substrates prior to exposure, contained in Figures B2-S8. Dominant structures, corresponding RE cation information, measured densities, and average porosity are listed in Table 3.2. Minor phases, including rare-earth monosilicates (REMS; RE<sub>2</sub>SiO<sub>5</sub>) and non-dominant REDS structures, were detected but not quantified in the APS coating materials. In addition to the effect of RE cation size, the effect of coating microstructure, composition, porosity, and surface roughness on CMAS wettability was explored. These results are presented in the following sections.

Rare-earth Silicate	Dominant REDS Structure	RE Cation Site(s) CN	Average RE Cation Size [Å]	Measured Density [g/cm³]	Average Porosity [vol%]
APS LaDS*	Tetragonal (A)	9, 9, 8, 7	1.173	4.344	12.507
APS NdDS	Tetragonal (A)	9, 9, 8, 7	1.118	4.990	7.646
APS GdDS*	Triclinic (α)	8, 8, 8, 8	1.053	5.420	7.698
APS YDS	Monoclinic (γ)	6	0.900	3.742	7.236
APS LuDS	Monoclinic (β)	6	0.861	5.816	7.307
APS YbDS	Monoclinic (β)	6	0.868	6.036	9.576
APS YbDS – A	Monoclinic (β)	6	0.868	Not Measured	5.746
APS YbDS – C	Monoclinic (β)	6	0.868	Not Measured	15.863
APS YbDS – F	Monoclinic (β)	6	0.868	Not Measured	29.014
SPS YbDS	Monoclinic (β)	6	0.868	6.056	~2-6+
SPS 20YbMS/YbDS	Monoclinic (β)	Mixed	0.875	6.293	~2-6+
APS (Y+Yb)DS	Monoclinic (β)	6	0.884	4.779	11.184
APS YbMS	Monoclinic (X2)	7,6	0.897	3.742	Not Measured

Table 3.2: Dominant REDS structure, RE coordination in associated REDS, average cation size, and average porosity content for APS and SPS RE-silicate substrates

\* = strong REMS presence in addition to REDS structures; + = measurements used from prior chapter.

#### 3.3.1. Effect of Rare-earth Cation Size

Wetting measurements on nominally dense freestanding APS REDS materials consisted of CMAS contact angle, width, height, and spreading measurements (Figures 3.3, 3.4, 3.5, and 3.6 respectively). Wetting data at 1150°C was analyzed to evaluate the effect of unreacted coating composition on CMAS wetting shortly after melting and prior to reaction with the substrate. The lack of variability in CMAS contact angle at 1150°C indicated CMAS has a similar affinity for wetting for each substrate regardless of RE size (Figure 3.3a). CMAS contact angle measurements decreased as temperature increased to 1250°C and remained similar to one another at the start of the hold (Figure 3.3b). CMAS contact angle measurements did not change significantly between 2- and 4-hours at 1250°C (Figures 3.3c and 3.3d). The difference in CMAS contact angles of small- and large-RE cations after 2- and 4-hours at 1250°C indicate a potential shift in CMAS wettability. Explanation of RE size effects on CMAS contact angle and implications to coating performance will be addressed in the discussion.



Figure 3.3: Molten CMAS contact angle measurements on dense rare-earth silicate materials at (a) ~1150°C, (b) 0 hours at ~1250°C, (c) 2 hours at ~1250°C, and (d) 4 hours at ~1250°C. Measurements are plotted as a function of average RE cation size. NOTE: y-axis in (a) is adjusted to best depict trend in data; (a)-(c) are averages while (d) plots data from the single 4h experiment. Legend in (a) applies to all plots.

Molten CMAS width measurements were shown to increase over time (Figure 3.4). The dual cation (Y+Yb)DS substrate showed an increase in molten CMAS width measurements relative to the rest of the substrates at 1150°C and the start of the 1250°C hold (Figures 3.4a and 3.4b). The YDS substrate showed the least increase in molten CMAS width measurements after 2- and 4-hour holds at 1250°C (Figures 3.4c and 3.4d).



Figure 3.4: Molten CMAS width measurements on dense rare-earth silicate materials at (a) ~1150°C, (b) 0 hours at ~1250°C, (c) 2 hours at ~1250°C, and (d) 4 hours at ~1250°C. Measurements are plotted as a function of average RE cation size. NOTE: y-axes in (a) and (b) are adjusted to best depict trends in data; (a)-(c) are averages while (d) plots data from the single 4h experiment. Legend in (a) applies to all plots.

Molten CMAS height measurements were shown to decrease over time (Figure 3.5). The APS YbDS – Blend A substrate showed a notable decrease in molten CMAS height measurements relative to the rest of the substrates at 1150°C and the start of the 1250°C hold (Figures 3.5a and 3.5b). The APS GdDS and APS LaDS substrates produced the greatest molten CMAS height measurements after 2- and 4-hours at 1250°C (Figures 3.5c and 3.5d). APS NdDS was the only substrate to show a notable decrease in molten CMAS height measurements after 4-hours relative to measurements after 2-hours.



Figure 3.5: Molten CMAS height measurements on dense rare-earth silicate materials at (a) ~1150°C, (b) 0 hours at ~1250°C, (c) 2 hours at ~1250°C, and (d) 4 hours at ~1250°C. Measurements are plotted as a function of average RE cation size. NOTE: y-axes in (a), (b) and (c), (d) are adjusted to best depict trends in data; (a)-(c) are averages while (d) plots data from the single 4h experiment. Legend in (a) applies to all plots.

Quantification of CMAS spreading minimized variability and improved trend observation with average RE cation size (Figure 3.6) compared to other CMAS wetting measurements. APS LuDS was the only sample to have a 3-hour measurement and, therefore, has two datapoints plotted instead of an average and standard deviation for quantification of spreading after 2-hours. CMAS spreading stayed approximately the same for all species between the 2- and 4-hour measurements except for APS LaDS. APS LaDS increased spreading after 4-hours of CMAS exposure. A potential explanation of this phenomenon will be addressed in the discussion.



Figure 3.6: Normalized residual CMAS area measurements on dense rare-earth silicate materials after exposure at ~1250°C for (a) 2 and (b) 4 hours. Measurements were normalized to the CMAS loading and are plotted as a function of average RE cation size. NOTE: (a) are averages on at least three trials, except for the two LuDS specimens, while (b) are measurements on individual 4h experiments; Legend in (a) applies to both plots.

# 3.3.2. Effect of Processing Method, Composition, and Porosity of Yb-silicate Materials

CMAS wetting on dense (>95%) phase-pure SPS YbDS and phase-mixture SPS 20YbMS/YbDS were compared to APS YbDS, APS YbMS, APS (Y+Yb)DS, and APS YDS substrates. Wetting was evaluated through the quantification of CMAS contact angle, width, height, and spreading evolution. Appendix B contains figures adjusted to the narrow range of cation sizes (Figures B15, B16, B17, and B18 respectively). The only significant differences between SPS YbDS and SPS 20YbMS/YbDS were increases in CMAS spreading area from 2- to 4-hours (Figure 3.6). The only significant differences between the two dense APS YbDS substrates were observed in molten CMAS height at 1150°C and 0-hours at 1250°. A 4-hour CMAS exposure on the polished APS YbDS was not completed, but a 4-hour CMAS exposure on the APS YbDS – A was and is used as the nominally dense APS equivalent at this instance. SPS YbDS was the only YbDS-base substrate to increase CMAS spreading after 4-hours. Processing method and grain size (Table 3.1) did not have significant effect on CMAS wetting, as shown by the lack of variability in wetting results between APS and SPS Yb-silicate substrates.

Porosity of all substrates was measured individually and no trends with the wetting measurements were observed with substrates of varying compositions. The addition of porosity to the APS YbDS substrates largely did not affect CMAS wetting measurements. The lesser porous APS YbDS Blend C (APS YbDS – C) substrate behaved similarly to the denser APS YbDS substrates at all instances for all wetting measurements. However, the highly porous APS YbDS Blend F (APS YbDS – F) substrate increased contact angle measurements after a hold of 0- and 2-hours at 1250°C. Only one of the 2-hour CMAS exposures at 1250°C on APS YbDS – F substrates yielded measurable wetting data due to the CMAS infiltrating

completely into the substrate. Similarly, CMAS wetting measurements were not detected on the 4-hour exposure on the APS YbDS – F substrate.

Video recordings for APS YbDS – F from the wetting experiment software paired with plan view imaging indicated a shift from spreading to rapid infiltration. This phenomenon resulted in a crater-like CMAS affected area with a residual CMAS bead at the center and is not directly comparable to the denser APS YbDS substrates. A comparison of Yb-silicate substrates after 2-hour CMAS exposures at 1250°C are shown in Figure 3.7 to illustrate the change in CMAS interaction with the APS YbDS – F substrate (highlighted). Information on CMAS infiltration of polished APS YbDS – F substrates is contained in Table 3.3. CMAS transport phenomena will be addressed in the discussion.



Figure 3.7: Plan view back-scattered SEM micrographs of Yb-silicate substrates after 2-hour CMAS exposures at 1250°C for (a) SPS YbDS, (b) SPS 20YbMS/YbDS, (c) APS YbDS, (d) APS YbDS – A, (e) APS YbDS – C, (f) APS YbDS – F, (g) APS (Y+Yb)DS, and (h) APS YbMS.

Trial No.	Hold Time [h]	CMAS Load [mg]	Time to complete infiltration [min]	Affected area [mm²/mg]
1	4	10.51	33	2.12
2	2	10.85	>120*	1.63
3	2	11.10	66	2.08
4	2	10.31	113*	1.86

Table 3.3: CMAS Infiltration of Polished APS YbDS – F Substrates at 1250°C

\* = The silhouette of a CMAS dome was observable in the video at the conclusion of the 2-hour hold; however, a contact angle of 0° was measured in Trial 4.

APS YbMS was the only substrate to show a notable decrease in CMAS contact angle and increase in CMAS spreading from 2- to 4-hours exposure at 1250°C. This indicates that changes in the silica chemistry (from YbDS to YbMS in this case) of the APS RE-silicate can increase CMAS wetting (by decreasing contact angle and increasing CMAS spreading area). Substrate reactivity, which also changes with the number of silicate groups in addition to the RE-cation, and their effects on CMAS wetting will be addressed in the discussion.

The dual cation APS (Y+Yb)DS substrate did not show consistent or predictable behavior with respect to dense APS YbDS and APS YDS substrates across all instances and all CMAS wetting measurements with the exception of CMAS spreading area. CMAS spreading on APS (Y+Yb)DS lies firmly between the dense APS YDS and YbDS substrates (Figure 3.6). Relative to all single cation Yb-silicate substrates, APS YDS measured similar CMAS contact angles at all instances, decreased in width after 2- and 4-hours at 1250°C, measured similar molten CMAS heights at all instances, and decreased CMAS spreading.

## 3.3.3. Effect of Surface Roughness on CMAS Wetting of APS Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> Substrates

CMAS contact angle generally increased with surface roughness during the 1250°C hold (Figure 3.8b, 3.8c, and 3.8d). Surface roughness effects on CMAS wetting of APS YbDS substrates varied depending on porosity. Unpolished dense APS YbDS substrates showed similar CMAS contact angle measurements to their polished counterparts at all instances. Unpolished porous APS YbDS – F increased CMAS contact angle relative to its unpolished counterparts at the start of the 1250°C hold (Figure 3.8b). Unpolished porous APS YbDS – C increased CMAS contact angle relative to both polished and unpolished YbDS substrates after 4-hours at 1250°C (Figure 3.8d).

Appendix B contains molten CMAS width and height measurements on unpolished dense APS YbDS substrates (Figures B19 and B20). Generally, molten CMAS width and height measurements decreased with surface roughness on unpolished dense APS YbDS substrates. Molten CMAS width and height measurements on unpolished APS YbDS – A increased relative to its polished counterpart. Molten CMAS width measurements of unpolished porous APS YbDS substrates decreased with surface roughness. However, molten CMAS height measurements on unpolished not show consistent behavior.



Figure 3.8: Molten CMAS contact angle measurements on polished and unpolished YbDS substrates of various porosity contents after exposure at (a) ~1150°C, (b) 0 hours at ~1250°C, (c) 2 hours at ~1250°C, and (d) 4 hours at ~1250°C. Measurements are plotted against root mean square (RMS) roughness. Polished specimens are plotted at the corresponding unpolished RMS measurement to visualize the effect of surface roughness. Legend in (a) applies to all plots. NOTE: shift in y-axis between top and bottom plots.

There is not enough data to comment on or identify a trend between CMAS spreading and surface roughness on unpolished APS specimens (due to differences in porosity content). However, significant differences were observed in CMAS spreading between polished and unpolished APS YbDS (Figure 3.9). Unpolished APS YbDS substrates showed a 100% increase (~2.5-2.7 mm<sup>2</sup>/mg CMAS) in CMAS spreading

when compared directly to their polished counterparts. Plan view BSE SEM micrographs of the unpolished APS YbDS substrates are compared to their polished APS YbDS counterparts to visualize surface roughness effects on CMAS spreading (Figure 3.10). Polished APS YbDS – A was the only substrate to form a uniform CMAS wetting perimeter. The presence of porosity in polished APS YbDS – C resulted in a non-uniform CMAS wetting perimeter. However, CMAS is shown to flow through channels in the unpolished surface of APS YbDS coupons, increasing the non-uniformity of the CMAS wetting perimeter and residual CMAS pool size. The porosity level in unpolished APS YbDS – C synergized with the surface roughness to increase molten CMAS contact angle after 4-hours at 1250°C despite having similar spreading measurements to its denser counterparts. Implications of residual CMAS distribution on coating performance will be addressed in the discussion.



Figure 3.9: Residual CMAS spreading area measurements on polished and unpolished YbDS substrates of various porosity contents after a 4-hour exposure at ~1250°C. Measurements are plotted against root mean square (RMS) roughness. Polished specimens are plotted at the corresponding unpolished RMS measurement to visualize surface roughness effects. NOTE: a 4-hour exposure at ~1250°C was not completed on the polished APS YbDS substrate provided with the array of REDS substrates.


Figure 3.10: Plan view back-scattered SEM micrographs of YbDS substrates after 4-hour CMAS exposures at 1250°C for (a) polished APS YbDS – A, (b) polished APS YbDS – C, (c) polished APS YbDS – F, (d) unpolished APS YbDS – small batch, (e) unpolished APS YbDS – A, (f) unpolished APS YbDS – C, and (g) unpolished APS YbDS – F. NOTE: a 4-hour CMAS exposure was not conducted on the polished APS YbDS – small batch; the polished APS YbDS – F specimen fractured upon removal from epoxy.

#### 3.4. Discussion

Molten CMAS contact angle, width, and height measurements on unreacted APS REDS substrates at 1150°C behaved similarly to one another, indicating REDS have similar CMAS wettability despite different dominant REDS phases. CMAS spreading after 2-hours at 1250°C correlates indirectly with RE-apatite stability,<sup>27, 84</sup> indirectly with RE-apatite formation kinetics,<sup>98, 99</sup> and directly with RE cation diffusivity.<sup>100</sup> With the exception for APS LaDS, this trend also applies to the 4-hour CMAS spreading measurements. As a result, the observed trend in CMAS wetting is attributed to the interplay of degree of CMAS reactivity and RE diffusivity with each substrate. Where the comparatively rapid diffusivity of small RE cations into the CMAS melt combined with slower RE-apatite formation kinetics allows for increased CMAS spreading.

CMAS transport on REDS is hypothesized to be reaction-limited with wettability directly tied to RE cation diffusivity. CMAS reactivity with rare-earth silicate materials also increases as the number of silicate groups decreases (i.e. RE<sub>2</sub>O<sub>3</sub> is most reactive).<sup>23, 26</sup> Tran et al.<sup>101</sup> calculated surface energies of over 100 polymorphs of ~70 elements and showed surface energy decreased as atomic packing and crystal structure symmetry increased (true for both cubic and non-cubic lattices). Broughton et al.<sup>102</sup> reported similar findings in a Molecular Dynamics study. Therefore, the increase in atomic packing and crystal structure symmetry of RE<sub>2</sub>O<sub>3</sub> (compared to RE<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> or RE<sub>2</sub>SiO<sub>5</sub>) would also decrease the substrate surface energy, magnifying the driving force for CMAS wetting. The increased reactivity of APS YbMS and presence of Yb<sub>2</sub>O<sub>3</sub> (due to APS non-equilibrium process) likely explains the decreased molten CMAS contact angle and increased spreading after 4-hours at 1250°C.

APS LaDS was the only REDS to increase in spreading after 4-hours, likely due to having more porosity (~12  $\pm$  0.5%) compared to the other APS substrates which ranged from ~7-9% porosity (Table 3.2). The porosity likely acted as a network of channels for CMAS to transport at the surface of the substrate via capillary action.<sup>83</sup> This is also observed, albeit not significantly, with CMAS spreading on the polished porous APS YbDS – C substrate compared to its denser counterparts after 2-hours at 1250°C (Figure B18a). Therefore, the increased reactivity of LaDS could have worked in synergy with the porosity to perpetuate spreading. This study showed that surface roughness in unpolished APS YbDS substrates increased CMAS spreading. These trends in surface roughness were also observed in molten silicate wetting experiments (synthetic CMAS, volcanic ash, and fly ash) on YSZ.<sup>89, 90, 95</sup> Use of EBCs in turbine engines will contain porosity, even in nominally dense coatings. The use of abradable coatings will increase porosity content relative to the dense coatings with interconnected networks of porosity likely contributing to surface roughness. These features are shown to increase CMAS spreading relative to lab-controlled CMAS exposures on polished, dense substrates.

The relationship between CMAS wetting measurements (Figures B12-B14 in Appendix B) is addressed here and used to make predictions on CMAS infiltration. Molten CMAS width vs. height plots are shown in Figure B12. Looking at these measurements after 2-hours at 1250°C, a large overlap in width measurements is apparent. However, APS LaDS, NdDS, GdDS, and YbMS have taller residual CMAS glass pools. This implies that the more reactive substrates with taller residual CMAS glass pools have less infiltration. Molten CMAS contact angle, width, and height measurements vs. CMAS spreading are shown in Figure B13. As noted, molten CMAS width measurements are generally uniform at both 2- and 4-hour instances. Molten CMAS contact angle and height measurements generally mirror the RE-apatite stability trend, except for LaDS after 4-hours. Small cation REDS showed the smallest contact angles, smallest heights, and largest CMAS spreading areas. Provided that CMAS volume should be conserved, then small RE cation REDS likely experienced increased CMAS infiltration. Future work for publication will involve cross-sectional analysis of APS YbDS and LaDS substrates after the 2-hour exposure.

Trends in substrate surface energy can be identified from contact angle measurements using Equation 3.2. Coatings looking to employ a non-reactive, CMAS-phobic approach should utilize low surface energy substrates which will have less adhesion with CMAS, increasing molten CMAS contact angle and resulting in partial wetting. However, coatings looking to employ a reactive, CMAS-philic approach should utilize high surface energy substrates that will have greater adhesive interaction with CMAS, decreasing molten CMAS contact angle and encourage CMAS wetting. The small RE cation REDS (RE = Y, Yb, Lu) measured the lowest molten CMAS contact angles, indicating their reaction product(s) (predominantly RE-apatite) have high interfacial energy. This phenomenon was also validated through CMAS spreading measurements.

CMAS interaction with coating materials can have both thermochemical and thermomechanical consequences that result in premature coating failure. Minimizing CMAS affected areas of the coating

material is desired to minimize changes in coating microstructure.<sup>19</sup> However, a concentrated area or thick layer of CMAS can increase in-plane tensile stresses, promoting penetrating through-coating cracks, coating delamination, and coating spallation.<sup>41, 48, 103</sup> Reducing the thickness of the high CTE mismatch material is shown to decrease the magnitude of in-plane tensile stresses and driving force for cracking (Figure 3.11). Therefore, designing coatings to maximize CMAS spreading area could minimize residual CMAS thickness at the coating surface. Decreasing the thickness of residual CMAS is expected to prolong the lifetime of the coating from a thermomechanical standpoint. Hypothetically, if CMAS is dispersed over a greater area, there is less CMAS available for infiltration. Decreasing infiltration depth (provided the CMAS achieves complete reaction) is also expected to prolong coating lifetime from a thermochemical standpoint. The most ideal case for both EBC and TBC materials results in minimal coating recession, a thin reaction layer, and minimal in-plane tensile stresses. This study found that small RE cation REDS (RE = Y, Yb, Lu) increased CMAS wetting while large RE cation REDS (RE = Gd, Nd, La) decreased CMAS wetting.



Figure 3.11: Schematic illustrating effect of high CTE mismatch material thickness (Yb<sub>2</sub>SiO<sub>5</sub> on Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) on crack behavior. Increasing coating toughness will decrease cracking. Work originally published by Summers et al.<sup>41</sup> Reprinted with permission from Elsevier.

CMAS flow properties and reactivity will change with temperature and glass composition. The nominal 0.73 CaO-SiO<sub>2</sub> ratio used in this study is a low viscosity CMAS, where decreasing CaO-SiO<sub>2</sub> ratio will increase CMAS surface tension (or liquid surface energy), increasing viscosity which would decrease CMAS wetting and spreading. However, increasing temperature will also decrease CMAS surface tension and viscosity – increasing wetting and spreading as a result – while also increasing reactivity with and diffusivity of the substrate.<sup>104</sup> The presence of water vapor, a critical combustion biproduct, has been shown to lower glass surface tension, which will decrease viscosity.<sup>62</sup> Changes to CMAS composition occur through the addition of modifying cation species (like RE<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, or TiO<sub>2</sub>) and/or fluctuating the CaO-SiO<sub>2</sub> ratio. Reaction products with certain coating materials can be predicted using phase diagrams and computational thermodynamics databases,<sup>105–107</sup> but that does not guarantee favorable kinetics, microstructure, or precipitation mechanisms. Additionally, increasing CMAS compositional complexity

(through the presence of additional oxides) increases the difficulty of predicting reaction products due to a limited thermodynamic knowledge of molten silicate interactions with its constituent oxides and coating materials. Lastly, changes in CMAS load (via deposition area: mg/cm<sup>2</sup>; or ingestion volume: mg/cm<sup>3</sup>) will also impact interactions with the coating material.

