EQUILIBRIUM RELATIONSHIPS BETWEEN THERMAL BARRIER OXIDES AND SILICATE MELTS

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ABSTRACT

The phase equilibria between thermal barrier coating (TBC) materials and calcium–magnesium–aluminosilicate melts (CMAS, representing deposits formed when siliceous debris is ingested into modern turbine engines), were investigated at 1300°C. The primary goal was to understand the influence of the deposit and thermal barrier oxide compositions on the melt solubility limits and reaction product constitution. Model deposit compositions with SiO₂ to CaO ratios from 1.4 to 4.7 and with or without MgO were reacted with yttria- and gadolinia-zirconia thermal barrier oxides ranging from pure ZrO₂ to the pure yttria and gadolinia. The reactions formed various crystalline silicate phases; rare earth–calcium–silicate apatite and zircon (ZrSiO₄) were observed most frequently. Following the reactions, the residual melts were depleted in SiO₂ and generally enriched in CaO, MgO, and Al₂O₃. The implications of the anticipated changes in the melt viscosity and the cation partitioning between the melt and various solid solution phases on the efficacy of degradation-mitigating crystallization reactions are discussed.

Keywords: Thermal barrier coatings (TBC); Rare earth; Phase equilibria; CMAS; Solid solution

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1. INTRODUCTION

Modern turbine engines employ thermal barrier coatings (TBC) to protect metallic structures in the hot section. Increased operating temperatures have expanded the menu of failure mechanisms impacting the durability of these ceramic coatings [1, 2]. Several failure modes involve interaction between the coatings and molten deposits that arise when siliceous debris (volcanic ash, sand, dust) ingested into the engine adhere to hot gas path components and impregnate their TBCs. These deposits are generically termed ‘CMAS’ owing to their basis in the CaO-MgO-AlO_{1.5}^c-SiO₂ system. The deposit compositions, which may also include NaO_{0.5}, KO_{0.5}, FeO_x, TiO₂, etc vary regionally based on the geological sources and wear of upstream components [2, 3]. These composition variations make this degradation mode (and selection of an effective mitigation strategy) particularly complex because a coating material/architecture may exhibit drastically different behavior depending on the nature of the deposit.

Reactions with the deposit reduce the stability/adherence of the TBC as the melt wicks into the coating porosity, where it solidifies. Upon thermal cycling, the reduced in-plane compliance of the infiltrated layer increases thermal misfit stresses leading to premature coating failure. Thermomechanical analysis suggests that the stored elastic strain energy available to drive coating delamination/spallation increases nonlinearly with the depth of penetration [2, 4, 5]. To improve the coating durability following in-service CMAS deposition, mitigation strategies aim to minimize the depth of melt penetration by modifying the coating composition (to promote melt crystallization) or microstructure (to slow infiltration).

The melt crystallization behavior is determined by multi-component phase equilibria acting in concert with local temperature gradients. In the absence of coating/melt interaction the melt may crystallize if it drops significantly below its liquidus while infiltrating against the thermal gradient. These reactions are hereafter termed ‘intrinsic’ crystallization as they involve only oxides from the deposit; typical crystallization products are summarized in Table 1.

Alternatively, TBC dissolution into the melt may promote the crystallization of phases containing constituents from both the coating and deposit. This pathway, termed ‘reactive’ crystallization, has been the focus of efforts to develop thermal barrier oxides (TBOs) with improved resistance to degradation by silicate deposits. It is desired to maximize the ratio of the volume crystallized (V_{crys}) per volume of dissolved coating (V_{TBO}), as long as the crystallization

^c For convenience in interpreting molar concentrations, all oxides are represented in terms of single cation formula units. When appropriate, compact notation using the first letter of the cation symbol is employed (e.g. C = CaO, A = AlO_{1.5}, S=SiO₂, etc).

reactions occur on a timescale faster than infiltration. This behavior is exemplified by rare earth (RE) zirconate pyrochlores (e.g. $\text{Gd}_2\text{Zr}_2\text{O}_7$ [6]). Within tens of seconds [2] the $\text{REO}_{1.5}$ reacts with SiO_2 and CaO from the melt to crystallize a silicate with the oxyapatite structure, nominally $(\text{RE,Ca,Zr})_{10}(\text{SiO}_4)_6\text{O}_2$ [6]. Excess ZrO_2 concomitantly ‘reprecipitates’ as a $\text{REO}_{1.5}$ -depleted cubic (fluorite) or tetragonal ZrO_2 phase [7]. The consumption of SiO_2 and CaO from the melt via apatite crystallization may trigger subsequent intrinsic crystallization processes. Apatite and fluorite have been observed as initial reaction products for $\text{Gd}_2\text{Zr}_2\text{O}_7$ exposed to a variety of deposit compositions [6, 8, 9].