#### 3.5. Conclusions

The following conclusions can be drawn from this work:

- CMAS spreading on EBC materials imaged in plan view found to be a stronger indicator of CMAS-EBC interactions than contact angle measurements using a heating microscope.
- 2. Reactive substrates with high propensity to form a rare-earth apatite resulted in less spreading.
- Surface roughness increased CMAS wetting by increasing CMAS spreading. Unpolished EBC surface features acted as channels to facilitate CMAS spreading.
- 4. EBC porosity had no effect on CMAS spreading until a critical porosity value was achieved, presumably related to the percolation threshold, when CMAS infiltration dominated over spreading.

## 4. Experimental Investigation of Fifth Oxide Effect on CMXAS Glass Properties

#### 4.1. Background

Molten silicate properties are relevant to several different fields including volcanology and the flow of magmatic liquids,<sup>108</sup> slag formation during ferrous and non-ferrous alloy synthesis,<sup>109</sup> containment and transport of nuclear waste products,<sup>110</sup> as well as thermochemical degradation of hot-section components in air-ingesting turbine engines.<sup>111</sup> The following work was completed in the context of air-ingesting turbine engines, where hot-section components are subject to multiple thermochemical degradation processes that must be mitigated to maximize their lifetime. A prominent form of degradation in jet engines occurs by ingesting siliceous debris (sand, volcanic ash, or runway dust) on take-off, at cruise, and upon landing. The debris enters the engine hot section, melts and forms a calcium-magnesiumaluminosilicate (CMAS) glass. The molten CMAS impacts and adheres to coated components in the engine hot-section, where infiltration into the coating materials can change coating chemistry and microstructure, modifying coating properties and performance, resulting in premature coating failure.<sup>20,</sup> <sup>21, 43</sup> Debris with higher melting points can pass through the engine without melting, while debris close to a eutectic melt composition are more likely to adhere to coated components.<sup>19</sup> Thus, the threat of thermochemical degradation of engine hot-section components by CMAS attack increases as engine operating temperatures increase; however, increases in engine operating temperatures improves fuel efficiencies and mitigates harmful  $CO_2$  and  $NO_x$  emissions. Therefore, it is important to understand the effects of temperature and composition on CMAS glass properties.

The primary glass property of importance to coating infiltration is CMAS viscosity ( $\eta$ ), which is defined as the ability of a liquid to resist fluid flow, and therefore can be used as a relative indication of coating infiltration threat.<sup>28, 36–40</sup> Other glass properties of interest due to the nature of the aero-engine thermal cycling include the linear coefficient of thermal expansion (CTE), softening temperature (or deformation temperature;  $T_d$ ), and glass transition temperature ( $T_g$ ). CMAS infiltration via intergranular transport, while also subjected to thermal cycling, will induce deleterious stresses at sites of CMAS attack. The threat of premature coating failure via through-coating crack formation will increase as CMAS CTE mismatch with the coating increases.<sup>41</sup> Whereas higher T<sub>d</sub> and T<sub>g</sub> are associated with earlier onset of stress accumulation on cooling, <sup>42</sup> lower T<sub>d</sub> and T<sub>g</sub> are associated with earlier onset of intergranular CMAS transport on heating.<sup>20</sup> Understanding the relationships of these properties with CMAS composition is key in improving the predictive capacity of thermochemical attack across the broad and compositionally complex CMAS-forming materials system. While simplification of CMAS compositional space to Ca-Mg-Al-Si oxide constituents is convenient, constraining the compositional space often ignores the influences of minor constituents and their potentially large impact on the glass structure and CMAS glass properties. Natural-forming CMAS glasses are compositionally complex, often containing six or more constituents, with composition dependent on geographic location as well as debris type.<sup>36, 112–115</sup> Additionally, dissolution of coating materials into the CMAS glass melt can further modify CMAS composition.<sup>22, 36</sup> Common coating-derived constituents include: Gd<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, Sc<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>. Their known effects on glass properties are limited to viscosity.<sup>31, 116, 117</sup> Coating constituent effect on network modifying or forming behavior is dependent on the glass composition, where coating dissolution increased viscosity in glass compositions rich with network modifying species.

Changes in CMAS composition will change the glass structure and allow cation species to be classified as glass network formers (which strengthen the network through the formation of bridging oxygens (BO)) or glass network modifiers (which weaken the network through the formation of non-bridging oxygens (NBO)).<sup>34, 35</sup> The more BO present in the solid structure, the more rigid it is, constraining vibrations of

individual atoms, and lowering CTE. T<sub>d</sub> and T<sub>g</sub> are intimately connected to the glass network structure, increasing with BO content or network rigidity. However, it should be noted that T<sub>g</sub> is not a fixed thermodynamic property of a material but instead a kinetic phenomenon dependent on the heating or cooling rate of the material.<sup>34</sup> Compositionally, the CaO-SiO<sub>2</sub> ratio has the greatest influence on CMAS viscosity,<sup>19, 31–33</sup> where Ca<sup>2+</sup> and Si<sup>4+</sup> are predominant glass network modifying and forming cations, respectively. Mg<sup>2+</sup> functions as a glass modifying species. However, MgO content in CMAS forming debris is relatively minor compared to CaO content.<sup>113, 115, 118</sup>

There also exist intermediate, or amphoteric, cation species where network modifying or forming behavior is dependent on glass composition.<sup>32, 119–121</sup> Al<sup>3+</sup> is one of these intermediate species. Al<sup>3+</sup> interactions with network modifying cations, such as Ca<sup>2+</sup> in the context of CMAS, can stabilize [AlO<sub>4</sub>]<sup>-</sup> tetrahedra which incorporates Al<sup>3+</sup> cations into the network, increases BO content and network rigidity, and affects glass properties. As a result, the total ratio of modifying glass species (i.e. Ca<sup>2+</sup>, Mg<sup>2+</sup>, or Na<sup>+</sup>) to intermediate species content, such as Al<sup>3+</sup>, should also be considered. Controlled changes in composition via fifth oxide additions to CMAS glass properties can be depicted as an effect of cation size. Cation size dictates the cation's coordination behavior with surrounding oxygen<sup>122</sup> and the ability to engage as an edge vs. corner sharing polyhedron in the network.<sup>123</sup>

Prior work has shown that controlled addition of Fe<sup>3+</sup> and Ti<sup>4+</sup> natural-forming oxides behave as glass network modifiers to the CMAS melt and lower viscosity.<sup>31</sup> However, the effect of coating-derived oxide additions used in existing and prospective thermal/environmental barrier coating (T/EBC) systems – such as yttria-stabilized zirconia, gadolinium zirconate, and rare-earth silicates – on CMAS glass properties has been primarily limited to viscosity.<sup>116, 117, 124</sup> In addition, the use of dilatometry to measure CMAS glass properties has been primarily limited to natural-forming CMAS materials. <sup>37, 125</sup> This study fills a key knowledge gap by evaluating the relationship between viscosity and dilatometric CMAS glass properties.

Increasing CMAS compositional complexity by introducing a fifth oxide was done to explore the effects of cation size on individual CMAS glass properties. Review of glass properties in both molten liquid (viscometry) and condensed amorphous (dilatometry) states allowed for implications of fifth oxide additions to glass network behavior to be inferred. This work specifically elucidates the effects of the iron oxide valence (Fe<sup>2+</sup> versus Fe<sup>3+</sup>), group IV metal cations (Ti<sup>4+</sup>, Zr<sup>4+</sup>, Hf<sup>4+</sup>), and RE metal cations (Gd<sup>3+</sup>, La<sup>3+</sup>, Lu<sup>3+</sup>, Nd<sup>3+</sup>, Sc<sup>3+</sup>, Y<sup>3+</sup>, and Yb<sup>3+</sup>; or RE<sup>3+</sup>) on measured viscosity, CTE, T<sub>d</sub>, and T<sub>g</sub>. Implications to coating performance will address the interplay of the properties explored in this study and then discuss the additional considerations for coating design: (i) coating effect on solubility within the melt, and (ii) precipitation behavior.

#### 4.2. Experimental

#### 4.2.1. Materials

The Ca 33 – Mg 9 – Al 13 – Si 45 (single cation mol%) CMAS composition used by Krämer et al.<sup>36</sup> is the nominal baseline composition for this study and is referred to as 0.73 C:S CMAS based on the 0.73 CaO-SiO<sub>2</sub> (C:S) ratio. Three nominal 0.73 C:S baseline CMAS glasses were investigated. Each was synthesized from different precursor powder providers and had their properties measured using viscometry and dilatometry. The first is the colorless baseline glass used in this study, the second turned red after synthesis and is thus termed 'red CMAS', and the third is the nominal 0.73 C:S baseline from the study by Webster and Opila.<sup>31</sup> Investigation of the effect of a fifth cation, denoted by X, was assessed by adding 5 or 10 mol% of oxide species X through changing relative amounts of Ca and Si while maintaining an 0.73 C:S ratio and holding Mg and Al content constant. Nominal compositions of synthesized CMAS and CMXAS

glasses are listed in Table 4.1 with the fifth oxide additions listed in Table 4.2. CMAS and CMXAS glasses were fabricated by mixing stoichiometric amounts of CaO, MgO, AlO<sub>1.5</sub>, SiO<sub>2</sub>, and XO<sub>Y</sub> – where Y is the number of stable oxygen anions bonded to a single metal cation X. Fifth oxide species were selected from naturally occurring siliceous debris compositions and coating species capable of dissolution into the glass melt.<sup>36, 112–115</sup> Color and transparency of bulk CMAS and CMXAS glasses are listed in Table C1, contained in Appendix C. Coordination with NBO and BO content was not identifiable with the experimental and computational techniques available during this study, literature on cation behavior in comparable materials systems was explored to evaluate realistic coordination with BO and NBO for each cation addition as a result.

Species (X <sup>n+</sup> )	Са	Mg	AI	Si	х	C:S Ratio	(C+M+X):A Ratio
0.73 C:S Baseline	33	9	13	45	0	0.73	3.23
0.73 C:S + 5%	30.75	9	13	42.25	5	0.73	3.44
0.73 C:S + 10%	28.75	9	13	39.25	10	0.73	3.67

Table 4.1: Nominal CMAS, CMXAS compositions studied (in single cation mol%)

Table 4.2 lists the metal oxides used in this study, their suppliers, and metal cation radii in the most likely predicted coordination states.<sup>97</sup> The  $(Y+Yb)^{3+}$  dual cation addition is an equimolar mixture of 5 single cation mol% of each  $Y^{3+}$  and  $Yb^{3+}$  oxides. Powder mixtures were ball milled with zirconia media ( $\geq$ 95% purity, Glen Mills Inc.; Clifton, NJ) for ~24 hours to mix the constituents. Ball milled powders were transferred to a 95% Pt-5% Au crucible (Heraeus Precious Metals; Santa Fe Springs, CA), underwent an isothermal hold for at least 4 hours at 1500°C to allow the melt to homogenize, and then were quenched in water.

Quenched glass was allowed to dry before densities were measured using Archimedes' method (Mettler Toledo, Model XSE205DU; Suwanee, GA) in DI water. Table 4.3 lists the compositions (as measured by semi-quantitative energy dispersive X-ray spectroscopy in single cation mol%), resultant C:S ratio, and measured densities for each glass composition investigated in this study.

Oxide Species	Classification	Cation Radii [Å] (CN) <sup>a</sup>	Supplier	Purity	Comments
Al <sub>2</sub> O <sub>3</sub>	Base constituent	0.39 (4); 0.535 (6)	Alfa Aesar	99.9%	Metals basis; <1 micron APS
					powder
			Thermo Fisher	99.997%	Metals basis; 40 micron
			Scientific		crystalline
	Base constituent	1.0 (6)	Alfa Aesar	99.95%	Metals basis
CaO			Spectrum Chemical	Reagent grade (100%)	N/A
			Mfg Corp		
MgO	Base	0.72 (6)	Alfa Aesar	99.99%	Metals basis
	constituent		GFS Chemicals	99.95%	
SiO2	Base	0.40 (4)	Alfa Aesar	99.9%	1.5 micron
0.02	constituent		Thermo Scientific	99.9%	1.5 micron
FeO	Natural-	0.63 (4); 0.78 (6)	Sigma Aldrich	99.6%	Trace metals basis
	forming				
Fe <sub>2</sub> O <sub>3</sub>	Natural-	0.49 (4);	Alfa Aesar	99.6%	Metals basis
-	forming	0.645(6)			
Gd <sub>2</sub> O <sub>3</sub>	Coating-	0.938 (6)	Praxair Surface	99.9%	
	derived	0.50(4)	Technologies		
HfO <sub>2</sub>	Coating- derived	0.58 (4); 0.71 (6)	Alfa Aesar	99.995%	(typically <0.2% Zr)
	Coating- derived	1.032 (6)	Praxair Surface	00.0%	SiO <sub>2</sub> content accounted for
La2312U7			Technologies		during synthesis
$Lu_2O_3$	Coating- derived	0.861 (6)	Praxair Surface	99 9%	
			Technologies		
$Na_2CO_3$	Natural- forming	1.0 (5)	Alfa Aesar	99.5%	Granular; Used to
					incorporate Na <sub>2</sub> O into the
					network, CO <sub>2</sub> volatilized
					during synthesis

Table 4.2: List of powders, suppliers, and cation radii for base constituents and fifth oxide additions used to synthesize CMXAS glasses

Nd <sub>2</sub> O <sub>3</sub>	Coating- derived	0.983 (6)	Praxair Surface Technologies	99.9%	
Sc <sub>2</sub> O <sub>3</sub>	Coating- derived	0.745 (6)	Elemental Metals	99.998%	
TiO <sub>2</sub>	Natural- forming	0.42 (4); 0.605 (6)	Alfa Aesar	99.8%	Rutile, metals basis
Y <sub>2</sub> O <sub>3</sub>	Coating- derived	0.9 (6)	Praxair Surface Technologies	99.9%	
Yb <sub>2</sub> O <sub>3</sub>	Coating- derived	0.844 (6)	Praxair Surface Technologies	99.9%	
(Y+Yb) <sub>2</sub> O <sub>3</sub>	Coating- derived	0.868 (6)	Praxair Surface Technologies	Same as above	Used Y <sub>2</sub> O <sub>3</sub> and Yb <sub>2</sub> O <sub>3</sub> powders to synthesize ~5 mole% each of Y <sup>3+</sup> & Yb <sup>3+</sup> ; average of cation radii
ZrSiO₄	Coating- derived	0.59 (4); 0.72 (6)	Alfa Aesar	Not listed	<2 micron powder; SiO <sub>2</sub> content accounted for during synthesis

<sup>a</sup>: CN stands for coordination number, which affects cation radius; reported Fe<sup>n+</sup> cation radii are from the high spin state

Species (X <sup>n+</sup> )	Са	Mg	AI	Si	х	C:S Ratio	Density [g/cm³]
0.73 C:S							
(this	30.1	9.3	13.6	47.0		0.64	2.807
study)							
Webster							
& Opila	33.7	9.0	13.7	43.6		0.77	2.781
0.73 C:S							
'red'	21.6	9.3	13.6	45.5		0.70	2.801
0.73 C:S	51.0						
5 Fe <sup>2+</sup>	27.6	9.8	14.2	42.9	5.6	0.64	2.905
5 Fe <sup>3+</sup>	29.5	8.2	12.6	43.9	5.8	0.67	2.904
10 Fe <sup>3+</sup>	29.9	8.6	12.9	41.8	6.9	0.71	2.951
5 Gd <sup>3+</sup>	26.1	10.5	14.6	44.0	5.0	0.59	3.143
5 Hf <sup>4+</sup>	30.0	7.4	12.0	45.5	5.0	0.66	3.176
10 La <sup>3+</sup>	24.9	9.2	13.3	41.1	11.6	0.61	3.283
10 Lu <sup>3+</sup>	26.4	8.3	11.8	44.1	9.5	0.60	3.536
5 Na⁺	29.3	9.7	13.6	42.8	4.6	0.69	2.789
10 Nd <sup>3+</sup>	25.0	9.2	12.9	38.7	14.4	0.65	3.265
10 Sc <sup>3+</sup>	28.2	9.0	12.9	41.7	8.3	0.68	2.907
5 Ti <sup>4+</sup>	28.5	9.4	13.4	43.1	5.7	0.66	2.882
10 Y <sup>3+</sup>	28.2	9.2	13.9	41.7	7.0	0.68	2.943
10 Yb <sup>3+</sup>	28.7	7.2	11.2	42.8	10.1	0.67	3.623
5Y <sup>3+</sup> &	20.7	7.1	10.3	42.6	4.6 (Y);	0.72	2.264
5Yb <sup>3+</sup>	30.7				4.8 (Yb)		3.301
5 Zr <sup>4+</sup>	32.8	8.0	12.8	42.6	3.8	0.77	2.942

Table 4.3: Composition (mole %) as measured by EDS and density of CMXAS fifth oxide additions

#### 4.2.2. Characterization Techniques

Scanning electron microscopy (SEM; FEI Technologies Inc., Quanta 650; Hillsboro, OR) was performed in a high vacuum setting (<0.25 mTorr) in back-scattered electron (BSE) mode and semi-quantitative energy dispersive X-ray spectroscopy (EDS; Oxford Instruments Aztec X-MaxN 150; Abingdon, Oxfordshire, UK) were used to evaluate homogeneity and quantify elemental composition of bulk CMXAS glass materials synthesized. CMAS and CMXAS glasses were prepared for SEM by affixing a variety of sized and shaped glass fragments which formed during the quenching process to a stub with carbon tape. The CMAS and CMXAS glass fragments were sputter coated with Au-Pd to ensure a conductive surface for SEM/EDS. EDS was performed on fragments with flat surfaces. Reported EDS measurements are area measurements (<100  $\mu$ m) from at least three sites per fragment from at least two fragments. The use of multiple fragments was done to improve statistical randomization. The elemental sensitivity of EDS was reported to be >0.1 wt%.

Bulk glasses were powdered using a mortar and pestle and X-ray diffraction (XRD; PANalytical, Empyrean; Royston, UK) was performed on powdered glasses to confirm all compositions were amorphous. Select compositions are shown in Figure C1, contained in Appendix C. Cu K $\alpha$  radiation in a Bragg-Brentano geometry with a linear detector was used in an ambient, lab air environment over a 2 $\theta$  range of 15° to 70° with a step size of 0.0140°.

X-ray fluorescence spectroscopy (XRF; Panalytical, Epsilon 3x; Ivyland, PA), which can measurably detect individual elements at <10 ppm, was conducted on powdered baseline CMAS glasses and allowed for more accurate C:S ratio measurements than those reported by EDS. Concentrations were determined by loading powdered glass material in an 18 mm sample cup with a ~2.5 um Mylar foil lining the bottom. The OMNIAN (internal standards) methodology was used. Applied corrections accounted for finite thickness effects and effects due to fluorescence volume geometry. Processing parameters included the loose powder state of the sample as well as the theoretical density before normalizing the data to 100%. The Compton intensity was used to validate the analysis. All data was measured as oxide wt% to account for the presence of oxygen in the material and then converted to single cation mol% for comparison with EDS results. XRF samples with elemental content reported as 5 ppm to 9.9 ppm were rounded to 0.001%. No compositional constraints were used.

Viscosities of molten CMAS and CMXAS glasses were measured using an Orton RSV-1600 viscometer furnace (Westerville, OH) and a Brookfield HA-DV2T viscometer unit (Middleboro, MA). A 50 mL 95% Pt-5% Au crucible (Heraeus Precious Metals) was filled with 31.6 mL of glass. Molten CMAS and CMXAS glasses were held at 1550°C for at least 60 minutes to allow the melt to equilibrate. Viscosity measurements were performed between furnace temperatures of 1550°C and 1300°C in 25°C intervals, where measurements occurred during a 30-minute hold, and glass was cooled at a rate of 2.5°C/min between holds. The furnace was shut off at the end of the run and air-cooled to room temperature. Viscosity ( $\eta$ ) is determined from the constant angular velocity of the spindle (RPM) and spindle torque ( $\tau$ ), shown below in Equation 4.1.

$$\eta = \frac{100}{RPM} \times TK \times SMC \times \tau \tag{4.1}$$

Where TK and SMC are the torque constant and spindle multiplier constant, respectively. Equation 1 and the values pertaining to each constant were provided by the Orton RSV-1600 instrument manual and viscometer software, respectively. The viscosity of a borosilicate glass standard (NIST SRM 717a, Sigma Aldrich; St. Louis, MO) was measured on cooling between 1360°C and 1000°C using a cooling rate of 2°C/min and compared to a calibration curve. Equipment accuracy was evaluated between 1250°C to 1350°C because CMAS melts ~1200°C and the possibility of the glass increasing viscosity outside of the measurable limit of the instrument greatly increases at temperatures less than  $1250^{\circ}$ C. The viscosity standard was measured once at the beginning of the study and again at the end of the study, resulting in a % error of  $2.03 \pm 0.276\%$  and  $0.418 \pm 0.152\%$ , respectively, confirming accuracy of the supplied constants (Figure C2). Additionally, viscosity measurements were shown to be repeatable on a second batch produced of a  $10Fe^{3+}$  specimen (Figure C3).

In-situ precipitation events occurred during viscometry of some glasses. Precipitation of crystallites from the CMXAS glasses were investigated through isothermal holds in an open-air box furnace (CM Furnaces; Bloomfield, NJ). Excess CMXAS glasses were melted in 95% Pt-5% Au crucible and held at 1500°C for 4 hours to allow the melt to homogenize before the furnace temperature was lowered to perform the isothermal hold for ~16 hours at temperatures listed in Table 4.4. Samples were pulled from the furnace at temperature and water quenched to avoid crystallization during slow cooling. SEM/EDS and XRD, following approaches previously outlined, were used to characterize CMXAS precipitates. Phase identification of the XRD spectra used PANalytical HighScore Plus (version 4.9) analysis software and ICDD PDF-5+ database.<sup>126</sup> In some cases XRD of precipitates resulting from viscometry experiments were used as precipitates from the isothermal hold did not yield enough material to overcome background signal from the CMXAS glass.

Dilatometry (NETZSCH, DIL402c; Burlington, MA) of condensed amorphous CMAS and CMXAS glass rods was performed on a cylindrical glass rod to measure linear CTE,  $T_d$ , and  $T_g$  of each glass composition. A calibration run was performed on an Al<sub>2</sub>O<sub>3</sub> standard of 15 mm in length and 6 mm in diameter. Glass rods were drawn from the melt using a COE 33 borosilicate glass rod as the molten glass air-cooled from ~1500°C through a workable temperature. Drawn CMXAS rods were cut to 15mm lengths with a diameter of 2.5 ± 0.5 mm and loaded into the dilatometer horizontally. Dilatometry was performed with alumina differential scanning calorimetry (DSC) pans (MSE Suppliers; Tucson, AZ) protecting the alumina pushrod from reacting with the CMXAS glass rods. The NETZSCH DIL402c software was used to collect data while Proteus analysis software (version 5.2) was used to analyze and export data. The temperature precision of the DIL402c is 0.1K and resolution of the pushrod is 1.25 nm.

The CMXAS rods were heated from room temperature to 900°C at 10°C/min in two consecutive runs. The first run softened the glass rod faces, creating a flush interface on the dilatometer components and allowed each sample to undergo identical thermal treatment prior to characterizing glass properties on the second run. Therefore, the data collected from the second runs can be considered directly comparable for each glass composition. At least three trials, consisting of individual specimens, with two runs conducted on each specimen were performed for each glass composition. All reported values are averages and standard deviations from the second run of each trial. Linear CTE was determined over the temperature range of 200-600°C, averaging the difference in the change in length with respect to temperature between the datapoints collected in this temperature range (2 pts/°C). The contact forces involved in pinning the sample in the dilatometer allowed for determination of T<sub>d</sub>, which is defined as the temperature at which the glass rod achieved maximum expansion before mechanically deforming due to compression from the 25 cN contact force.  $T_g$  was determined as the onset temperature at which the glass rod began to increase its rate of thermal expansion. It should be noted that Tg as measured by dilatometry is not equivalent to T<sub>g</sub> as measured by calorimetry due to the contact forces employed in dilatometry. Figure 4.1 displays the dilatometry heating curve of a glass rod and visualizes CMAS CTE, T<sub>d</sub>, and T<sub>g</sub> feature identification.



Figure 4.1: CMXAS dilatometer data with CMAS CTE,  $T_d$ , and  $T_g$  properties visualized.

#### 4.3. Results

#### 4.3.1. Baseline CMAS Glass Properties

Figure 4.2 contains the (a) compositions as determined by XRF of the as-made glasses, (b) temperature dependence of measured baseline CMAS viscosities, (c) average CMAS CTE measurements, and (d) dilatometric  $T_g$  vs  $T_d$  of the condensed amorphous glassy baseline CMAS specimens. The measurements captured in Figure 4.2 shows how small changes in C:S ratio are accompanied by measurable changes in glass properties. The C:S ratio as determined by XRF (Figure 4.2a) yielded a direct relationship with CMAS CTE and an indirect relationship with CMAS viscosity,  $T_d$ , and  $T_g$ . The variability between measured viscosities of the three nominal baseline CMAS glasses was ~0.2 Log (Pa-s) across all temperatures, which indicates the glass melt structure functioned similarly between specimens (Figure 4.2b). Significant variability of the baseline CMAS samples was not exhibited for CMAS CTE due to overlap of the stand deviation (Figure 4.2c) but was observed for  $T_d$  and  $T_g$  (Figure 4.2d).

The following results investigate fifth oxide species additions on CMXAS glass properties, where the results are depicted as the effect of an assumed cation size on the investigated property. Since cation coordination with NBO and BO content was not identifiable during this study, as mentioned previously, literature on cation behavior in comparable materials systems was consulted to inform realistic assumptions of coordination for each cation addition. Effective radii for various coordination geometries of each cation species<sup>97</sup> are listed in Table 4.2. Cation size selection will be addressed in the discussion. Natural-forming additions and coating-derived additions were separated to identify differences in their behaviors.



Figure 4.2: Characterization of 0.73 CaO-SiO<sub>2</sub> CMAS made from variable powder sources demonstrates how small changes in CaO-SiO<sub>2</sub> ratio measurably affect glass properties as depicted by (a) glass composition in single cation mol% quantified by XRF, (b) temperature dependence of viscosity measurements, (c) average linear CTE between 200-600°C vs. CaO-SiO<sub>2</sub> ratio as measured by XRF, and (d) dependence of measured T<sub>d</sub> on T<sub>g</sub>. Legend in (b) also applies to (c) and (d). Lines connecting symbols in (b) are only to serve as a visual aid.

### 4.3.2. Viscometry of Fifth Oxide Additions

Figure 4.3 contains the (a, b) temperature dependence of measured viscosities as a function of assumed cation radius and (c, d) the temperature dependence of the difference in measured viscosity between species additions and the baseline composition. Results are categorized by natural-forming species

additions (a, c) and coating-derived species additions (b, d). The solid horizontal lines in Figures 4.3a and 4.3b represent the measured average value for the baseline CMAS composition at each of the temperatures explored. Viscosity measurements are plotted in 50°C increments to improve the readability of the figure. Figure 4.3a shows natural-forming oxide additions to CMAS – which included  $X = 10Fe^{3+}$ ,  $5Fe^{3+}$ ,  $5Ti^{4+}$ ,  $5Fe^{2+}$ , and  $5Na^+$  – decreased CMAS viscosity and operate as network modifying species where CMXAS viscosity generally increased as assumed cation size increased. The formation of crystalline precipitates can be used to indicate stability of the glass melt. The glass melt remained homogeneous for all natural-forming species additions across all temperatures explored.

Figure 4.3c shows the Na<sup>+</sup> addition had the least effect on viscosity of natural-forming additions. There were notable decreases in viscosity as temperature increases for the 5Fe<sup>2+</sup> (~0.2-0.25 Log (Pa-s)), 5Fe<sup>3+</sup> (~0.3-0.35 Log (Pa-s)), and 10 Fe<sup>3+</sup> (~0.4-0.5 Log (Pa-s)) additions, with the 5Fe<sup>3+</sup> addition showing a greater decrease than the 5Fe<sup>2+</sup> addition. Figure 4.3c also shows how the difference in viscosities of the 5Fe<sup>2+</sup>, 5Fe<sup>3+</sup>, and 10Fe<sup>3+</sup> additions decreased as temperature increased. The temperature dependence of this difference in viscosity indicated the Fe<sup>n+</sup> additions have a greater modifying effect on the network structure at lower temperatures. The Ti<sup>4+</sup> addition decreased viscosity measurements by ~0.25 Log (Pa-s) across all temperatures. It was observed that Ti<sup>4+</sup> additions behave difference are described in the discussion.

Figure 4.3b shows coating-derived species additions – which included X =  $5Gd^{3+}$ ,  $5Hf^{4+}$ ,  $10La^{3+}$ ,  $10Nd^{3+}$ ,  $10Sc^{3+}$ ,  $10Yb^{3+}$ ,  $10Y^{3+}$ ,  $5Zr^{4+}$ , and  $(5Y+5Yb)^{3+}$  – generally decreased viscosity as cation size increased, opposite to what is seen in the natural-forming species additions.  $Hf^{4+}$  and  $Zr^{4+}$  additions both increased CMAS viscosity, with the  $Hf^{4+}$  addition having the greater effect, compared to the 0.73 C:S CMAS. Differences in behavior between Group IV and  $RE^{3+}$  additions will be addressed in the discussion. All measured CMXAS viscosities are contained in Table C3.

Figure 4.3d shows Y<sup>3+</sup>, Yb<sup>3+</sup>, Lu<sup>3+</sup>, Sc<sup>3+</sup>, and (Y+Yb)<sup>3+</sup> additions exhibited an increase in the difference in viscosities as temperature increased, indicating these species additions have a greater modifying effect on the network structure at higher temperatures. Lu<sup>3+</sup> and Y<sup>3+</sup> additions showed an increase in viscosity at lower temperatures, 1315°C and 1290°C respectively, compared to the 0.73 C:S CMAS. Precipitation was observed to affect viscosities of some CMXAS compositions as temperatures were decreased and are addressed in depth in the following section. Hf<sup>4+</sup>, La<sup>3+</sup>, Nd<sup>3+</sup>, Yb<sup>3+</sup>, (Y+Yb)<sup>3+</sup>, and Zr<sup>4+</sup> additions all exceeded solubility limits where in-situ precipitation changed glass composition resulting in an increase in viscosity. As a result, viscosity measurements at temperatures after precipitation occurred are not shown in Figure 4.3b, but are shown in Figure 4.3d and reported in Table C3.



Figure 4.3: Temperature dependence of (a, b) measured viscosities and (c, d) differences from comparable baseline CMAS compositions of (a, c) natural-forming and (b, d) coating-derived CMXAS fifth oxide additions. The solid horizontal lines in (a) and (b) represent the measured average value for the baseline CMAS composition at each of the temperatures explored. Whereas the line at 0 Log (Pa-s) in (c) and (d) represents the average value for baseline CMAS composition. Lines connecting symbols in (c) and (d) are only to serve as a visual aid. Legend in (b) applies to all graphs. Shaded portion of (d) applies to the inset. NOTE: X-axes in (a) and (b) as well as y-axes in (c) and (d) are dissimilar to best depict trends in the data.

#### 4.3.3. Dilatometry of Fifth Oxide Additions

Dilatometry was performed on CMXAS glasses to measure CTE,  $T_d$ , and  $T_g$  (Figures 4.4, 4.5, and 4.6, respectively) and are plotted against the assumed cation size of fifth oxide additions. It should be noted that the solid horizontal lines represent the measured average value for the baseline CMAS composition, where the dashed lines surrounding it represent one standard deviation. CMXAS CTE measurements had the greatest variability which resulted in large error bars. As a result, general observations are made with respect to trends in average CTE measurements. CMXAS CTE measurements of 5% natural-forming additions appeared to increase as assumed cation size increased, with the 5Na<sup>+</sup> addition being the only composition to significantly differentiate from the baseline CMAS (Figure 4a). CMXAS CTE measurements of coating-derived additions generally increased as assumed cation size increased, with the CTE of lanthanide species additions generally trending inversely with atomic mass (Figure 4b). The 5Hf<sup>4+</sup> addition had the greatest effect on CMXAS CTE of all fifth oxide additions. The 5Gd<sup>3+</sup> addition had no effect on CMXAS CTE, while 10La<sup>3+</sup> and 10Nd<sup>3+</sup> additions were the only species to increase CMXAS CTE. All smaller RE<sup>3+</sup> additions showed significant effects on CMXAS CTE, decreasing CTE relative to the baseline CMAS. This delineation between RE<sup>3+</sup> species will be addressed in the discussion.



Figure 4.4: Measured CTE between 200-600°C of (a) natural-forming and (b) coating-derived CMXAS fifth oxide additions. The solid horizontal lines represent the measured average value for the baseline CMAS composition with the dashed line being one standard deviation. NOTE: X-axis range in (b) is reduced to highlight the range of coating-derived cation radii.

CMXAS T<sub>d</sub> and T<sub>g</sub> measurements of natural-forming additions, shown in Figures 4.5a and 4.6a respectively, do not have enough datapoints to confidently state a trend. However,  $10Fe^{3+}$ ,  $5Fe^{3+}$ ,  $5Fe^{2+}$ , and  $5Na^+$ additions decreased CMXAS T<sub>d</sub> and T<sub>g</sub>.  $5Fe^{2+}$  had a greater effect than  $5Fe^{3+}$ , which is opposite to what was observed in viscometry. The Ti<sup>4+</sup> specimen increased CMXAS T<sub>d</sub> but had little-to-no effect on CMXAS T<sub>g</sub>. Discussion of glass properties will be grouped by periodic families (i.e. Ti<sup>4+</sup> is discussed among group IV additions) with implications to coating performance to follow in the discussion. CMXAS T<sub>d</sub> and T<sub>g</sub> of coating-derived species, shown in Figures 4.5b and 4.6b respectively, generally decreased as assumed cation radius increased. All coating-derived species significantly increased CMXAS T<sub>d</sub> and T<sub>g</sub> relative to the baseline CMAS, except for  $5Gd^{3+}$ ,  $10La^{3+}$ , and  $10Nd^{3+}$  additions which had little effect on CMXAS T<sub>g</sub> measurements.  $10Y^{3+}$  and  $10Yb^{3+}$  additions were the only single cation  $RE^{3+}$  species to show observable deviations from the trend in CMXAS T<sub>g</sub> measurements. The separation of  $RE^{3+}$  additions into two categories based on their cation size based on the dilatometric glass properties covered here will be addressed in the discussion. All CMXAS CTE, T<sub>d</sub>, and T<sub>g</sub> measurements are contained in Table C4.



Figure 4.5: Measured T<sub>d</sub> of (a) natural-forming and (b) coating-derived CMXAS fifth oxide additions. The solid horizontal lines represent the measured average value for the baseline CMAS composition with the dashed line being one standard deviation. NOTE: X-axis range in (b) is reduced to highlight the range of coating-derived cation radii.



Figure 4.6: Measured T<sub>g</sub> from dilatometry of (a) natural-forming and (b) coating-derived CMXAS fifth oxide additions. The solid horizontal lines represent the measured average value for the baseline CMAS composition with the dashed line being one standard deviation. NOTE: X-axis range in (b) is reduced to highlight the range of coating-derived cation radii.

#### 4.3.4. Relationships Between Glass Properties

Figure 4.7 shows the relationship between measured glass properties for all compositions investigated and demonstrates how condensed amorphous glass properties are correlated amongst one another (Figures 4.7a-c). A linear trend was observed between CMXAS  $T_d$  and  $T_g$ , where an increase in  $T_g$  generally corresponds with an increase in  $T_d$  (Figure 4.7a). The Yb<sup>3+</sup> and (Y+Yb)<sup>3+</sup> additions are shown to follow the broad trends of all compositions contained in Figure 4.7a despite their notable increase in  $T_g$  (see Figure 4.6b). Figures 4.7b and 4.7c show that decreases in CTE are generally accompanied by increases in  $T_d$  and  $T_g$ . The relationship between CMXAS viscosity at 1500°C (prior to any precipitation events occurring) against CTE was found to have a weaker trend relative to comparisons between dilatometric glass properties (Figure 4.7d). The compositional effect of fifth oxide additions on glass structure as well as implications to coating performance will be addressed in the discussion.



Figure 4.7: Glass property correlation of (a) T<sub>d</sub> versus T<sub>g</sub>, (b) T<sub>d</sub> versus CTE, (c) T<sub>g</sub> versus CTE, and (d) viscosity measured at 1500°C versus CTE measurements of CMXAS glasses. CTE was determined between 200 and 600°C.

# 4.3.5. Precipitation and Crystallization of CMXAS Glasses

XRD of crystalline CMXAS precipitates was completed (Figure 4.8a). XRD was conducted on  $Hf^{4+}$  and  $Zr^{4+}$  precipitates from viscometry experiments as precipitates from the isothermal hold did not yield enough material to overcome background signal from the glass.  $Hf^{4+}$  and  $Zr^{4+}$  additions precipitated their constituent oxides (monoclinic  $HfO_2$  and  $ZrO_2$ ).<sup>127</sup> Precipitation in  $Hf^{4+}$  and  $Zr^{4+}$  additions occurred

homogenously, leaving no crystalline products on any interfaces of the crucible post-viscosity measurement. The solubility limits for Hf<sup>4+</sup> and Zr<sup>4+</sup> were identified by measuring residual glass composition from the surface of the melt after cooling using semi-quantitative EDS. Hf<sup>4+</sup> and Zr<sup>4+</sup> composition in the glass ranged between 3.2 to 3.7 mol% and 3 to 3.5 mol%, respectively. XRD patterns of all RE<sup>3+</sup> precipitate materials shown in Figure 4.8a are from the isothermal hold conducted in an open-air box furnace and are consistent with XRD conducted on precipitates that formed during viscometry. La<sup>3+</sup>, Nd<sup>3+</sup>, Yb<sup>3+</sup>, and (Y+Yb)<sup>3+</sup> additions precipitated a Ca-stabilized RE-apatite (Ca<sub>2</sub>RE<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>)<sup>128</sup> during viscometry and on cooling, where heterogeneous precipitation occurred along the surface of the glass and walls of the crucible. Solubility limits for La<sup>3+</sup>, Nd<sup>3+</sup>, Yb<sup>3+</sup>, and (Y+Yb)<sup>3+</sup> additions were not determined due to the nature of heterogenous precipitation creating a non-uniform concentration gradient throughout the material container. It should be noted that RE-apatite growth occurred to a greater amount during the gradual air-cooling process concluding viscometry compared to the limited amount of precipitation that occurred during the isothermal box furnace hold.

Figure 4.8b shows the temperature dependence of measured viscosities for Hf<sup>4+</sup>, La<sup>3+</sup>, Nd<sup>3+</sup>, Yb<sup>3+</sup>, (Y+Yb)<sup>3+</sup>, and Zr<sup>4+</sup> additions, including the change in viscosity post-precipitation. Precipitation in the La<sup>3+</sup> and Nd<sup>3+</sup> additions occurred at the highest temperature of ~1440°C, while the Yb<sup>3+</sup> addition had precipitation occur at the lowest temperature of ~1290°C. No trends with the delta viscosity of each fifth oxide addition affected by in-situ precipitation were observed when compared against cation size (Figure 4.8c). Delta viscosity was quantified as the difference in the melt stabilized viscosity measurement post-precipitation and the extrapolation of the viscosity measurement in-solution to the temperature at which post-precipitation viscosity stabilized (i.e. the temperature after precipitation was observed). The average of the slope between each datapoint in-solution was used to perform this extrapolation. Delta viscosity for the Yb<sup>3+</sup> addition, which did not measure viscosity beyond initiation of precipitation, was estimated based

on the post-precipitation measurement for the (Y+Yb)<sup>3+</sup> addition. The striped bar indicates the initial change due to precipitation measured in the Yb<sup>3+</sup> addition between ~1315°C and ~1290°C, while the open bar indicates the extrapolation from the (Y+Yb)<sup>3+</sup> addition to achieve melt stabilization between ~1365°C and ~1340°C. These results are summarized for all compositions in Table 4.4. No RE<sup>3+</sup> specimens crystallized during dilatometry, while the 5Fe<sup>2+</sup> specimen showed minor crystallization at the glass rod contact points.

Extrapolated Δη **Species** T<sub>precipitation</sub> [°C] T<sub>dwell</sub> [°C] Phase(s) Identified (X<sup>n+</sup>) [Log (Pa-s)] 5Hf<sup>4+</sup> Monoclinic HfO<sub>2</sub> [Ref. 127] 0.57 1410 1390 5La<sup>3+</sup> 1440 1425 Ca2La8(SiO4)6O2 [Ref. 128] 0.71 10Nd<sup>3+</sup> Ca2Nd8(SiO4)6O2 [Ref. 128] 1440 1425 0.65 10Yb<sup>3+</sup> 0.48-0.80\* Ca<sub>2</sub>Yb<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> [Ref. 128] 1290 1275 10(Y+Yb)<sup>3+</sup> 0.70 1365 1350 Ca<sub>2</sub>(0.5Y+0.5Yb)<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> 5Zr<sup>4+</sup> 0.13 1390 1350 Monoclinic ZrO<sub>2</sub> [Ref. 127]

Table 4.4: Summary of precipitation phenomenon

\*: Viscosity measurement of a stabilized melt post-precipitation did not occur;  $(Y+Yb)^{3+}$  showed similar initial increases in viscosity to  $Yb^{3+}$  so the final increase to achieve melt stabilization in  $(Y+Yb)^{3+}$  viscosity (~0.32 Log (Pa-s)) was used to approximate a delta viscosity of ~0.80 Log (Pa-s) for  $Yb^{3+}$ .



Figure 4.8: Characterization of in-situ precipitation in molten CMXAS glasses via (a) XRD of precipitates, (b) viscosity measurements of CMXAS specimens displaying in-situ precipitation, and (c) delta viscosities of the post-precipitation measurement from an extrapolation of viscosity in-solution. Shaded portion of (b) refers to the inset. Lines connecting symbols in (b) are only to serve as a visual aid. Striped portion of Yb delta viscosity in (c) reflects the initial change in viscosity measurement before melt stabilization was achieved and the open portion reflects the extrapolation to achieve melt stabilization applied from Y+Yb addition.