Not all rare earth-zirconia TBOs behave the same way. Some coatings (e.g., yttria stabilized zirconia, YSZ) do not contain enough $\text{REO}_{1.5}$ to saturate the melt and precipitate apatite. Similarly, coatings with smaller RE cations (e.g. Yb, Y) favor crystallization of slower-growing silicates such as garnet [7, 10] or cuspidine [11] (Table 1) rather than apatite. Additionally, the ratio $V_{\text{crys}}:V_{\text{TBO}}$ for a given reaction depends on the TBO solubility in the melt and the partitioning between the crystalline silicate(s) and reprecipitated fluorite [7, 12]. Studies on the behavior of YSZ coatings indicate that these processes are sensitive to the composition of the deposit. When exposed to silica-lean melts, YSZ dissolves and reprecipitates $\text{YO}_{1.5}$ -depleted tetragonal ZrO_2 that transforms to monoclinic ZrO_2 upon cooling [13]. Deposits with higher silica content react with YSZ to form ZrSiO_4 [4, 14] or $\text{Ca}_2(\text{ZrY})\text{Si}_4\text{O}_{12}$ [15]. Although these phases yield a high $V_{\text{crys}}:V_{\text{TBO}}$, they do not effectively block melt infiltration, presumably due to unfavorable crystallization kinetics or morphology.

The cumulative evidence indicates that the effectiveness of crystallization reactions to mitigate TBC degradation depends on both the TBO identity and the composition of the deposit. Efforts are currently underway to develop integrated, science-based understanding of the process with models to efficiently predict and optimize coating behavior upon exposure to a variety of deposits. This development has focused on characterizing the melting/crystallization behavior of relevant deposits [16], investigating and modeling the infiltration and failure behavior under thermal gradients [4], and elucidating the phase equilibria in key ternary subsystems [17] to support the development of thermodynamic databases. The further development of these databases to enable integration with thermomechanical models is hindered by a lack of data regarding the phase equilibria in higher-order systems (e.g. quinary/senary CMAS+TBO mixtures). This investigation is motivated by the need to identify relevant trends in reaction behavior and generate a dataset to benchmark new thermodynamic databases.

This study systematically investigates the equilibrium phases resulting from reactions between a range of silicate melts and candidate TBOs (or their constituents) under conditions relevant to the early-stage deposit-TBC interactions. Emphasis is placed on elucidating the interplay between the Si:Ca ratio and presence of MgO in the initial silicate deposit as well as the RE:Zr ratio in the TBO and the $\text{REO}_{1.5}$ identity on:

- (i) the evolution of the residual melt composition following reactions, including the solubility limits of the TBO constituents in the melt relative to particular reaction product assemblages,
- (ii) the propensity to form apatite relative to other crystalline silicates, and
- (iii) the nature and crystal chemistry origins of variations in reaction product composition and the implications of cation partitioning between various reaction products on the reaction efficiency.

2. EXPERIMENTAL APPROACH

Mixtures of thermal barrier oxides and synthetic silicate deposit powders were equilibrated at 1300°C and characterized to determine the equilibrium phase assemblage and solution phase compositions.