#### 4.4. Discussion

#### 4.4.1. Characterization of CMAS Glass Properties

The measured viscosities of baseline CMAS glasses are less than those reported in a similar C:S ratio glass (35Ca-10Mg-7Al-48Si) by ~1.3 Log (Pa-s) at ~1515°C.<sup>116</sup> This is likely due to the increased total modifier cation content used in this study, and therefore decrease in silica content, further reinforcing how small fluctuations in silica content can result in measurable changes to CMAS viscosity. The Tg reported in this study is not comparable to calorimetric Tg. Dilatometric Tg relies on thermal expansion, where the use of mechanical contact forces results in observation of Tg at lower temperatures compared to calorimetry. Where calorimetry relies on differences in heat flow without any mechanical interactions. However, the relationship between dilatometric Tg with composition has been shown to yield nearly identical trends with calorimetric Tg.<sup>129</sup> The CTE reported by Ericks et al. calculated with the Fluegel model ( $8.81°C^{-1} \times 10^{-6}$ )<sup>130</sup> is significantly lower than the CTEs measured in this study for all three CMAS glasses ( $9.27-9.88°C^{-1} \times 10^{-6}$ ). This could be due to differences in temperature range of CTE (range not stated in Ericks et al. calculation) or the nature of the Fluegel model relying on a statistical analysis of commercial glass compositions to calculate glass properties rather than a thermodynamic approach.<sup>31</sup> As a result, investigation of the composition – structure – property relationships are needed to improve prediction of CMAS glass properties and material performance.

Figure 4.7 shows that small variations in CMAS and CMXAS compositional complexity can be correlated among the condensed amorphous CMAS/CMXAS glass properties. Natural-forming CMAS debris often spans a large compositional space in addition to being compositionally complex. They also often contain multiple modifying cation constituents (like Ca, Fe, Na, K, or Mg), which can negatively impact CMAS properties (decrease viscosity, increase CTE, decrease Tg/Td), and increase the risk of premature coating failure. <sup>37, 125</sup> For example, Wiesner and Bansal performed dilatometry on several natural-forming CMAS compositions (23.3CaO–6.4MgO–3.1Al<sub>2</sub>O<sub>3</sub>–62.5SiO<sub>2</sub>–4.1Na<sub>2</sub>O–0.5K<sub>2</sub>O–0.04Fe<sub>2</sub>O<sub>3</sub> and 7.8CaO–4MgO–5Al<sub>2</sub>O<sub>3</sub>–61.6SiO<sub>2</sub>–0.6Fe<sub>2</sub>O<sub>3</sub>–1K<sub>2</sub>O, both in mol%).<sup>37, 125</sup> with dilatometric CTE, T<sub>d</sub>, T<sub>g</sub> measurements of 9.32 x 10<sup>-6</sup> °C<sup>-1</sup> (25 to 690°C), 751°C, 691°C and 9.8 x 10<sup>-6</sup> °C<sup>-1</sup> (25 to 700°C), 764°C, 706°C, reported respectively for each composition. Despite having much lower C:S ratios, the natural-forming CMAS glasses performed similarly to the baseline CMAS reported in this study likely due to the presence of additional modifying cations. The CTE, T<sub>d</sub>, T<sub>g</sub> measurements of the natural-forming CMAS agree with the range of data reported in Figure 4.7. Therefore, property relationships between CMAS and CMXAS glasses porferies can be expensive with respect to physical, monetary, and temporal resources. Computational thermodynamics, such as FactSage<sup>73</sup> and Thermo-Calc<sup>74</sup> property models, and compositionally driven descriptors, such as cation field strength<sup>34, 131</sup> and optical basicity,<sup>132</sup> pose promise to predict glass properties while minimizing resource consumption.<sup>31, 40</sup> Investigation of some of these non-experimental approaches will be made in the following chapter.

#### 4.4.2. Effects of Iron Cations

This work assumed Fe<sup>3+</sup> adopted high spin complexes which would increase the number of unpaired electrons (due to crystal field splitting) and allow cation incorporation into the glass network by forming tetrahedral structures with BO.<sup>133–136</sup> Crystal field theory dictates a high-spin Fe<sup>3+</sup> will have five unpaired electrons, and therefore operate as an amphoteric species, competing with Al<sup>3+</sup> for Ca<sup>2+</sup> to stabilize the [FeO<sub>4</sub>]<sup>-</sup> tetrahedral structure to adopt 4-fold coordination with surrounding oxygen. While it is possible

for Fe<sup>2+</sup> to stabilize tetrahedral structures, it is most likely to occur in basic, alkaline-rich glasses and, therefore, unlikely to have occurred in this work.<sup>137, 138</sup> Fe<sup>2+</sup> typically functions as a network modifier and stabilizes an octahedral structure.<sup>133–136</sup>

Decoupling iron valence post-synthesis – which was not performed for this study – requires specialized methods and equipment, such as Mössbauer absorption spectroscopy,<sup>139, 140</sup> electron spin resonance,<sup>141</sup> or X-ray absorption fine structure.<sup>142</sup> It is noted that Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios can fluctuate with Fe<sup>3+</sup> forming from oxidation of Fe<sup>2+</sup> at the atmospheric interface. Conversely, it is possible for Fe<sup>3+</sup> to be reduced to Fe<sup>2+</sup> in oxygen deficient environments. It is highly likely that FeO oxidized to form Fe<sub>2</sub>O<sub>3</sub> during synthesis. EDS measurements of glass composition of 5Fe<sup>2+</sup> and 5Fe<sup>3+</sup> specimens, contained in Table 4.3, show slight differences in iron cation content and CaO-SiO<sub>2</sub> ratios (5.6 and 5.8; 0.64 and 0.67, respectively). Where the differences in viscosity measurements between the 5Fe<sup>2+</sup> and 5Fe<sup>3+</sup> specimens are similar to the differences in viscosities measurements between CMAS glasses with differing CaO-SiO<sub>2</sub> ratios (Figure 4.9).



Figure 4.9: Difference of measured CMXAS viscosities from the baseline CMAS of (a) Fe-additions varying in amount and initial valence as well as (b) CMAS glasses with different measured CaO-SiO<sub>2</sub> ratios. The solid horizontal line represents the measured values for the baseline CMAS composition at each of the temperatures explored.
The greater iron content and CaO-SiO<sub>2</sub> ratio would also explain why the  $5Fe^{3+}$  addition has a lower CTE as well as greater T<sub>d</sub> and T<sub>g</sub> than the  $5Fe^{2+}$  addition in the condensed amorphous state (Figures 4.4a, 4.5a, and 4.6a). The interaction between  $Fe^{3+}$  with  $Al^{3+}$  in the condensed amorphous state increases glass network polymerization, or formation, at temperatures near and below T<sub>g</sub>. This same phenomenon has a strong modifying effect in the liquid state, where cation diffusion allows the amphoteric  $Fe^{3+}$  ions to disrupt the network and decrease CMAS viscosity as shown by work on iron-containing sodium-aluminosilicate melts.<sup>140</sup> This also explains why trends observed in molten viscosity measurements for  $5Fe^{3+}$  and  $5Fe^{2+}$  additions were reversed when measuring properties in the condensed amorphous glass state. Similar trends in  $5Fe^{3+}$  impact on viscosity relative to the  $5Ti^{4+}$  have been shown.<sup>31</sup>

Literature on iron valence shows significant differences in measured glass properties.<sup>140, 143–145</sup> Fe<sup>3+</sup> has been shown to decrease viscosity and depolymerize the melt structure,<sup>124</sup> while also increasing solubility of Zr<sup>4+</sup> and Hf<sup>4+</sup> coating constituents<sup>130</sup> relative to simpler glass compositions.<sup>146</sup> The results reported in this study have shown the presence of iron is unequivocally disadvantageous to CMAS viscosity with the 10Fe<sup>3+</sup> addition having the greatest effect on viscosity out of any CMXAS composition while also increasing CMAS CTE. Figure 4.3c shows how increasing Fe<sup>3+</sup> content from 5% to 10% decreases viscosity by ~0.15 Log (Pa-s), which is greater than the difference between the 5Gd<sup>3+</sup> and any 10RE<sup>3+</sup> addition. Spontaneous crystallization in all CMFAS glasses synthesized was also observed on cooling post-viscometry. Additionally, the Fe<sup>2+</sup> specimen crystalized if a large enough thermal gradient was present during quenching, further indicating the severity CMFAS harbors to coating performance in the thermal cycling aero-engine environment.

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## 4.4.3. Effects of Group IV Metal Cations

Mysen and Neuville<sup>147</sup> showed that Ti<sup>4+</sup> coordination within Ti-bearing sodium silicate glasses and melts has a temperature dependence. Near T<sub>g</sub> the Ti<sup>4+</sup> is tetrahedrally coordinated but increasing temperature above T<sub>g</sub> decreased the amount of tetrahedrally coordinated Ti<sup>4+</sup> by increasing NBO coordination, which allowed formation of 5- and 6-fold coordinated Ti<sup>4+</sup>. This explains the deviation in Ti<sup>4+</sup> specimen property measurements between the molten liquid and condensed amorphous glass states. As a result, trends in this study were shown assuming Ti<sup>4+</sup> cation sizes in 4-fold coordination for the condensed amorphous glassy state and 6-fold coordination for the liquid melt. Ti<sup>4+</sup> had little effect on CTE and T<sub>g</sub> (Figure 4.4a and 4.6a) implying it functions as a weak network former in the condensed amorphous state. This is expected as Ti<sup>4+</sup> should have very little NBO coordination while in the tetrahedral coordination structure.<sup>148</sup> The effect of Ti<sup>4+</sup> on CMAS melt viscosity has been explored previously, where increases in TiO<sub>2</sub> content decreased viscosity, which is consistent with the results from this study.<sup>31, 149</sup>

 $Zr^{4+}$  has been shown to operate in 6-fold coordination in peralkaline aluminosilicate glass systems.<sup>123, 150–</sup> <sup>154</sup> Molecular Dynamics simulations have shown similar behavior of Hf<sup>4+</sup> cations in aluminosilicate melts, justifying the extension of these assumptions to Hf<sup>4+</sup> coordination at all temperatures as well.<sup>155</sup> However,  $Zr^{4+}$  and Hf<sup>4+</sup> have been shown to integrate into the network through edge sharing<sup>152–154</sup> despite having 6-fold coordination and therefore behave as glass network formers for all properties investigated. This is visually represented in Figure 4.9 where the structural illustration shows how edge sharing increases network polymerization. A comparison of Group IV cations reveals that the Ti<sup>4+</sup> specimen deviates from the other Group IV cation species by decreasing viscosity and remaining soluble at all temperatures explored during viscometry.  $Zr^{4+}$  and Hf<sup>4+</sup> increased viscosity but only remained soluble at temperatures greater than ~1390°C and ~1415°C, respectively. TiO<sub>2</sub>, ZrO<sub>2</sub>, and HfO<sub>2</sub> are known to be insoluble in SiO<sub>2</sub> with line compounds present for only ZrSiO<sub>4</sub> and HfSiO<sub>4</sub>.<sup>156–158</sup> Interestingly, the precipitates were solely

 $ZrO_2$  and  $HfO_2$ , not  $ZrSiO_4$  and  $HfSiO_4$ . The improved solubility of Ti in the silica glass network is likely explained by the cation sizes of these species in both 4-fold and 6-fold coordination. Ti<sup>4+</sup> [0.42 Å & 0.605 Å] is closer to that of Si<sup>4+</sup> [0.26 Å & 0.4Å], while  $Zr^{4+}$  [0.59 Å & 0.72 Å] and  $Hf^{4+}$  [0.58 Å & 0.71 Å] are larger. While bonding strengths with the oxygen nearest neighbors have previously been proposed as a mechanism for network polymerization,<sup>159</sup> cation size is likely the greater contributor as polyhedron size and the capability of edge sharing will have greater effects on network polymerization.<sup>152, 155</sup> This explains why the Ti<sup>4+</sup> addition does not have the same effect on the glass structure and properties as  $Zr^{4+}$  and  $Hf^{4+}$ additions.

This study has shown Zr<sup>4+</sup> dissolution increases viscosity at higher temperatures relative to the baseline CMAS (Figure 4.3d). This behavior is notably different from that of yttria-stabilized zirconia (YSZ) and gadolinium zirconate (GZO) dissolution in several molten CMAS and CMFAS compositions of varying compositional complexity, which typically increased viscosity at lower temperatures but decreased viscosity at higher temperatures relative to the baseline glass compositions.<sup>116</sup> While the Zr<sup>4+</sup> addition by itself increased viscosity, precipitation behavior must also be considered. TiO<sub>2</sub> and ZrO<sub>2</sub> are well known nucleating agents in MAS glass-ceramic systems,<sup>151, 152</sup> but re-precipitation of ZrO<sub>2</sub> in CMAS interactions with YSZ coating systems does not mitigate further infiltration and reaction with the coating.<sup>21, 36, 116, 160</sup> In contrast, alloying ZrO<sub>2</sub> with RE<sub>2</sub>O<sub>3</sub> increases reactivity and limits further CMAS infiltration through the formation of a Ca-RE-apatite phase at the interface.<sup>21, 107, 130</sup>

#### 4.4.4. Effects of RE Cations

All RE<sup>3+</sup> additions were assumed to operate in 6-fold coordination for simplicity, however, coordination has been shown to increase as atomic mass decreases and cation size increases.<sup>122</sup> RE<sup>3+</sup> additions in this study showed mixed behaviors between the liquid melt and condensed amorphous states. Literature has shown that RE<sup>3+</sup> species will increase 5- and 6-fold coordination of Al<sup>3+</sup> in aluminosilicate glasses,<sup>161</sup> where higher coordinated Al<sup>3+</sup> polyhedron can maintain polymerization of the glass network in the condensed amorphous state. However, increases in temperature could increase NBO content or Al<sup>3+</sup> coordination in the molten liquid state and work to depolymerize the network.<sup>162</sup> RE<sup>3+</sup> are also expected to coordinate with at least 3 NBO, with NBO coordination increasing with RE<sup>3+</sup> size.<sup>163</sup>

Figure 4.7 (and by design also Figure 9) indicate two groupings among lanthanide series additions where increases in CMXAS CTE are accompanied by decreases to viscosity,  $T_d$ , and  $T_g$  due to the assumed increase in oxygen coordination and NBO content.<sup>122, 163</sup> The small cation RE<sup>3+</sup> additions (Lu<sup>3+</sup>, Sc<sup>3+</sup>, Y<sup>3+</sup>, Yb<sup>3+</sup>) had notable effects on CMXAS CTE and  $T_d$  when compared to the baseline CMAS. Whereas the larger cation RE<sup>3+</sup> additions (Gd<sup>3+</sup>, Nd<sup>3+</sup>, La<sup>3+</sup>) did not have a significant effect on CMXAS CTE and  $T_d$  (see Figure 7b). As noted previously, the selected boundary between small and large cation radii (~0.9 Å) is conveniently close to the average modifier cation radius of the baseline composition (~0.87 Å). It is hypothesized that the small RE<sup>3+</sup> species ( $\leq 0.9$  Å) integrate into the network fundamentally in the same manner as large RE<sup>3+</sup> species but their lower coordination number with surrounding oxygen introduces fewer NBO into the network, resulting in improved polymerization of the network and the observed trends in glass properties.

The improved incorporation into the network is also likely to improve range of melt stability, as shown by  $Lu^{3+}$ ,  $Sc^{3+}$ , and  $Y^{3+}$  additions being the only  $10RE^{3+}$  additions to forgo precipitation over the temperature

range explored (Figure 4.3d). Addition of these species in a multi-RE coating material could help to increase the range of melt stability as is shown in comparing the 10Yb<sup>3+</sup> addition to the dual cation (Y+Yb)<sup>3+</sup> addition (Figure 4.3d). The 5Gd<sup>3+</sup> and 10Y<sup>3+</sup> additions explored in this study did not precipitate apatite during viscometry despite being known to form apatite in CaO-rich silicate melts<sup>164</sup> and being more stable in the apatite phase than Yb<sup>3+</sup>.<sup>27, 84</sup> EDS measurements conducted post-viscosity measurement on the Gd<sup>3+</sup> and Y<sup>3+</sup> CMXAS showed lower RE<sup>3+</sup> content, 5% and 7% respectively, than other RE<sup>3+</sup> specimens. This illustrates how apatite precipitation during viscometry depended on saturation of RE<sup>3+</sup> in the melt.

Comparing the dual cation (Y+Yb)<sup>3+</sup> and 10Yb<sup>3+</sup> additions reported in this study to a 5% Yb<sup>3+</sup> addition from literature<sup>31</sup> indicates that an additional 5% of Y<sup>3+</sup> or Yb<sup>3+</sup> can destabilize the melt structure by precipitating apatite and lowering viscosity relative to the baseline. These results imply that a mixed RE<sup>3+</sup> coating could be tailored to mitigate CMAS infiltration depending on diffusivity of the RE<sup>3+</sup> cations and solubility limits of the glass melt. Coating material reactivity, or resistance to CMAS attack, has been shown to correlate with increasing exothermic contribution of the enthalpies of solution and mixing for the binary oxide components; consequently, the same work shows that enthalpic differences between an oxide addition and the silicate melt correlate with NBO formation.<sup>107</sup>

The results reported in this study are in good agreement with a similar study investigating 13.5 wt% RE<sup>3+</sup> additions to a similar 0.73 C:S CMAS glass (35Ca–10Mg–7Al–48Si) with all compositions decreasing viscosity.<sup>117</sup> However, crystallization was only observed in the ~2.7 mol% Nd<sup>3+</sup> addition (~1215°C) and not for the La<sup>3+</sup> or Gd<sup>3+</sup> additions. Work investigating the effect of La<sup>3+</sup> content on a CMFAS melt showed increases in viscosity as La<sup>3+</sup> supplanted Fe<sup>3+</sup> content, which is consistent with results we report here (Figure 4.3c and 4.3d). Similar trends in T<sub>g</sub> dependence on cation size are seen in various studies on RE-aluminosilicate glasses<sup>165–167</sup> and follow the same correlation displayed in Figure 4.7a. The increase in T<sub>g</sub> for Yb<sup>3+</sup> and (Y+Yb)<sup>3+</sup> specimens relative to the trend with RE<sup>3+</sup> additions could be the result of increased

BO content associated with Yb<sup>3+</sup> due to the small cation size and resultant lower coordination number which would allow for improved crosslinking throughout the glass network,<sup>122, 163, 167</sup> but this cannot be confirmed without structural analysis.

# 4.4.5. Hypotheses of Fifth Oxide Cation Effect on Glass Structure

As previously stated, the use of experimental or computational methods to determine cation coordination with the surrounding oxygen as well as quantifying NBO or BO content of specific cation species was unavailable for this study. However, it is known that trends in glass properties can be used to infer effects on glass network structure.<sup>34, 161, 168</sup> Prior studies by An et al.<sup>124</sup> and Wang et al.<sup>169</sup> show viscosity decreases as network modification increases (via NBO content). Kang et al.<sup>170</sup> showed that decreases in CMAS CTE as well as increases in CMAS T<sub>d</sub> and T<sub>g</sub> corresponded with increases in network formation (via Si tetrahedral connectivity). Clausell et al.<sup>171</sup> also showed that CTE decreases and T<sub>g</sub> increases as network formation increases (via increasing crosslink density) in complex CMAS glass systems. As a result, the most-likely explanation for changes in CMXAS glass properties is a change in network connectivity. Where CMAS viscosity, T<sub>d</sub>, and T<sub>g</sub> increase as network formation increases. While CMAS CTE increases as network modification increases.

Both fifth oxide (X) cation valence and size were observed to correlate with trends on CMXAS viscosity, CTE,  $T_d$ , and  $T_g$ . Some network modifying cation additions displayed opposite behaviors between the molten liquid and condensed amorphous states. This behavior is assumed to result from the formation of higher coordination states of  $AI^{3+}$  or  $RE^{3+}$  cations, which would strengthen the network at temperatures

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close to T<sub>g</sub> (while the material is in the condensed state) but ultimately increase NBO content and disrupt the network in the molten liquid state. Effects on glass structure were inferred by evaluating CMXAS properties relative to the 0.73 C:S CMAS baseline composition and are hypothesized below:

- 1.  $Fe^{3+}$  additions have strong modifying effects on the glass in the molten state with  $Fe^{2+}$  expected to have a greater modifying effect than  $Fe^{3+}$ . However,  $Fe^{3+}$  is expected to have a greater modifying effect than  $Fe^{2+}$  in the condensed amorphous state, increasing CMXAS CTE while decreasing CMXAS T<sub>d</sub> and T<sub>g</sub>. Although, in the rare case  $Fe^{2+}$  adopts a tetrahedral coordination structure and incorporates into the network then these trends should reverse.
- Ti<sup>4+</sup> addition operated as a glass network modifier in the molten liquid state, decreasing viscosity (as a weak network former in the condensed amorphous state) and decreasing CMXAS CTE while increasing CMXAS T<sub>d</sub> but having little effect on CMXAS T<sub>g</sub>.
- Zr<sup>4+</sup> and Hf<sup>4+</sup> additions operated as strong glass network formers in both molten liquid and condensed amorphous states for all properties explored – decreasing CMXAS CTE while increasing CMXAS viscosity, T<sub>d</sub>, and T<sub>g</sub>.
- Small RE<sup>3+</sup> (e.g. Sc, Lu, Yb, Y) additions had strong network modifying effects in the molten liquid state, decreasing viscosity. However, they acted as network formers in the condensed amorphous state, decreasing CMXAS CTE while increasing CMXAS T<sub>d</sub> and T<sub>g</sub>.
- 5. Large RE<sup>3+</sup> (e.g. Gd, Nd, La) additions had strong modifying effects in the molten liquid state, decreasing viscosity. However, they acted as weak network modifiers in the condensed amorphous state, increasing CMXAS CTE and having little effect on CMXAS T<sub>d</sub>. Interestingly, CMXAS T<sub>g</sub> also increased relative to the baseline 0.73 C:S CMAS, but had the lowest increase among all RE<sup>3+</sup> additions.

Figure 4.10 depicts the hypothesized oxygen coordination of each cation classification and placement of each structural illustration corresponds to the clustering of data shown in Figure 7d. The baseline material structural schematic is shown without Mg<sup>2+</sup> for simplicity. It should be noted that the effect of alkaline species, like Na<sup>+</sup>, on glass network structure is not contained in Figure 4.10 as multiple alkaline compositions were not investigated and their effect on glass structure is generally well understood.<sup>172</sup> Given Al<sup>3+</sup> is an amphoteric species, each category of cation addition is expected to interact with Al<sup>3+</sup> differently.



Figure 4.10: Fifth oxide additions can be classified based on their measured glass properties. Illustration of assumed oxygen coordination of various fifth oxide additions are positioned relative to CMXAS CTE and viscosity measured glass properties. Tg, Td, and BO content are generally expected to increase as CTE decreases and viscosity increases.

#### 4.4.6. Implications to Coating Performance

This work demonstrated the compositional influence of fifth oxide additions on CMAS/CMXAS glass properties, where the relative threat of CMAS attack of coatings can be deduced from the relationships between glass properties and inform the coating selection process (Figure 4.7). Lower viscosities imply faster infiltration of the coating.<sup>28, 36–40</sup> Higher CTE mismatch with the coating material is indicative of threat to through-coating cracking.<sup>41</sup> Higher T<sub>d</sub> and T<sub>g</sub> indicate earlier onset of thermal stresses,<sup>42</sup> while lower T<sub>d</sub> and T<sub>g</sub> are indicative of earlier onset of intergranular diffusion.<sup>20</sup> Figures 4.7a-c can be used in predicting dilatometric glass properties of condensed amorphous CMXAS compositions. Additionally, the relationships between dilatometric glass properties are shown to translate across a wide range of compositional space,<sup>37, 125, 165, 166</sup> allowing for inferences to be made if only one of the glass properties (CTE,  $T_d$ ,  $T_g$ ) is known. However, this is not the same for comparison of properties between viscometry and dilatometry as is shown by the scatter in Figure 4.7d. The 10Fe<sup>3+</sup> addition was shown to decrease CMXAS viscosity the most while also increasing CTE, indicating it has the greatest threat to coating infiltration (viscosity) and spallation (CTE, T<sub>d</sub>, T<sub>g</sub>). The 5Hf<sup>4+</sup> addition was shown to increase CMXAS viscosity the most while also decreasing CTE, indicating it has the greatest ability to mitigate premature coating failure. However, coatings often contain multiple constituents and their combined effect on CMAS glass properties and melt behavior cannot be easily predicted as indicated by the dual cation (Y+Yb)<sup>3+</sup> composition. Coating performance predictions should consider coating constituent solubility as well as precipitation behavior of crystalline reaction products.

This work also investigated the effect of coating constituent dissolution on CMXAS glass melt solution and the relative threat of individual constituents to CMAS attack (Figure 4.7). As indicated by this study, the following phenomena are also important considerations for coating design: (i) coating constituent solubility within the melt and (ii) precipitation behavior. Müller and Dingwell found dissolved mixtures of  $Zr^{4+}$  with Y<sup>3+</sup> and Gd<sup>3+</sup> (in the form of YSZ and GZO) increased CMAS viscosity at lower temperatures. The GZO addition followed a rule of mixtures prediction consistent with trends extrapolated from this study, yielding a higher viscosity and lower temperature of precipitation.<sup>116</sup> However, predicting precipitation behavior after dissolution of several amphoteric cation additions of varying roles or strengths – such as with mixed rare-earth silicates – to a compositionally complex glass system is difficult. For example, the (Y+Yb) dual cation addition from this study exhibited behavior of a nonideal solution for CMXAS viscosity, CTE, and T<sub>d</sub> but exhibited a rule of mixtures for CMXAS T<sub>g</sub> measurements. This could be explained by the dissimilar Y-O and Yb-O bonding working to disorder the structure, resulting in a minimum for viscosity and T<sub>d</sub> while increasing CTE.<sup>105, 107, 173, 174</sup>

Constituent dissolution rates and solubility limits in the glass melt are also crucial in evaluating the threat of CMAS attack. Use of multi-component coatings can result in dissimilar dissolution rates into the glass melt with solubility limits that may not even being reached depending on dissolution rate. Understanding of dissolution of HfO<sub>2</sub>, ZrO<sub>2</sub>, and RE<sub>2</sub>O<sub>3</sub> into CMAS and CMFAS systems is limited to Hf<sup>4+</sup> and Zr<sup>4+</sup> species,<sup>130</sup>, <sup>160</sup> with a critical knowledge gap existing on the dissolution rates and precipitation behaviors of lowcontent (~5 mol%) mixed cation RE<sup>3+</sup> additions to CMAS and CMFAS glass melts. Predictive capabilities exist as quantified by Costa et al., where the enthalpic difference, or exothermicities, between the oxide addition and silicate melt correlate with oxide constituents that introduce more NBO, depolymerizing melt structure and limiting species solubility.<sup>107</sup> The same source of thermodynamic data can be used to predict coating material reactivity, or resistance to CMAS attack, where reactivity is often coupled with precipitation behavior.

Precipitation behavior, which was touched on previously in context of Zr<sup>4+</sup> in YSZ, is another crucial phenomenon to consider in coating design. Re-precipitation of ZrO<sub>2</sub> from YSZ is nonprotective due to re-precipitation occurring homogeneously. Homogeneous precipitation during CMAS-coating interactions is

undesirable for several reasons: no cessation of reaction with coating materials, continuous infiltration of coating materials, increased high temperature solubility associated with decreases in viscosity, and compromising coating design due to continuous coating dissolution. However, tailoring coatings to undergo spontaneous heterogenous precipitation at the CMAS interface can address these concerns by creating an inert barrier capable of ceasing reaction and infiltration while also creating a gradient of thermal expansion mismatch between the coating material and the residual glass. Coating materials using rare-earth oxides are state-of-the-art for their ability to form a RE-apatite reaction product and mitigate CMAS infiltration.

# 4.5. Conclusions

The following conclusions can be drawn from this work:

- 1. Small changes in CMAS C:S ratio are measurably reflected in CMAS glass viscosity, CTE,  $T_d$ , and  $T_g$ . However, fifth oxide additions showed greater impact on glass properties.
- 2. Coating material selection must also consider the effect of coating dissolution on melt structure, solubility limits, and precipitation behaviors.
- Effects of fifth oxide additions on glass properties can be used to indicated effect on the glass network:
  - Natural-forming additions behaved as glass network modifiers in both the condensed amorphous and molten liquid glass states, which is fundamentally different from coating-derived additions.
  - b. RE<sup>3+</sup> additions behavior varied, where they behaved as glass network formers in the condensed amorphous state and glass network modifiers in the molten liquid state.
  - c. However, Hf<sup>4+</sup> and Zr<sup>4+</sup> additions consistently behaved as glass network formers in both the condensed amorphous and molten liquid states.
- Relationships between CMAS and CMXAS glass properties can be used to indicate compositional threat to premature coating failure via infiltration (viscosity) and spallation (CTE, T<sub>d</sub>, T<sub>g</sub>).

# 5. Computational and Numerical Investigation on CMXAS Glass Properties

# 5.1. Background

Experimental measurement of glass properties is often expensive with respect to time, energy, and fiscal resources. As a result, computational methods are often implemented to provide insights at the fraction of a cost as experimental measurements. The primary glass property of importance to coating infiltration is viscosity. But other pertinent properties include coefficient of thermal expansion (CTE), softening temperature (T<sub>d</sub>), and glass transition temperature (T<sub>g</sub>). Han<sup>175</sup> compiled an excellent literature review of viscosity models relevant to the CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, highlighting the wide array of methods being explored to calculate CMAS viscosity: statistical, empirical, structural, thermodynamic, and combinations of these methods are reviewed. Prior work by Webster and collaborators<sup>28, 31, 40</sup> assessed three viscosity models (Fluegel,<sup>176</sup> Giordano,<sup>72</sup> and FactSage<sup>73</sup> viscosity models) and determined FactSage to have better accuracy over both a broader range of CaO-SiO<sub>2</sub> ratios as well as more complex compositional spaces. Even thermodynamic databases have their downsides: compositional limitations can mean databases often lack additions relevant to coating materials systems or plumet in accuracy as compositional complexity increases. This addresses a need to improve the understanding of CMAS glass composition – structure – property relationships.

Numerical descriptors, such as Cation Field Strength, show promise in developing glass composition – structure – property relationships. The concept of cation field strength (F) relates the cation charge (Z) of species i to the sum of the squares of cation and anion radius ( $r_c$  and  $r_a$ , respectively). This relationship is shown in Equation 5.1:

$$F_i = \frac{Z_i}{r_c^2 + r_a^2} \tag{5.1}$$

If the glass system has only one anion present (e.g.  $O^{2-}$ ) and the interatomic bond distance between the cations and anion is assumed to be constant throughout the system, the anionic radius can be removed to provide a simplified cation field strength relationship (Equation 5.2):

$$F_i = \frac{Z}{r_c^2} \tag{5.2}$$

A series of fifth oxides, denoted as X in CMXAS, are selected for study due to their prevalence in the natural environment, e.g. FeO, or their presence in coating materials, e.g. Yb<sub>2</sub>O<sub>3</sub>. Net cation field strength is used to form trends with viscosity and composition and is expected to corelate with T<sub>g</sub>, T<sub>m</sub>, and CTE as a function composition. An increase in net cation field strength will result in an increase in viscosity, T<sub>d</sub>, and T<sub>g</sub>, but will decrease CTE. The predictive capabilities of the Giordano, FactSage, and Thermo-Calc viscosity models as well as net cation field strength are evaluated against experimental viscosity measurements. This work expands on prior work done on the fifth oxide effect<sup>31</sup> with the addition of net cation field strength. Additionally, FactSage and Thermo-Calc viscosity calculations for equivalent fifth oxide constituents are compared against measured viscosities for the first time.

#### 5.2. Methods

Viscosities were calculated using Giordano,<sup>72</sup> FactSage,<sup>73</sup> and Thermo-Calc<sup>74</sup> viscosity models. The Giordano model is of interest due to including water in its database, which is not available in FactSage or Thermo-Calc. Giordano predicts non-Arrhenian Newtonian viscosity of silicate melts as a function of temperature and melt composition from a database of more than 1770 measurements of anhydrous and

volatile-rich magmatic silicate melts using the Vogel-Fulcher-Tammann (VFT) equation,<sup>177–179</sup> shown in Equation 5.3.

$$\log \eta = A + \frac{B}{T(K) - C} \tag{5.3}$$

Where viscosity ( $\eta$ ) is determined through the relationship of T (temperature in Kelvin), A (a constant independent of composition), B and C (adjustable parameters compositionally determined from the database). The Giordano model uses calculated viscosity to predict  $T_g$ .

The FactSage viscosity model contains both a melts and glasses setting, which utilizes a Modified Quasichemical Model for short-range ordering to calculate viscosity data.<sup>180-182</sup> The FactSage 8.0 software utilized thermodynamic data from the FToxid database, used the melts setting, and input compositions as a mole percent of the single metal cation oxide when calculating viscosities. The Thermo-Calc viscosity model uses the ionic two-sublattice liquid model, which functions similarly to the Modified Quasichemical Model by identifying the concentration of second-nearest-neighbor cation bonds – given that every first-nearest-neighbor is an oxygen anion – to identify the structure of the melt.<sup>183, 184</sup> The Thermo-Calc 2022a software utilized thermodynamic data from the TCOX11 (v11.1) database, loaded materials as oxide components, input compositions as a mole percent of the single metal cation oxide component when calculating viscosities. FactSage and Thermo-Calc are of interest due to their thermodynamic computational approach and expansion of compositional inputs relevant to effects of coating dissolution. Thermo-Calc is specifically of interest due to its database containing coating constituents. Compositions used mirrored the nominal CMAS and CMXAS compositions from Chapter 4. The system parameters and thermodynamic inputs are summarized for each viscosity model in Table 5.1.

Table 5.1: Database descriptors and thermodynamic parameters used to calculate viscosities in various viscosity models

Viscosity Model	Database	Compositional Input Format	Reference Pressure	Temperature Range
Giordano	Made with >1770 measurements	wt% converted from single cation oxide mole%	1 atm*	1100°C-1600°C, 50°C increments
FactSage	FTOxid	single cation oxide mole%	1 atm	1200°C-1600°C, 25°C increments
Thermo-Calc	TCOX11: Metal Oxide Solutions v11.1	single cation oxide mole% and set O to 0%; all available phases selected	1 atm	1150°C-1600°C, 25°C increments

\* = pressure is not a variable that can be changed in the Giordano viscosity model

Given a good understanding of constituent behavior in the glass network and several intelligent assumptions on the structure, one can empirically determine a net cation field strength representative of the glass composition. Net cation field strength is therefore defined as the sum of the products between glass composition and the field strength of the constituent cation (Equation 5.4).

$$F_{net} = \sum_{i}^{n} F_{i} y_{i} = F_{1} y_{1} + \dots + F_{n} y_{n}$$
(5.4)

The net cation field strength evaluated in this work utilized the simplified cation field strength relationship defined by Equation 5.2 and nominal CMAS and CMXAS compositions from Chapter 4.

#### 5.3. Results

Viscosities calculated using the Giordano model were inaccurate and are not included in the results.

# 5.3.1. Evaluation of Computational Methods

FactSage and Thermo-Calc calculated viscosities were compared to experimentally measured viscosities for naturally-forming oxide (Figure 5.1) and coating-derived oxide (Figure 5.2) additions. FactSage viscosity calculations of naturally-forming oxide additions were more accurate than Thermo-Calc calculations (Figure 5.1d). Thermo-Calc calculations overapproximated CMXAS viscosities of both naturally-forming (Figure 5.1d) and coating-derived oxide additions (Figure 5.2d).



Figure 5.1: (a) FactSage and (b) Thermo-Calc calculated viscosities for  $X = NaO_{0.5}$ , TiO<sub>2</sub>, FeO, FeO<sub>1.5</sub> additions while maintaining a 0.73 CaO-SiO<sub>2</sub> ratio. (c) Experimentally measured viscosities for  $X = NaO_{0.5}$ , TiO<sub>2</sub>, FeO, FeO<sub>1.5</sub> additions while maintaining a 0.73 CaO-SiO<sub>2</sub> ratio. (d) A direct comparison of (a-c) at T = 1290°C.



Figure 5.2: (a) Thermo-Calc calculated viscosities for X = Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> additions using the nominal composition. (b) Experimentally measured viscosities for X = Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub> additions while maintaining a 0.73 Ca-Si ratio. (c) A direct comparison of (a) to (b) at T = 1290°C, withholding the La<sub>2</sub>O<sub>3</sub> addition. (d) Comparison of Thermo-Calc calculated viscosity for X = ZrO<sub>2</sub> addition to experimentally measured viscosities for X = HfO<sub>2</sub>, ZrO<sub>2</sub> additions.

# 5.3.2. Evaluation of Cation Field Strength

The simplified net cation field strength is shown to develop a good trend with CMS, CAS, and CMAS glass viscosities over a wide compositional range and several temperatures (Figure 5.3a). This trend begins to weaken when the compositional range is reduced but compositional complexity increases. Increases in temperature of the CMXAS compositions continue to weaken the trends (Figure 5.3b). When applying the simplified cation field strength calculation to net cation field strength of dilatometric glass properties, the trend also weakens for CTE but forms a moderate trend with T<sub>d</sub> and T<sub>g</sub>. Reasons for this behavior and potential paths to improve the model are addressed in the discussion.



Figure 5.3: (a) Measured CMS, CAS, and CMAS viscosities as well as (b) measured CMXAS viscosities as a function of net cation field strength and their respective regressions at 1300°C, 1400°C, and 1500°C. Data in (a) measured by Webster and Opila.<sup>31</sup>



Figure 5.4: Measured dilatometric glass properties as a function of net cation field strength. (a) Coefficient of thermal expansion (CTE) as well as (b) softening temperature ( $T_d$ ) and glass transition temperature ( $T_g$ ).

# 5.4. Discussion

Poerschke et al.<sup>19</sup> introduced a computational framework to assess coating durability through a series of integrated thermodynamic, thermochemical, and thermomechanical models. The work reported here aims to provide feedback on available models and ensure quality input to the computational framework is utilized. Evaluation of Thermo-Calc computational methods is of importance for its ability to calculate other glass properties (i.e. surface tension, thermal expansivity, etc.).

Net cation field strength using the simplified cation field strength relationship (Equation 5.2) was shown to trend well in simplified CAS, CMS, and CMAS molten viscosity measurements (Figures 5.3a). However, increasing compositional complexity decreased the fit of CMXAS glass property measurements with net cation field strength (Figure 5.4). This likely could be improved by accounting for cation interactions with  $O^{2-}$  throughout the network. While this increases the complexity of the cation field strength calculation, and as a result net cation field strength calculation, it would also likely increase its accuracy. Things to account for include but are not limited to: i) geometric influence of oxygen on the cation field strength value (corner sharing versus edge sharing); ii) influence of glass state (molten liquid versus condensed amorphous) on the cation behavior; iii) dissimilar bond lengths between cations and anions. These should be addressed and validated before extending use of the model to more compositionally complex glass systems or broadening its application to evaluate other glass properties (especially if they're in the condensed amorphous state).

Another empirical relationship of use to coating materials is the concept of optical basicity (OB or  $\Lambda$ ), which is described as the quantification of the oxygen anion's ability to donate electrons and has been shown to be an indicator of CMAS dissolution of the coating material.<sup>132, 185</sup> OB can be calculated using Equation 5.5, shown below:

$$\Lambda_{th} = \sum_{i}^{n} X_{i} \Lambda_{i} \tag{5.5}$$

Where the theoretical OB ( $\Lambda_{th}$ ) of a complex silicate glass can be calculated from the summation of n constituent oxides, with each constituent denoted with i, of the product of the fraction of total oxygen contribution ( $X_i$ ) and the OB of the oxide constituent ( $\Lambda_i$ ) for each oxide species. Some common  $\Lambda_i$  are tabulated here.<sup>186</sup> OB can be calculated for multiple CMAS systems and preliminary attempts at gauging coating reactivity have also used optical basicity for select materials systems.<sup>185–187</sup> However this model does not account for the cation coordination structure and, as a result, should be limited to the evaluation of stability of the glass melt and the propensity for coating constituents to diffuse into the melt.<sup>19</sup> It is understood the driving force for crystalline product formation is better explained by the difference in free energies of the crystalline products and the melt.<sup>186, 187</sup> These concepts can work in synergy to improve

accuracy of property predictions and coating-melt interactions while minimizing the work vested into the time-intensive process of experimental assessment.

# 5.5. Conclusions

The following conclusions can be drawn from this work:

- FactSage is shown to be the more accurate thermodynamics-based computational viscosity model compared to Thermo-Calc. Thermo-Calc has several coating-derived constituents of interest, but overapproximated the calculated viscosities of all coating-derived species additions.
- 2. The application of the simple net cation field strength to glass property trends shows promise in predicting glass properties with limited confidence.
- Improving CMAS glass composition structure property relationships is pertinent to predicting CMAS – EBC interactions.

#### 6. Scientific Contribution and Impact

#### 6.1. Summary of Work

This dissertation investigated CMAS-EBC interactions from multiple angles: environmental effects on CMAS-EBC interactions, EBC composition on CMAS wetting, fifth oxide effect on CMAS glass properties, and predicting CMAS glass properties through computational methods and numerical descriptors. The completed work takes into consideration key variables of the engine environment, including: temperature, pressure, coating composition, and CMAS chemistry. Understanding CMAS-steam synergy on molten CMAS-EBC interactions was accomplished through a systematic evaluation of environmental effect on two model EBC materials. Compositional and microstructural effects on CMAS reactive wetting mechanisms were observed by investigating CMAS wetting across a variety of freestanding APS rare-earth silicate coating materials (using rare-earths across the lanthanide series; Y and La  $\rightarrow$  Lu). The effects of coating dissolution as well as naturally occurring oxides on molten liquid and condensed amorphous CMXAS glasses were evaluated through the controlled addition of a fifth oxide, where the X in CMXAS represents the fifth oxide. CMXAS composition-property relationships were used to form a hypothesis on CMXAS glass structure. This hypothesis was then applied to the evaluation and interpretation of several known computational methods and numerical descriptors. It is the hopes of this author that the data obtained on CMAS infiltration, wetting, and glass properties (thermal expansion, dilatometric glass transition temperature, softening temperature, and viscosity) as well as evaluation of several known computational methods and numerical descriptors can be used to develop future lifetime prediction models for EBCs in service.

# 6.2. Novelty of Findings

The novelty of the work contained in this dissertation is as follows:

- Systematic evaluation of environmental effect on CMAS-EBC interactions to confirm the deleterious effect of CMAS-steam synergy on molten CMAS-EBC interactions (Chapter 2)
- Effects of coating composition and morphology informed CMAS transport and developed a wellinformed hypothesis of CMAS reactive wetting mechanism (Chapter 3)
- Systematic analysis of CMAS and CMXAS glass properties in both molten liquid and condensed amorphous states (Chapter 4)
- Analysis of CMAS and CMXAS glass properties through the lens of composition-structure-property relationships (Chapter 4 and 5)
- Evaluation of Thermo-Calc thermodynamic-based computational model through its comparison to FactSage and measured CMAS, CMXAS viscosities (Chapter 5)
- Development of a net cation field strength model for evaluating compositional effects and compositionally complexity of the glass on glass properties as well as predicting glass properties of compositionally complex glasses (Chapter 5)

# 6.3. Knowledge Gaps and Future Directions

# 6.3.1. Coating-CMAS Interactions

Assessment of coating material resistance and reactivity with CMAS/CMFAS should be quantified as per the knowledge gap identified by Ridley et al.<sup>188</sup> Suggested approaches to quantification include spreading

area, infiltration depth, reaction layer thickness in the event precipitation occurs, and crystallite or precipitate grain size distribution with identification of precipitate capacity to cease CMAS/CMFAS infiltration. Feature quantification should be normalized to mass of CMAS/CMFAS loading. There is a lack of CMAS/CMFAS exposure studies evaluating coating performance and durability relevant to safe flight operational limits (<2 mg/m<sup>3</sup>),<sup>67, 68</sup> a loading of <10 mg/cm<sup>2</sup> is recommended.

CMFAS compositional suggestions for evaluation of coating interactions include commercially available AFRL-02 test dust<sup>189</sup> as well as four exemplary CMFAS compositions selected from the analysis of chemical characteristics, calculated thermophysical properties, and reactions with common coating oxides.<sup>115</sup> Coating interactions with the four exemplary CMFAS compositions<sup>115</sup> are unpublished at the time of this dissertation's completion.

The solubility limits as well as dissolution rates of popular coating constituents (HfO<sub>2</sub>, ZrO<sub>2</sub>, and RE<sub>2</sub>O<sub>3</sub>) into CMAS and CMFAS melts have limited published investigations.<sup>130, 160</sup> Investigation of multi-RE coating materials performance under thermal cycling relevant to times and temperature ranges turbine blades experience during operation has not been published and is paramount in evaluating performance of a mixed RE<sup>3+</sup> cation coating material. Literature can be consulted for suggested mixed RE coating material compositions and synthesis methods.<sup>16, 190–194</sup> Reaction kinetics and formation mechanism of multi-RE coating materials and CMAS/CMFAS interaction are another area of interest that literature indicates is understudied.

# 6.3.2. Glass Composition-Structure-Property Relationships

As noted in this work, the expected effect of multiple network modifying species additions on the glass properties of a compositionally complex glass network can be difficult to predict. A large knowledge gap is the investigation of low-content (~5 mol%) mixed cation RE<sup>3+</sup> additions to CMAS and CMFAS glasses (both CaO-rich and CaO-poor) to evaluate structural impact of the RE<sup>3+</sup> species in the condensed amorphous and molten liquid states, their effect on amorphous glass properties (CTE, T<sub>d</sub>, T<sub>g</sub>), and their molten liquid solubility limit as a function of temperature as well as composition. The effect of HfO<sub>2</sub>, ZrO<sub>2</sub>, and RE<sub>2</sub>O<sub>3</sub> on CMAS/CMFAS melt viscosity are limited,<sup>116, 117</sup> where investigation into CaO-poor (<0.3 C:S) CMAS melts is understudied. Coating-derived constituent influence on other glass properties (CTE, T<sub>d</sub>, T<sub>g</sub>) is limited in aluminosilicate glass systems,<sup>165, 166</sup> but more work on boron- and alkaline earth-containing aluminosilicates is available.<sup>195–197</sup>

One key knowledge gap that should be addressed is the composition-structure-property relationship of compositionally complex glass systems. This is especially imperative for understanding natural forming CMAS debris that have widely varying compositions. Natural forming CMAS debris will vary in both ratio of network modifying species to network forming species as well as number of constituents in the composition. While CaO-to-SiO<sub>2</sub> ratio is frequently referenced in literature, the total ratio of network modifying species to network forming species should be referenced. Further development of the net cation field strength model to account for geometric influence of oxygen on the cation field strength value, the mathematical incorporation of various structural effects on net cation field strength value, and validation of the model for prediction of compositionally complex glass systems is needed to improve and broaden its application.

# 6.4. Scientific Communication

The work produced by this dissertation has been displayed, communicated, and recognized through the following list of presentations, publications (including expected), and awards.

## 6.4.1. Resulting Presentations

- 1. "Exploring the Effect of EBC Composition on CMAS Wetting Behavior," 48th International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, FL, January 2024
- 2. "Investigating Fifth Oxide Effect on CMXAS Glass Properties," *Materials Science & Technology Technical Meeting & Exhibition*, Columbus, OH, October 2023
- "Investigating Fifth Oxide Effect on CMXAS Glass Properties," (Invited Speaker) Gordon Research Seminar – High Temperature Corrosion, New London, NH, July 2023
- 4. "Exploring CMAS-Steam Synergy on Yb-silicate Degradation," 47th International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, FL, January 2023
- "Investigating Fifth Oxide Effect on CMXAS Glass Properties," (GEMS Finalist Sapphire Award Recipient) Materials Science & Technology Technical Meeting & Exhibition, Pittsburgh, PA, October 2022
- 6. "Exploring CMAS-Steam Synergy on Ytterbium Disilicate Degradation," 46th International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, FL, January 2022

# 6.4.2. Resulting Publications

- 1. Luckhardt, CA & Opila, EJ (2025). Experimental Investigation of Fifth Oxide Effect on Calcium-Magnesium-Aluminosilicate (CMAS) Glass Properties. Submitted for publication.
- Luckhardt, CA, Savage, M, Stokes, JL, & Opila, EJ (2025). Effect of EBC Composition on Molten Silicate Wetting Behavior. Manuscript in preparation.
- Luckhardt, CA & Opila, EJ (2025). CMAS-Steam Synergistic Effect on Yb-silicate Degradation. Manuscript in preparation.
- 4. Luckhardt, CA & Opila, EJ (2025). Experimental Investigation of Fifth Oxide Effect on Calcium-Magnesium-Aluminosilicate (CMAS) Glass Properties. Manuscript in preparation.
- 5. Luckhardt, CA, Stokes, JL, & Opila, EJ (2025). Calorimetric Study of Synthetic CMAS in Crystalline and Amorphous States. Manuscript in preparation.

#### 6.4.3. Awards

- 1. Gordon Research Seminar: High Temperature Corrosion Invited Speaker (July 2023)
- 2. Graduate Excellence in Materials Science Finalist Sapphire Award Recipient (Oct 2022)

# Appendices

Appendix A: Supplemental Materials for Chapter 2





Figure A1: XRD of SPS substrates prior to CMAS exposure. Patterns are labelled to the right of the figure. ICDD PDF #04-016-8936 (Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) and #00-040-0386 (Yb<sub>2</sub>SiO<sub>5</sub>).



Figure A2: Microstructures representative of (a) phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, (b) 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, and (c,d) 25Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>/Yb<sub>2</sub>SiO<sub>5</sub> substrates densified by SPS. The light contrasted phase is Yb<sub>2</sub>SiO<sub>5</sub> and dark contrasted phase is Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.



Figure A3: Stitched plan view BSE micrographs of phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates after CMAS exposure at 1300°C in stagnant lab air for (a,b,c,d) 4-, (e,f,g) 24-, and (h,i,j,k) 96-hour durations. Trial numbers proceed numerically from left-to-right.



Figure A4: Stitched plan view BSE micrographs of phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates after CMAS exposure at 1300°C in flowing dry O<sub>2</sub> for (a,b,c) 4-, (d,e,f,g) 24-, and (h,I,j,k) 96-hour durations. Trial numbers proceed numerically from left-to-right.



Figure A5: Stitched plan view BSE micrographs of phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates after CMAS exposure at 1300°C in flowing steam for (a,d,g) 4-, (b,e,h) 24-, and (c,f,i) 96-hour durations. Trial numbers proceed numerically from left-to-right.



Figure A6: Stitched plan view BSE micrographs of mixed  $20Yb_2SiO_5/Yb_2Si_2O_7$  substrates after CMAS exposure at 1300°C in stagnant lab air for (a,b) 4- and (c) 96-hour durations. Two trials occurred for the 4-hour duration.



Figure A7: Stitched plan view BSE micrographs of mixed 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates after CMAS exposure at 1300°C in flowing dry O<sub>2</sub> for (a,b,c) 4-, (d,e,f) 24-, and (g,h,i) 96-hour durations. Trial numbers proceed numerically from left-to-right.



Figure A8: Stitched plan view BSE micrographs of mixed 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates after CMAS exposure at 1300°C in flowing steam for (a,b,c) 4-, (d,e,f) 24-, and (g,h,i) 96-hour durations. Trial numbers proceed numerically from left-to-right.


Figure A9: Stitched plan view BSE micrographs of mixed  $25Yb_2Si_2O_7/Yb_2SiO_5$  substrates after CMAS exposure in stagnant lab air at 1300°C for (a) 24- and (b,c) 96-hour durations. Two trials occurred for the 96-hour duration.



Figure A10: Stitched cross-section BSE micrographs comparing (a) 20 vol% Yb<sub>2</sub>SiO<sub>5</sub> in Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and (b) 25 vol% Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> in Yb<sub>2</sub>SiO<sub>5</sub> after a 4-hour CMAS exposure in stagnant lab air at 1300°C. The light contrasted phase is Yb<sub>2</sub>SiO<sub>5</sub> and dark contrasted phase is Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.



Figure A11: Stitched cross-section BSE micrographs of 25 vol% Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> in Yb<sub>2</sub>SiO<sub>5</sub> after CMAS exposure in stagnant lab air at 1300°C for (a) 4-, (b) 24-, and (c,d) 96-hour durations. The light contrasted phase is Yb<sub>2</sub>SiO<sub>5</sub> and dark contrasted phase is Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.

## A.2. Raw Data and Statistics

Environment	Time [h]	Trial No.	CMAS Load [mg]	Spreading Area [mm <sup>2</sup> ]	Normalized Spreading Area [mm²/ mg]	Apatite Ring Area [cm <sup>2</sup> / mg]	Norm. Apatite Ring Area [cm²/ mg]	Average Infiltration Measurement [µm]	Std. Dev. of Infiltration Measurement [µm]
		4	38.41	1.10831	0.02885	0.81329	0.02117	155.19455	48.15791
	4	5	42.18	0.98262	0.02330	0.86939	0.02061	TBD	TBD
		6	39.11	1.33788	0.03421	0.94905	0.02427	TBD	TBD
90% H₂O/		3	41.72	1.31389	0.03149	0.91380	0.02190	TBD	TBD
10% O <sub>2</sub> ,	24	5	39.80	DNE	N/A	DNE	N/A	1623.26729	117.07464
~1000 sccm,	24	6	41.52	1.41986	0.03420	0.77407	0.01864	TBD	TBD
~1.6 cm/s		7	39.44	1.36257	0.03455	0.80625	0.02044	TBD	TBD
		2	41.32	1.29664	0.03138	0.94723	0.02292	1386.38844	84.65541
	96	3	40.43	1.48332	0.03669	1.08897	0.02693	TBD	TBD
		4	38.60	1.58446	0.04105	0.97784	0.02533	TBD	TBD
		4	38.90	0.85217	0.02191	0.65760	0.01690	155.84223	46.27117
	4	5	38.80	0.60863	0.01569	0.55363	0.01427	TBD	TBD
		6	39.96	0.69460	0.01738	0.60004	0.01502	TBD	TBD
		3	40.02	DNE	N/A	DNE	N/A	804.02618	116.67978
100% 0		4	39.73	1.03774	0.02612	0.67729	0.01705	TBD	TBD
$100\% 0_2$ ,	24	5	40.24	0.96366	0.02395	0.66815	0.0166	TBD	TBD
$\sim 1.6 \text{ cm/s}$		6	41.76	0.83887	0.02009	0.58208	0.01394	TBD	TBD
1.0 CIT/S		7	43.16	1.16406	0.02697	0.62354	0.01445	TBD	TBD
		1	38.61	1.32587	0.03434	0.72174	0.01869	TBD	TBD
	06	2	40.53	1.40233	0.03460	0.63976	0.01578	1363.33838	173.01418
	90	3	37.86	1.30318	0.03442	0.71630	0.01892	TBD	TBD
		4	38.02	1.03128	0.02712	0.66830	0.01758	TBD	TBD

Table A1: CMAS spreading and infiltration measurements on individual SPS phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates

		2	39.79	0.85541	0.02150	0.64589	0.01623	TBD	TBD
	4	3	39.07	0.88666	0.02269	0.64811	0.01659	TBD	TBD
	4	4	39.87	0.82272	0.02064	0.62545	0.01569	239.20589	27.45039
		5	42.02	0.92319	0.02197	0.74156	0.01765	TBD	TBD
Lab Air,		2	39.13	1.17261	0.02997	0.65507	0.01674	545.89025	114.50903
No Flow	24	3	41.76	1.06181	0.02543	0.66824	0.01600	TBD	TBD
(stagnant)		4	38.97	1.28856	0.03307	0.61260	0.01572	TBD	TBD
		1	38.75	1.39598	0.03603	0.58460	0.01509	1594.94318	264.82832
	06	2	38.99	1.13156	0.02902	0.85950	0.02204	TBD	TBD
	90	3	40.52	1.47841	0.03649	0.55579	0.01372	TBD	TBD
		4	39.33	1.13173	0.02878	0.60160	0.01530	TBD	TBD

Table A2: CMAS spreading and Infiltration measurements on SPS 25 vol% Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> in Yb<sub>2</sub>SiO<sub>5</sub> substrates

Environment	Time [h]	Trial No.	CMAS Load [mg]	Spreading Area [cm²]	Normalized Spreading Area [cm²/ mg]	Apatite Ring Area [cm²/ mg]	Norm. Apatite Ring Area [cm²/ mg]	Average Infiltration Measurement [µm]	Std. Dev. of Infiltration Measurement [µm]	Average Reaction Layer Thickness [µm]	Std. Dev. Reaction Layer Thickness [µm]
	4	1	40.63	DNE	N/A	DNE	N/A	95.88594	29.49483	47.11918	11.34865
Lab Air,	24	1	40.58	DNE	N/A	DNE	N/A	TBD	TBD	TBD	TBD
No Flow	24	2	42.57	0.67642	0.01589	0.64166	0.01507	160.19007	37.58443	110.25007	23.57741
(stagnant)	06	1	44.44	0.86664	0.0195	0.56014	0.0126	198.33961	52.88971	229.60594	55.26557
	90	2	40.34	TBD	TBD	TBD	TBD	DNE	N/A	DNE	N/A

Environment	Time [h]	Trial No.	CMAS Load [mg]	Spreading Area [cm²]	Normalized Spreading Area [cm <sup>2</sup> / mg]	Apatite Ring Area [cm²/ mg]	Norm. Apatite Ring Area [cm²/ mg]	Average Infiltration Measurement [µm]	Std. Dev. of Infiltration Measurement [µm]	Average Reaction Layer Thickness [µm]	Std. Dev. Reaction Layer Thickness [µm]
		2	40.21	0.67370	0.01675	0.62173	0.01546	56.43500	24.59948	26.37567	8.34131
	4	3	39.67	0.69232	0.01745	0.63475	0.01600	TBD	TBD	TBD	TBD
		4	38.14	0.70842	0.01857	0.65313	0.01712	TBD	TBD	TBD	TBD
90% П <sub>2</sub> О/ 10% О-		2	38.55	0.95901	0.02488	0.72743	0.01887	106.97852	33.48858	63.61433	22.1721
$10\% 0_2$ ,	24	3	41.77	0.86727	0.02076	0.74336	0.01780	TBD	TBD	TBD	TBD
$\sim 1.6 \text{ cm/s}$		4	39.82	0.96012	0.02411	0.73150	0.01837	TBD	TBD	TBD	TBD
1.0 cm/3		1	41.12	1.06446	0.02589	0.89704	0.02182	180.32261	83.93623	113.88596	28.0437
	96	2	39.58	1.06784	0.02698	0.88191	0.02228	TBD	TBD	TBD	TBD
		4	40.43	1.09759	0.02715	0.84335	0.02086	TBD	TBD	TBD	TBD
		1	38.63	0.80483	0.02083	0.72362	0.01873	99.23505	38.04074	38.13895	30.79044
	4	2	41.89	0.90336	0.02157	0.75772	0.01809	TBD	TBD	TBD	TBD
		3	38.32	0.76368	0.01993	0.78177	0.02040	TBD	TBD	TBD	TBD
100% O <sub>2</sub> ,		1	37.74	0.98439	0.02608	0.69066	0.01830	TBD	TBD	TBD	TBD
~1000 sccm,	24	3	37.58	1.12969	0.03006	0.71961	0.01915	TBD	TBD	TBD	TBD
~1.6 cm/s		4	38.17	1.09789	0.02876	0.77037	0.02018	113.92104	37.43524	54.23296	26.21065
		1	40.33	1.01378	0.02514	0.81904	0.02031	180.32261	83.93623	28.0437	101.75895
	96	2	40.87	0.81534	0.01995	0.76684	0.01876	TBD	TBD	TBD	TBD
		3	41.19	0.88062	0.02138	0.91037	0.02210	TBD	TBD	TBD	TBD
	Л	2	40.83	0.87821	0.02151	0.85838	0.02102	82.36137	22.20871	33.45832	9.56552
Lab Air,	4	3	38.91	0.90069	0.02315	0.78931	0.02029	TBD	TBD	TBD	TBD
(stagnant)	24	1	40.58	DNE	N/A	DNE	N/A	TBD	TBD	TBD	TBD
(stagnant)	96	3	37.73	1.00310	0.02659	0.78008	0.02068	TBD	TBD	TBD	TBD

Table A3: CMAS spreading, infiltration, and reaction layer thickness measurements on individual SPS 20 vol% Yb<sub>2</sub>SiO<sub>5</sub> in Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrates

Substrate	Environment	Time [h]	Average Normalized Spreading Area [mm <sup>2</sup> ]	Std. Dev. Normalized Spreading Area [mm²/ mg]	Average Normalized Apatite Ring Area [cm²/ mg]	Std. Dev. Normalized Apatite Ring Area [cm²/ mg]
	90% H₂O/	4	0.02879	0.00546	0.02202	0.00197
	10% O <sub>2</sub> , ~1000 sccm,	24	0.03341	0.00167	0.02033	0.00163
	~1.6 cm/s	96	0.03637	0.00484	0.02506	0.00202
	100% O2	4	0.01833	0.00322	0.01540	zed ea   Std. Dev. Normalized Apatite Ring Area [cm²/ mg]     0.00197     0.00163     0.00202     0.00136     0.00154     0.00143     8.26905E-4     5.27296E-4     0.00374     8.4822E-4     5.37063E-4     0.00119     9.42587E-4     0.00167     N/A     N/A     N/A
Phase-pure Yb <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	~1000 sccm,	24	0.02428	0.00307	0.01551	0.00154
/	~1.6 cm/s	96	0.03262	0.00367	0.01774	0.00143
	Lab Air.	4	0.02170	8.63364E-4	0.01654	8.26905E-4
	No Flow	24	0.02949	0.00384	0.01615	5.27296E-4
	(stagnant)	96	0.03258	0.00425	0.01654	0.00374
	90% H₂O/	4	0.01759	9.18057E-4	0.01620	8.4822E-4
	10% O <sub>2</sub> , ~1000 sccm,	24	0.02325	0.00219	0.01835	5.37063E-4
	~1.6 cm/s	96	0.02667	6.84708E-4	0.02165	Area   Apatite Ring Area     [cm²/ mg]   0.00197     0.00163   0.00202     0.00136   0.00136     0.00154   0.00143     8.26905E-4   5.27296E-4     0.00374   8.4822E-4     5.37063E-4   0.00119     9.42587E-4   0.00167     N/A   N/A     N/A   N/A
	100% O <sub>2</sub> .	4	0.02078	8.19567E-4	0.01907	0.00119
20Yb <sub>2</sub> SiO <sub>5</sub> / Yb <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	~1000 sccm,	24	0.02830	0.00203	0.01921	9.42587E-4
- 2 - 2 - 7	~1.6 cm/s	96	0.02216	0.00268	0.02039	0.00167
	Lab Air.	4	N/A	N/A	N/A	N/A
	No Flow	24	N/A	N/A	N/A	N/A
	(stagnant)	96	N/A	N/A	N/A	N/A

Table A4: Statistics on CMAS spreading measurements on EBC substrates densified by SPS



Figure A12: CMAS spreading area measurements normalized per mg of CMAS loaded after exposures varying in length and environment on (a) phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> as well as (b) mixed 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and 25Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>/Yb<sub>2</sub>SiO<sub>5</sub> substrates at 1300°C. Lines are included only as a visual tool.



Figure A13: Apatite ring area measurements normalized per mg of CMAS loaded after exposures varying in length and environment on (a) phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> as well as (b) mixed 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and 25Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>/Yb<sub>2</sub>SiO<sub>5</sub> substrates at 1300°C. Lines are included only as a visual tool.



Figure A14: CMAS infiltration measurements after exposures varying in length and environment on (a) phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> as well as (b) mixed 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and 25Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>/Yb<sub>2</sub>SiO<sub>5</sub> substrates at 1300°C. (c) Reaction layer thicknesses of apatite formation on mixed material 20Yb<sub>2</sub>SiO<sub>5</sub>/Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and 25Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>/Yb<sub>2</sub>SiO<sub>5</sub> substrates. Phase-pure Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> substrate thickness limited CMAS infiltration during 96-hour exposures. NOTE: the change in scale from (a) to (b). Lines are included only as a visual tool.

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Appendix B: Supplemental Materials for Chapter 3



## B.1. Materials Characterization

Figure B1: XRD of heat-treated APS and SPS substrates prior to CMAS exposure. Patterns are labelled to the right of the figure



Figure B2: XRD of heat-treated APS LaDS substrate prior to CMAS exposure and reference patterns. Patterns are labelled to the right of the figure.



Figure B3: XRD of heat-treated APS NdDS substrates prior to CMAS exposure and reference patterns. Patterns are labelled to the right of the figure.



Figure B4: XRD of heat-treated APS GdDS substrates prior to CMAS exposure and reference patterns. Patterns are labelled to the right of the figure.



Figure B5: XRD of heat-treated APS YDS substrates prior to CMAS exposure and reference patterns. Patterns are labelled to the right of the figure.



Figure B6: XRD of heat-treated APS LuDS substrates prior to CMAS exposure and reference patterns. Patterns are labelled to the right of the figure.



Figure B7: XRD of heat-treated APS and SPS Yb-silicate substrates prior to CMAS exposure and reference patterns. Patterns are labelled to the right of the figure.



Figure B8: XRD of heat-treated APS (Y+Yb)DS and constituent REDS substrates prior to CMAS exposure as well as reference patterns. Patterns are labelled to the right of the figure.

RE	RE <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (structure)	RE₂SiO₅	RE <sub>9.33</sub> Si <sub>6</sub> O <sub>26</sub>
	04-009-9536 (tetragonal)		
La	04-010-8687 (monoclinic)	00-040-0234	00-049-0443
	04-012-2424 (triclinic)		
	04-015-1535 (tetragonal)		
Nd	04-009-8272 (monoclinic)	00-040-0284	01-084-9399
	00-038-1456 (orthorhombic)		
	04-014-8506 (triclinic)		
Gd	04-007-8972 (orthorhombic)	00-040-0287	00-038-0283
	00-062-0128 (tetragonal)		
Yb	04-016-8936 (monoclinic)	00-040-0386	04-007-9173
Lu	04-010-9417 (monoclinic)	00-041-9417	04-007-9174
	04-013-8417 (monoclinic)		
Y	00-045-0042 (orthorhombic)	00-052-1810	00-030-1457
	04-016-5897 (triclinic)		

Table B1: Reference patterns and corresponding ICDD reference numbers

Constituent	Site 1	Site 2	Site 3	Average
Са	30.0	30.1	30.1	30.1
Mg	9.1	9.3	9.4	9.3
Al	13.6	13.7	13.6	13.6
Si	47.2	46.9	47.0	47.0

Table B2: Point EDS Measurements on 0.73 C:S CMAS Glass



Figure B9: (a) Back-scatter electron micrograph of CMAS with labels corresponding with sites where point EDS was conducted; elemental maps for (b) Ca, (c) Mg, and (d) Si indicate a homogeneous mixture.

Substrate	Trial No.	Site 1 [%]	Site 2 [%]	Site 3 [%]	Average (Std. Dev.)
	1	12.577	11.878	12.773	12.409 (0.3841)
	2	11.603	10.937	11.396	11.312 (0.2783)
APS Lads	3	12.146	13.022	12.137	12.435 (0.4151)
	4	14.776	14.392	12.441	13.870 (1.0223)
	1	7.662	8.651	7.912	8.075 (0.4199)
	2	8.063	8.063 7.944		8.095 (0.1387)
APS NUDS	3	7.615	8.378	7.727	7.907 (0.3364)
	4	6.479	6.372	6.672	6.508 (0.1241)
	1*	8.200	7.643	5.343	7.132
	2	7.840	7.861	7.277	7.659
APS GdDS	3	8.992	7.962	8.470	8.475 (0.4205)
	4	8.197	8.329	7.961	8.162 (0.1522)
	1	7.137	7.276	6.993	7.135 (0.1155)
	2	8.967	8.091	8.543	8.534 (0.3577)
AF3 103	3	8.189	8.595	8.949	8.578 (0.3105)
	4*	5.784 6.339	6.091 5.975	5.837 6.141	6.028 (0.1881)
	1	7.292	7.190	7.378	7.287 (0.0768)
	2	7.276	7.797	7.441	7.505 (0.2174)
APS LUDS	3	7.690	7.850	7.726	7.755 (0.0685)
	4*	7.679 6.354	7.345 6.513	6.409 6.768	6.845 (0.4988)

Table B3: Porosity measurements on APS REDS substrates

	1	9.388	9.204	9.958	9.517 (0.3210)
	2	10.06	9.25	9.419	9.576 (0.3489)
APS YDDS	3	8.304	8.099	8.465	8.289 (0.1498)
	1   2   3   4   1   2   3   4   1   2   3   4*   1   2   3   4*   1   2   3   4   1   2   3   4   1   2   3   4   1   2   3   4   1   2   3   4   1   2   3   4   1   2   3	10.349	11.95	10.461	10.920 (0.7298)
	1	6.790	6.615	7.099	6.835 (0.2001)
	2	5.730 6.190		4.806	5.575 (0.5755)
APS YbDS – A	3	5.697	5.948	6.026	5.890 (0.1404)
	4*	4.544 4.792	4.676 4.761	4.835 5.006	4.769 (0.1417)
	1	15.969	15.676	16.415	16.020 (0.3038)
	2	15.719	15.965	16.183	15.956 (0.1895)
ΑΡΣ ΥΔΟΣ – Ο	3	16.677	15.413	16.000	16.030 (0.5165)
	4	15.419	15.802	15.120	15.447 (0.2791)
	1	19.392	19.457	19.756	19.535 (0.1585)
	2	32.800	33.648	33.913	33.454 (0.4747)
APS די – געמז APS - ר	3	32.521	32.176	33.073	32.590 (0.3694)
	4	31.911	29.906	29.614	30.477 (1.0210)
	1	9.233	10.866	10.712	10.270 (0.7362)
	2	11.356	12.472	12.060	11.963 (0.4608)
ΑΡ3 (1+τυ)υ3	3	12.091	9.413	11.043	10.849 (1.1019)
	4	12.248	11.349	11.360	11.652 (0.4212)

\* = Some substrates had porosity measurements on two corners of the same coupon.



Figure B10: Porosity measurement conducted on APS YbDS – A (Trial 1) unreacted corner. Numbered regions correspond to site measurements in Table B3. Each tile was cropped from the original micrograph, adjusted contrast/brightness levels, and measured porosity by thresholding.

## B.2. Raw Data and Statistics

	Trial		Contact /	Angle [°]			Width	ι [μm]		Height [µm]			
Substrate	No.	1150°C	0h @ 1250°C	2h @ 1250°C	4h @ 1250°C	1150°C	0h @ 1250°C	2h @ 1250°C	4h @ 1250°C	1150°C	0h @ 1250°C	2h @ 1250°C	4h @ 1250°C
	1	87.167	45.449	28.090	39.499	2111.405	2352.355	3606.001	3762.131	1402.454	1313.178	613.266	558.822
	_	106.333	47.433	29.132	29.155							01001200	
	2	113.256	37.286	35.822	N/A	1980.659	2413.104	3762.348	N/A	1509.059	1397.294	651.047	N/A
APS LaDS	_	105.914	38.470	29.407	,				,				,
7	3	94.064	26.074	26.584	N/A	2074.366	2426.595	3858.740	N/A	1446.272	1347,769	735.259	N/A
	•	120.040	44.062	31.775	,				,				
	4	109.748	47.493	44.048	N/A	2128.536	2522.945	3845,184	N/A	1420.894	1303.899	701.285	N/A
		85.945	47.667	51.322	,				,				,
	1	106.526	62.089	22.621	32.660	2010.766	2142,594	3257.093	3458,179	1163.337	923.616	417.090	292.348
	-	107.715	59.852	17.017	13.518	20100.00	2112.0001	0207.0000	0 10012/0	1100.007	5201010	1271050	202.010
	2	115.745	44.496	25.051	N/A	1975.522	2266,990	3976,228	N/A	1253,183	1160,770	550,160	N/A
APS NdDS	_	109.622	43.245	18.897		13731322	2200.550	00701220	,//	12001200	11000,70		,//
	3	79.172	60.118	81.410+	N/A	2009.913	2539.040	4194,456	N/A	962,692	916.367	592,714	N/A
		91.548	44.700	36.092	,	2003.515	23031010	110 11100	,//	502.052	5101007	5521721	,//
	4	121.692	48.787	37.582	N/A	1977,965	2231,163	4266,490	N/A	1178,180	1112,229	611,896	N/A
		123.642	45.964	43.547	,				,				,
	1	139.179	47.321	28.479	51.192	2208,592	2328,160	4502.080	4755,963	1721,135	1617,661	792,681	611.522
	_	84.922	48.014	29.756	57.228								
	2	117.693	47.160	35.603	N/A	2059.454	2350.238	3880.752	N/A	1373.986	1263.331	689.327	N/A
APS GdDS	_	97.834	43.268	41.003	,				,				,
APS GdDS	3	75.546	40.892	34.740	N/A	2024.305	2350.255	3790.295	N/A	1435.660	1297.776	673.731	N/A
		105.113	43.932	37.322	N/A 2024.	202 1.000	2000.200	0,00.200	,//	1 1001000	1257.070	0/01/01	,//
	4	100.436	43.876	40.109	N/A 2001 71	2001.711	2223.657	3930.289	N/A	1472.428	1363.620	627.052	N/A
	•	114.720	44.062	43.097	,,,	2001.711	2220.007	0000.200		172.120	1000.020	027.002	,,,

Table B4: Raw data for molten CMAS contact angle, width, and height measurements on polished EBC substrates

	1	104.053 105.598	74.889 75.799	12.221 13.716	11.231 14.323	1981.697	2009.815	2297.993	2548.170	1170.308	1063.313	261.748	281.500
	2	118.703 128.147	59.795 59.018	15.741 16.869	N/A	1824.603	1941.118	3202.330	N/A	1487.120	1400.730	386.786	N/A
APS YDS	3	116.741 104.758	56.246 58.705	15.598 15.187	N/A	1852.148	2055.249	2911.627	N/A	1278.476	1156.478	375.865	N/A
	4	103.284 112.401	53.879 56.989	15.924 16.846	N/A	1941.770	2001.350	3704.974	N/A	1612.579	1502.251	425.418	N/A
	1	104.756 108.895	45.976 46.302	10.701 13.731	N/A	1873.710	2023.473	4043.357	N/A	1577.988	1504.341	417.657	N/A
	2	87.333 118.692	41.132 40.632	10.789 15.564	N/A	1887.588	2160.610	3528.258	N/A	1517.988	1433.863	579.425	N/A
AF3 LUD3	3	111.533 121.452	44.753 50.582	12.763 13.895	12.495 14.730	2016.188	2124.922	4078.601	4155.776	1578.591	1481.622	393.105	348.340
	4	108.707 107.289	76.858 74.831	12.265 13.056	N/A	2117.785	2109.450	2488.435	N/A	1270.728	1148.411	423.759	N/A
	1	105.953 115.798	N/A	N/A	N/A	1858.367	N/A	N/A	N/A	1312.554	N/A	N/A	N/A
	2	97.686 106.444	44.654 50.096	12.657 12.943	N/A	1797.822	2060.943	3614.223	N/A	1393.783	1292.146	343.988	N/A
AF3 TDD3	3	109.571 114.498	52.549 49.600	13.630 15.330	N/A	2101.162	2247.842	3938.352	N/A	1389.693	1282.978	378.323	N/A
	4	115.117 117.867	50.001 51.097	12.914 14.480	N/A	1972.423	2210.698	3492.260	N/A	1440.294	1347.372	318.883	N/A
	1	107.103 106.085	51.781 53.686	11.441 22.214	12.748 19.906	1956.689	2145.135	3409.731	3599.805	977.424	586.890	302.239	255.934
	2	118.523 120.490	46.952 48.595	20.867 16.613	N/A	1832.203	2257.220	4296.369	N/A	654.552	593.689	350.318	N/A
APS YbDS – A —	3	104.506 75.486	44.694 43.244	12.686 14.310	N/A	1759.205	2193.073	3543.937	N/A	690.213	585.733	279.062	N/A
	4	101.476 115.857	33.742 52.763	5.490 20.659	N/A	1935.677	2280.138	4126.576	N/A	761.488	682.031	325.815	N/A

	1	96.492 102.210	32.922 36.132	12.498 11.321	13.715 11.058	2247.964	2658.771	3776.166	3756.340	1323.512	1143.037	351.517	336.551
	2	104.333 114.041	36.648 41.199	14.142	N/A	2061.964	2623.096	3934.439	N/A	1532.832	1338.338	376.967	N/A
APS YbDS – C	3	107.877 121.157	47.503 51.122	11.835 14.900	N/A	2128.556	2399.760	3304.971	N/A	1510.386	1317.896	312.431	N/A
	4	145.948 142.488	63.159 62.613	15.187 10.258	N/A	1999.775	1953.662	3272.637	N/A	1660.176	1477.214	311.209	N/A
	1	108.521 102.614	80.992 86.029	Not Detected	Not Detected	2257.829	2171.724	Not Detected	Not Detected	1075.090	792.792	Not Detected	Not Detected
	2	108.237 124.634	100.146 96.234	Not Detected	N/A	2116.115	2044.638	Not Detected	N/A	1450.158	1220.712	Not Detected	N/A
APS TODS - P	3	144.598 162.305	112.704 123.232	35.608 25.339	N/A	2014.149	1960.369	566.493	N/A	1631.164	1344.219	299.666	N/A
	4	100.441 98.830	85.762 75.049	Not Detected	N/A	2169.312	2093.836	Not Detected	N/A	1385.326	1063.956	Not Detected	N/A
	1	103.184 110.179	53.791 55.145	14.856 13.146	N/A	1821.034	2047.524	2907.373	N/A	1279.812	1200.017	274.115	N/A
	2	108.701 112.554	54.588 55.368	14.715 13.462	N/A	1877.389	2010.295	3126.489	N/A	1494.431	1388.794	295.176	N/A
SPS 1005	3	91.395 95.069	50.662 53.354	13.351 13.000	N/A	1859.791	2003.689	3769.441	N/A	1370.150	1232.081	318.046	N/A
	4	135.268 119.379	43.410 42.266	14.029 14.147	18.977 13.681	1967.437	2087.953	3951.176	3874.581	1668.369	1523.376	328.543	269.926
	1	117.695 118.804	52.710 51.344	14.007 12.914	N/A	1881.639	2061.997	3364.263	N/A	1159.543	1042.197	326.392	N/A
SPS	2	107.382 104.417	41.057 41.917	12.526 15.215	N/A	2034.440	2284.715	4117.032	N/A	1436.583	1337.892	400.502	N/A
SPS 20YbMS/YbDS 3	3	105.152 102.382	63.669 64.954	11.318 12.885	N/A	1939.909	2024.238	3000.071	N/A	1343.243	1222.497	327.620	N/A
	4	122.512 110.860	40.397 43.432	19.005 18.402	13.606 12.776	2001.781	2202.459	3836.226	4374.333	1640.502	1536.073	656.736+	390.677

	1	99.381	32.078	18.831	15.217	2220 162	2936.342	3996.152	3999,781	1394 029	1163.516	458.566	450.925
	Ţ	99.266	33.525	17.245	18.053	2220.105			5999.761	1594.029			
	2	103.663	31.314	14.627	NI/A	2640.698	2800.474	1101 700	N/A	1581.063	1213.979	420.415	N/A
		117.729	33.359	17.807	N/A			4191.790					
	3	98.633	31.426	17.532	NI/A	2106 610	2000 215	4312.975	N/A	1420.323	1198.170	454.197	N/A
		108.780	32.980	19.202	N/A	2100.010	2900.215						
	4	133.221	44.876	16.349	NI/A	1990.806	2241.169	4276.663	N/A	1630.549	1506.532	447.835	N/A
		126.269	45.124	16.255	N/A								
APS YbMS	1	134.873	50.977	12.280	10.519	2023.361	2035.325	3407.080	3959.273	1738.866	1663.489	818.307	309.218
		151.153	55.718	14.303	8.783								
	2	114.825	58.601	16.061	N1 / A	2021.231		2150 204	N1 / A	1705 017	1505 207	061 010	
		138.940	62.544	16.205	N/A		1982.505	3159.304	N/A	1705.917	1090.387	801.210	N/A
	2	90.918	34.251	10.862		2132.598	2409.572	3807.290	N/A	1535.735	4 4 7 0 7 4 7	627.062	
	3	110.177	37.223	13.556	N/A						1470.717	627.863	N/A

<sup>+</sup> = considered outlier in dataset, not included in statistical analysis

		Co	ontact Angle	[°]		Width [µm]		Height [µm]			
Substrate	Statistic	1150°C	0h @ 1250°C	2h @ 1250°C	1150°C	0h @ 1250°C	2h @ 1250°C	1150°C	0h @ 1250°C	2h @ 1250°C	
APS LaDS	Ave.	102.808	41.742	34.523	2073.741	2428.750	3768.068	1444.670	1340.535	675.214	
	St. Dev.	12.432	7.519	8.798	66.045	70.612	116.142	46.533	42.287	53.872	
	Ave.	106.958	51.157	28.687	1993.542	2294.947	3923.567	1139.348	1028.246	542.965	
APS NUDS	St. Dev.	15.071	8.077	10.302	19.425	170.922	461.135	124.163	126.596	87.793	
	Ave.	104.430	44.816	36.264	2073.515	2313.077	4025.854	1500.802	1385.597	695.698	
APS GuDS	St. Dev.	19.871	2.450	5.221	93.132	60.516	322.732	152.400	160.206	69.859	
	Ave.	111.710	61.915	15.263	1900.054	2001.883	3029.231	1387.120	1280.693	362.454	
APS 1DS	St. Dev.	8.945	8.496	1.582	73.923	46.917	587.404	199.702	205.086	70.423	
	Ave.	108.582	52.633	12.846	1973.818	2104.614	3534.663	1486.324	1392.059	453.487	
APS LUDS	St. Dev.	10.313	14.671	1.625	115.440	58.181	741.457	146.515	165.067	84.998	
	Ave.	110.367	49.666	13.659	1932.444	2173.161	3681.612	1384.081	1307.498	347.065	
APS TUDS	St. Dev.	6.77904	2.675	1.052	133.759	98.942	230.555	52.920	34.834	29.839	
	Ave.	106.191	46.932	15.535	1870.943	2218.892	3844.153	770.919	612.085	314.358	
AFS TODS - A	St. Dev.	14.2362	6.530	5.704	92.248	61.446	433.249	144.670	46.762	30.643	
	Ave.	116.818	46.412	12.854	2109.565	2408.822	3572.053	1506.727	1319.121	338.031	
APS TODS - C	St. Dev.	18.503	11.811	1.755	106.199	324.366	333.651	138.815	137.076	32.003	
	Ave.	118.772	95.019	N/A	2139.351	2067.642	N/A	1385.435	1105.420	N/A	
APS TUDS - P	St. Dev.	23.322	16.469	N/A	88.247	76.740	N/A	231.579	237.888	N/A	
	Ave.	103.514	53.818	13.755	1852.738	2020.503	3267.768	1381.464	1273.631	295.779	
2601 242	St. Dev.	8.618	1.728	0.816	28.832	23.633	448.063	107.756	101.015	21.972	
SPS	Ave.	112.248	49.935	14.534	1964.442	2143.353	3579.398	1394.968	1284.665	427.813	
20YbMS/YbDS	St. Dev.	8.950	10.002	2.814	67.706	121.496	495.61	200.099	207.119	156.500	
	Ave.	110.868	35.585	17.231	2259.569	2739.550	4194.395	1506.491	1270.550	445.253	
APS (1+10)DS	St. Dev.	13.397	5.869	1.482	273.477	340.951	141.582	116.939	158.727	17.135	
ADS VHMC	Ave.	123.481	49.886	13.878	2059.063	2142.487	3457.891	1660.173	1576.531	769.127	
APS YDIVIS	St. Dev.	22.121	11.629	2.103	63.692	232.802	326.968	109.018	97.760	124.205	

Table B5: Statistics of molten CMAS contact angle, width, and height measurements on polished EBC substrates

Substrate	CMAS Load	Contact Angle [°]				Width [µm]					Normalized Spreading [mm <sup>2</sup> /mg]			
[mg	[mg]	1150°C	0h @ 1250°C	2h @ 1250°C	4h @ 1250°C	1150°C	0h @ 1250°C	2h @ 1250°C	4h @ 1250°C	1150°C	0h @ 1250°C	2h @ 1250°C	4h @ 1250°C	4h @ 1250°C
APS YbDS	9.87	118.235 112.532	51.309 48.970	13.468 13.529	18.977 7.764	1950.917	2064.565	4080.190	3872.184	1262.268	1184.579	377.813	266.825	5.441
APS YbDS – A	10.78	90.481 105.948	40.046 38.407	13.351 11.915	5.360 5.553	2145.728	2467.067	3836.262	3848.077	1569.073	1423.589	292.107	266.356	4.763
APS YbDS – C	10.88	124.795 132.453	57.266 64.444	21.597 39.837	72.035 107.969	2021.138	2009.433	3012.717	2319.827	1804.928	1593.395	223.009	188.366	4.820
APS YbDS – F	10.74	103.229 118.399	94.657 97.016	61.714 56.633	Did not measure	2001.700	1964.818	1084.367	361.097	1454.355	1226.958	389.838	166.933	2.685

Table B6: Raw data for molten CMAS contact angle, width, height, and spreading measurements on unpolished EBC substrates

Substrate	Trial No.	Time [h]	CMAS Load [mg]	Spreading Area [mm²]	Normalized Spreading Area [mm²/ mg]	Average Norm. Spreading Area [mm²/ mg]	Std. Dev. Norm. Spreading Area [mm²/ mg]	
	1	4	10.32	23.476	2.275	N/A	N/A	
	2	2	10.05	13.904	1.383			
APS LaDS	3	2	10.38	13.017	1.254	1.332	0.0562	
	4	2	10.24	13.920	1.359			
	1	4	10.20	16.876	1.655	N/A	N/A	
	2	2	10.20	15.983	1.567			
APS NODS	3	2	9.60	15.791	1.645	1.597	0.0343	
	4	2	10.75	16.973	1.579			
	1	4	13.40	17.262	1.288	N/A	N/A	
	2	2	9.95	12.956	1.302			
APS GuDS	3	2	9.60	13.367	1.392	1.347	0.0369	
	4	2	9.66	13.012	1.347			
APS YDS	1	4	10.05	17.272	1.719	N/A	N/A	
	2	2	10.09	17.109	1.696			
	3	2	10.74	18.302	1.704	1.739	0.0550	
	4	2	11.65	21.159	1.816			
	1	4	10.12	27.267	2.694		N/A	
	2	2	10.10	26.245	2.599	NI / A		
APS LUDS	3	2	9.80	28.457	2.904	IN/A		
	4	2	11.20	26.877	2.400			
	1*	~1.5	10.40	13.384	1.287	N/A	N/A	
	2	2	9.86	20.403	2.069		0.0645	
APS TUDS	3	2	10.46	21.678	2.072	2.025		
	4	2	10.55	20.405	1.934			
	1	4	9.71	20.321	2.093	N/A	N/A	
	2	2	10.05	20.229	2.013			
AFS TUDS - A	3	2	10.10	19.250	1.906	2.007	0.0799	
	4	2	9.48	19.920	2.101			
	1	4	10.55	24.664	2.338	N/A	N/A	
	2	2	10.80	22.871	2.118			
APS YDDS - C	3	2	10.75	22.395	2.083	2.197	0.1378	
	4	2	9.50	22.717	2.391			
	1	4	10.51	22.303	2.122	N/A	N/A	
	2	2	10.31	19.208	1.863			
Ar5 1003 - F	3	2	10.85	17.632	1.625	1.856	0.1860	
	4	2	11.10	23.093	2.080			

Table B7: Spreading measurements on polished EBC substrates

SPS YbDS	1	2	10.16	21.719	2.138			
	2	2	9.82	21.766	2.216	2.167	0.0354	
	3	2	10.32	22.144	2.146			
	4	4	9.65	23.979	2.485	N/A	N/A	
	1	2	10.15	20.436	2.013			
SPS	2	2	9.90	20.643	2.085	2.019	0.0517	
20YbMS/YbDS	3	2	10.25	20.078	1.959			
	4	4	10.15	23.203	2.286	N/A	N/A	
	1	4	10.15	19.852	1.956	N/A	N/A	
	2	2	10.55	20.837	1.975			
AP3 (1+10)03	3	2	10.45	19.883	1.903	1.946	0.0311	
	4	2	10.00	19.592	1.959			
APS YbMS	1	4	10.79	29.525	2.736			
	2	2	10.43	18.243	1.749	N/A	N/A	
	3	2	10.74	23.682	2.205			

\* = experiment failed due to computer software malfunction; all materials were used, and trial was unable to be repeated



Figure B11: Individual CMAS spreading measurements on APS REDS vs. porosity after (a) 2- and (b) 4hour exposures at 1250°C.



## B.3. Relationships Between CMAS Wetting Measurements

Figure B12: Molten CMAS width vs. height measurements of all substrates exposure at (a) ~1150°C, after (b) 0-hours at ~1250°C, (c) 2-hours at ~1250°C, and (d) 4-hours at ~1250°C. Legend in (a) applies to all plots. NOTE: break in y-axis of (c).



Figure B13: (a, b) Molten CMAS contact angle, (c, d) molten CMAS width, and (e, f) molten CMAS height vs. normalized spreading measurements of all substrates after exposure for (a, c, e) 2- and (b, d, f) 4- hours at ~1250°C. Legend in (a) applies to all plots. NOTE: break in y-axis of (c).



Figure B14: (a, b) molten CMAS contact angle and (c, d) normalized spreading measurements vs. CMAS width/height measurements of all substrates after exposure for (a, c) 2- and (b, d) 4-hours at ~1250°C. Legend in (a) applies to all plots.



Figure B15: Molten CMAS contact angle measurements of Yb-silicate substrates of various microstructures, compositions, and porosity contents at (a) ~1150°C, after (b) 0-hours at ~1250°C, (c) 2-hours at ~1250°C, and (d) 4-hours at ~1250°C. Measurements are plotted as a function of average RE cation size. NOTE: y-axis in (a) and (b) are adjusted to best depict trends in data; (a)-(c) are averages while (d) plots data from the single 4h experiment; No contact angle measurement was recorded during the 4-hour CMAS exposure on the highly porous APS YbDS – F specimen due to the CMAS achieving complete infiltration. Legend in (a) applies to all plots.



Figure B16: Molten CMAS width measurements of Yb-silicate substrates of various microstructures, compositions, and porosity contents at (a) ~1150°C, after (b) 0-hours at ~1250°C, (c) 2-hours at ~1250°C, and (d) 4-hours at ~1250°C. Measurements are plotted as a function of average RE cation size. NOTE: y-axis in (a) and (b) are adjusted to best depict trends in data; (a)-(c) are averages while (d) plots data from the single 4h experiment. Legend in (a) applies to all plots.



Figure B17: Molten CMAS height measurements on Yb-silicate substrates of various microstructures, compositions, and porosity contents at (a) ~1150°C, after (b) 0-hours at ~1250°C, (c) 2-hours at ~1250°C, and (d) 4-hours at ~1250°C. Measurements are plotted as a function of average RE cation size. NOTE: y-axis in (a) and (b) are adjusted to best depict trends in data; (a)-(c) are averages while (d) plots data from the single 4h experiment. Legend in (a) applies to all plots.


Figure B18: Residual CMAS spreading area measurements on Yb-silicate substrates of various microstructures, compositions, and porosity contents after exposure at ~1250°C for (a) 2- and (b) 4- hours. Measurements were normalized to the CMAS loading and are plotted as a function of average RE cation size. NOTE: (a) are averages on at least three trials, while (b) are measurements on individual 4h experiments; Legend in (a) applies to all plots.



Figure B19: Molten CMAS width measurements on polished and unpolished YbDS substrates of various porosity contents after exposure at (a) ~1150°C, after (b) 0-hours at ~1250°C, (c) 2-hours at ~1250°C, and (d) 4-hours at ~1250°C. Measurements are plotted against root mean square (RMS) roughness. Polished specimens are plotted at the corresponding unpolished RMS measurement to visualize the effect of surface roughness. Legend in (a) applies to all plots.



Figure B20: Molten CMAS height measurements on polished and unpolished YbDS substrates of various porosity contents after exposure at (a) ~1150°C, after (b) 0-hours at ~1250°C, (c) 2-hours at ~1250°C, and (d) 4-hours at ~1250°C. Measurements are plotted against root mean square (RMS) roughness. Polished specimens are plotted at the corresponding unpolished RMS measurement to visualize the effect of surface roughness. Legend in (d) applies to all plots.

# Appendix C: Supplemental Materials for Chapter 4

## C.1. Materials Characterization

Table C1: List of transparency and colors of as-made CMAS and CMXAS glass
---

Species (X <sup>n+</sup> )	Transparency	Color				
0.73 C:S						
(this	Clear	Colorless				
study)						
Webster						
& Opila	Clear	Colorless				
0.73 C:S						
'red'	Clear	Red tint				
0.73 C:S	Otea	Neu tint				
5 Fe <sup>2+</sup>	Opaque	Black				
5 Fe <sup>3+</sup>	Opaque	Black				
10 Fe <sup>3+</sup>	Opaque	Black				
5 Gd <sup>3+</sup>	Clear	Colorless				
5 Hf <sup>4+</sup>	Clear	Colorless				
10 La <sup>3+</sup>	Clear	Colorless				
10 Lu <sup>3+</sup>	Clear	Colorless				
5 Na⁺	Clear	Colorless				
10 Nd <sup>3+</sup>	Clear	Purple				
10 Sc <sup>3+</sup>	Clear	Colorless				
5 Ti <sup>4+</sup>	Clear	Yellow tint				
10 Y <sup>3+</sup>	Clear	Yellow tint				
10 Yb <sup>3+</sup>	Clear	Yellow tint				
5Y <sup>3+</sup> &	Clear	Vollow				
5Yb <sup>3+</sup>	Glear	renow				
5 Zr <sup>4+</sup>	Clear	Yellow				



Figure C1: XRD of select as-made CMAS and CMXAS glasses, compositions listed on the right.

### C.2. Equipment Calibrations



Figure C2: Viscosity measurement of NIST SRM 717a borosilicate glass standard and % error of measurements at the start and end of study.

Table C2: Statistics on % error of borosilicate glass standard viscosity measurement over the temperature range of 1250°C to 1350°C.

Point in Time	No. of Datapoints	Mean	One Std. Dev.	First Quartile	Median	Third Quartile	
Start of study	317	2.03	0.276	1.82	2.04	2.25	
End of Study	308	0.418	0.351	0.152	0.354	0.589	

## C.3. Raw Data

	Average Measured T <sub>Glass</sub> [°C] and η <sub>SetTemp</sub> [Log (Pa-s)] (± std. dev.)																					
Species (X <sup>n+</sup> )	T <sub>Glass</sub>	<b>1</b> 1300°C	T <sub>Glass</sub>	<b>ŋ</b> 1325°C	T <sub>Glass</sub>	<b>1</b> 1350°C	T <sub>Glass</sub>	<b>1</b> 1375°C	T <sub>Glass</sub>	<b>n</b> 1400°C	T <sub>Glass</sub>	<b>n</b> 1425°C	T <sub>Glass</sub>	<b>n</b> 1450°C	T <sub>Glass</sub>	<b>n</b> 1475°C	T <sub>Glass</sub>	<b>ŋ</b> 1500°C	T <sub>Glass</sub>	<b>1</b> 1525°C	T <sub>Glass</sub>	<b>1</b> 1550°C
0.73 C:S Baseline	1291	0.577 (0.003)	1316	0.456 (0.004)	1340	0.342 (0.002)	1365	0.232 (0.003)	1390	0.131 (0.004)	1415	0.035 (0.004)	1440	-0.052 (0.009)	1464	-0.138 (0.010)	1489	-0.223 (0.004)	1513	-0.319 (0.020)	1536	-0.401 (0.012)
'red' 0.73 C:S	1291	0.518 (0.004)	1316	0.399 (0.005)	1340	0.292 (0.004)	1365	0.187 (0.005)	1390	0.092 (0.005)	1415	-0.009 (0.010)	1440	-0.092 (0.009)	1464	-0.171 (0.015)	1489	-0.253 (0.016)	1513	-0.333 (0.020)	1536	-0.395 (0.015)
5 Fe <sup>2+</sup>	1289	0.316 (0.007)	1314	0.203 (0.003)	1339	0.0988 (0.005)	1364	-0.0005 (0.006)	1389	-0.092 (0.007)	1414	-0.180 (0.011)	1439	-0.264 (0.019)	1464	-0.351 (0.020)	1489	-0.425 (0.026)	1513	-0.501 (0.028)	1535	-0.577 (0.032)
5 Fe <sup>3+</sup>	1289	0.224 (0.005)	1314	0.113 (0.005)	1339	0.007 (0.004)	1364	-0.087 (0.007)	1389	-0.187 (0.011)	1414	-0.298 (0.005)	1439	-0.369 (0.024)	1464	-0.435 (0.027)	1488	-0.518 (0.045)	1513	-0.609 (0.057)	1536	-0.645 (0.055)
10 Fe <sup>3+</sup>	1289	0.0886 (0.007)	1314	-0.017 (0.007)	1339	-0.118 (0.008)	1364	-0.211 (0.006)	1389	-0.309 (0.016)	1414	-0.387 (0.022)	1439	-0.480 (0.029)	1464	-0.557 (0.036)	1489	-0.636 (0.042)	1513	-0.706 (0.037)	1536	-0.766 (0.057)
5 Gd <sup>3+</sup>	1290	0.538 (0.005)	1315	0.406 (0.004)	1340	0.289 (0.003)	1364	0.175 (0.003)	1389	0.071 (0.005)	1414	-0.025 (0.005)	1439	-0.121 (0.008)	1464	-0.199 (0.006)	1489	-0.298 (0.005)	1513	-0.357 (0.018)	1536	-0.446 (0.018)
5 Hf <sup>4+</sup>	1289	1.255* (0.006)	1314	1.135* (0.006)	1339	1.033* (0.005)	1364	0.933* (0.007)	1389	0.850* (0.008)	1414	0.772* (0.114)	1439	0.111 (0.009)	1464	0.017 (0.007)	1488	-0.065 (0.007)	1513	-0.138 (0.006)	1533	-0.210 (0.011)
10 La <sup>3+</sup>	1290	1.285* (0.027)	1315	1.136* (0.021)	1340	0.989* (0.010)	1365	0.837* (0.013)	1390	0.682* (0.016)	1414	0.522* (0.015)	1439	0.195* (0.206)	1464	-0.348 (0.030)	1489	-0.429 (0.027)	1514	-0.494 (0.031)	1537	-0.574 (0.035)
10 Lu <sup>3+</sup>	1292	0.632 (0.006)	1317	0.485 (0.004)	1342	0.347 (0.004)	1367	0.221 (0.006)	1392	0.094 (0.005)	1417	-0.019 (0.005)	1442	-0.127 (0.008)	1466	-0.230 (0.010)	1491	-0.341 (0.015)	1515	-0.434 (0.025)	1539	-0.532 (0.022)
5 Na⁺	1290	0.508 (0.006)	1315	0.392 (0.004)	1340	0.281 (0.003)	1365	0.175 (0.004)	1390	0.078 (0.003)	1414	-0.022 (0.003)	1439	-0.115 (0.007)	1464	-0.196 (0.007)	1489	-0.298 (0.004)	1513	-0.376 (0.023)	1536	-0.456 (0.002)
10 Nd <sup>3+</sup>	1290	1.289* (0.039)	1315	1.154* (0.025)	1340	0.990* (0.027)	1365	0.837* (0.014)	1390	0.683* (0.019)	1415	0.517* (0.017)	1440	0.212* (0.246)	1464	-0.301 (0.005)	1489	-0.377 (0.023)	1514	-0.463 (0.023)	1537	-0.546 (0.034)
10 Sc <sup>3+</sup>	1290	0.566 (0.004)	1315	0.418 (0.005)	1340	0.282 (0.005)	1365	0.157 (0.006)	1390	0.043 (0.007)	1415	-0.066 (0.008)	1439	-0.171 (0.007)	1464	-0.291 (0.015)	1489	-0.364 (0.023)	1513	-0.452 (0.034)	1537	-0.555 (0.036)
5 Ti <sup>4+</sup>	1290	0.325 (0.003)	1315	0.210 (0.003)	1341	0.101 (0.005)	1365	-0.004 (0.006)	1390	-0.106 (0.006)	1415	-0.202 (0.006)	1440	-0.300 (0.010)	1464	-0.382 (0.021)	1489	-0.472 (0.026)	1513	-0.568 (0.035)	1537	-0.677 (0.035)
10 Y <sup>3+</sup>	1289	0.589 (0.004)	1314	0.456 (0.004)	1339	0.333 (0.004)	1364	0.217 (0.004)	1389	0.107 (0.008)	1414	0.007 (0.007)	1439	-0.085 (0.007)	1463	-0.178 (0.008)	1489	-0.268 (0.016)	1512	-0.346 (0.005)	1535	-0.408 (0.018)
10 Yb <sup>3+</sup>	1291	1.009* (0.281)	1315	0.420 (0.004)	1341	0.288 (0.007)	1365	0.163 (0.004)	1390	0.049 (0.008)	1415	-0.059 (0.008)	1440	-0.159 (0.007)	1465	-0.262 (0.007)	1489	-0.347 (0.010)	1513	-0.440 (0.023)	1537	-0.522 (0.007)
5Y <sup>3+</sup> & 5Yb <sup>3+</sup>	1290	1.301* (0.017)	1315	1.119* (0.012)	1340	0.943* (0.011)	1365	0.624* (0.228)	1390	0.035 (0.009)	1415	-0.079 (0.005)	1439	-0.183 (0.010)	1464	-0.298 (0.004)	1489	-0.388 (0.023)	1513	-0.487 (0.031)	1536	-0.577 (0.033)
5 Zr <sup>4+</sup>	1290	0.740* (0.006)	1315	0.615* (0.004)	1340	0.499* (0.004)	1365	0.400* (0.005)	1390	0.265* (0.018)	1415	0.103 (0.008)	1440	0.007 (0.005)	1464	-0.078 (0.006)	1489	-0.155 (0.010)	1513	-0.226 (0.10)	1536	-0.301 (0.035)

#### Table C3: Viscosity measurements of CMAS and CMXAS glasses

\* = precipitation occurred in-situ, changing glass composition and increasing viscosity

Table C4: Coefficient of Thermal Expansion (CTE) from 200-600°C, Softening Temperature ( $T_d$ ), and Glass Transition ( $T_g$ ) of CMXAS Fifth Oxide Additions

CMAS or CMXAS (X <sup>n+</sup> ) Species	CTE [°Cx10 <sup>-6</sup> ] (± std. dev.)	Td [°C] (± std. dev.)	T <sub>g</sub> [°C] (± std. dev.)
0.73 C:S Baseline	9.446 (0.057)	762.7 (11.09)	714.3 (5.558)
Webster & Opila 0.73 C:S	9.271 (0.303)	787.7 (4.921)	742.3 (6.128)
'red' 0.73 C:S	9.880 (0.104)	745. 7 (4.714)	695.7 (6.650)
5 Fe <sup>2+</sup>	9.508 (0.030)	729.7 (0.471)	671.3 (1.247)
5 Fe <sup>3+</sup>	9.229 (0.597)	753.7 (0.943)	683.0 (2.828)
10 Fe <sup>3+</sup>	9.746 (0.256)	708.7 (8.654)	650.7 (9.741)
5 Gd <sup>3+</sup>	9.428 (0.141)	804.7 (1.700)	721.0 (4.320)
5 Hf <sup>4+</sup>	8.410 (0.053)	833.3 (2.494)	727.3 (0.471)
10 La <sup>3+</sup>	9.653 (0.098)	801.7 (6.944)	715.3 (0.471)
10 Lu <sup>3+</sup>	8.880 (0.214)	837.7 (2.494)	726.3 (2.357)
5 Na⁺	10.21 (0.311)	746.7 (12.28)	683.3 (6.549)
10 Nd <sup>3+</sup>	9.766 (0.090)	805.0 (2.828)	714.3 (1.247)
10 Sc <sup>3+</sup>	8.430 (0.270)	839.0 (3.559)	729.0 (0.817)
5 Ti <sup>4+</sup>	9.314 (0.186)	786.0 (6.683)	712.7 (2.867)
10 Y <sup>3+</sup>	8.975 (0.312)	814.3 (5.185)	734.0 (7.257)
10 Yb <sup>3+</sup>	9.023 (0.224)	818.7 (3.399)	769.0 (5.354)
5Y <sup>3+</sup> & 5Yb <sup>3+</sup>	8.649 (0.307)	807.7 (2.625)	759.7 (0.471)
5 Zr <sup>4+</sup>	8.813 (0.086)	817.7 (1.247)	726.3 (1.247)

C.4. Sensitivity of Glass Composition on Viscometry



Figure C3: Difference of measured CMXAS viscosities from the comparable baseline CMAS of Feadditions varying in amount and initial valence. The solid horizontal line represents the measured values for the baseline CMAS composition at each of the temperatures explored.



Figure C4: Difference of measured CMAS viscosities with different measured CaO-SiO<sub>2</sub> ratios from the baseline CMAS used in this study. The solid horizontal line represents the measured values for the baseline CMAS composition at each of the temperatures explored.

## Appendix D: Supplemental Materials for Chapter 5

## D.1. Computational Parameters

Table D1: Inputs specific to Thermo-Calc System Definer and Equilibrium Calculator for dynamic viscosity calculations

Configuration	Cor	nditions		Func	tions		ıs	
Compositions	Unit of Composition	Temp	System Size	Quantity Definitions	Selected Constituent	Max iterations	One axis: Global minimization	Phase Diagram: Global minimization
All* nominal and measured compositions in single cation mole%	Mole percent	1150°C	1 mole	Q1 = Activity of component	0	500	Checked; Every 10 <sup>th</sup> eq	Checked; At node points; Generate starting points automatically; No. of meshes: 3
Nominal and measured 5GdO <sub>1.5</sub> & 5FeO additions in single cation mole%	Mole percent	1150°C	1 mole	Q1 = Activity of component	0	1000	<i>Unchecked;</i> Every 10 <sup>th</sup> eq	Checked; At node points; Generate starting points automatically; No. of meshes: 3
Nominal and measured 5FeO <sub>1.5</sub> additions in single cation mole%	Mole percent	1150°C	1 mole	Q1 = Activity of component	0	500 (Global min. <i>turned</i> <i>off</i> )	Checked; Every 10 <sup>th</sup> eq	Checked; At node points; Generate starting points automatically; No. of meshes: 3

\* = Except for GdO<sub>1.5</sub>, FeO<sub>1.5</sub>, and FeO additions

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