2.1 Materials

Based on knowledge of the relevant phase equilibria, Zaleski et al. developed a set of synthetic deposits that captures a range of melting and crystallization behavior [16]. A subset of these compositions, identified in Table 2 and Figure 1, was selected to span a range of $\text{SiO}_2\text{:CaO}$ ratios and to probe the role of MgO on crystallization. For simplicity, other minor constituents expected to have only secondary influence on the reactions (e.g. oxides of Fe, Ti, Na, K) were not included. $\text{C}_{36}\text{A}_{14}\text{S}_{50}^{\text{d}}$, $\text{C}_{24}\text{A}_{17}\text{S}_{59}$, and $\text{C}_{15}\text{A}_{15}\text{S}_{70}$ have similar $\text{AlO}_{1.5}$ content but vary the Si:Ca ratio from 1.4 to 4.7. $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$, originally chosen based on the composition of the liquid that had infiltrated column gaps in ex-service airfoild [18], provides a useful comparison to many past studies. $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ maintains the same Ca:Al:Si proportions as $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ while removing MgO. $\text{C}_{24}\text{A}_{17}\text{S}_{59}$ is the lowest ternary eutectic^e in the CAS ternary [19]. The FactSage free energy

^d Abbreviated molar concentrations are used throughout the manuscript: $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ corresponds to 36mol% CaO, 14mol% $\text{AlO}_{1.5}$, and 50mol% SiO_2 .

^e This nominal eutectic composition, used by MaO et al. in their thermodynamic assessment [19], differs slightly from the eutectic calculated by the FTOxid database, $\text{C}_{26}\text{A}_{15}\text{S}_{59}$, which is shown in Figure 1(a) and used to calculate the temperatures in Table 2.

minimization software (with FTOxid database [20]) was used to provide additional insight into the CaO-(MgO)-AlO_{1.5}-SiO₂ phase equilibria.

The C(M)AS powders were produced by solid state reaction of mixed oxides below the respective incipient melting temperatures [16, 21]. The measured onsets of melting for the three CAS compositions were in the range 1125°C to 1140°C while that for C₃₃M₉A₁₃S₄₅ was 1233°C [16].

The equilibria were assessed between the four deposit compositions and ZrO₂, Y_{0.08}Zr_{0.92}O_{1.96} (7YSZ), Y₄Zr₃O₁₂ (δ -phase), Gd₂Zr₂O₇ (pyrochlore), YO_{1.5}, or GdO_{1.5}. The 7YSZ, Y₄Zr₃O₁₂, and Gd₂Zr₂O₇ represent current or prospective TBC materials and were synthesized by precipitation of hydroxides from a precursor solution followed by pyrolysis at 1000°C, as described elsewhere [7]. The pure oxides capture the reactivity of the individual coating components. YO_{1.5} (2 μ m, 99.9%) and GdO_{1.5} (<10 μ m, 99.9%) were procured from Alfa Aesar, Ward Hill, MA and ZrO₂ (-325 mesh, 99%) was obtained from Sigma-Aldrich, St. Louis, MO.

2.2 Equilibration

The deposit and thermal barrier oxide powders were combined to achieve a 25mol% concentration of the TBO cations, e.g. 0.75C₃₃M₉A₁₃S₄₅ + 0.25G₅₀Z₅₀, (Gd₂Zr₂O₇) has the overall composition C_{24.75}M_{6.75}A_{9.75}S_{33.75}G_{12.5}Z_{12.5}. This proportion captures the reactions relevant to early-stage CMAS-TBC interaction, where minor differences in the equilibria could have a pronounced influence on the mitigation efficiency. The composition was also selected to retain the liquid phase to measure the ZrO₂, YO_{1.5}, and GdO_{1.5} saturation limits with respect to various reaction products. Previous experiments showed that mixtures with higher TBO content (e.g. 50mol%) were less likely to yield residual melt [12]. To ensure a homogeneous mixture, ethanol-based slurries were ground in an alumina mortar and pestle until dry. The mixed powders were cold pressed into 6mm diameter pellets weighing approximately 0.15g (~1.5mm thick).

The pellets were wrapped in platinum foil, suspended by platinum wire from an alumina rack in a box furnace, annealed for 50h or 200h at 1300°C, and quenched by rapid withdrawal into air (< 30s to reach ambient temperature). This approach allowed for simultaneous equilibration and quenching of multiple molten samples in non-reactive containers. The longer annealing time was used in cases where partially reacted material remained trapped within the reaction products after 50h.

2.3 Analysis

The equilibrated specimens were mounted in epoxy, cross sectioned, and polished to a 0.5µm finish using diamond suspensions. The microstructures were characterized using backscattered electron imaging (BSE-SEM, XL30 Sirion FEG, FEI, Hillsboro, OR) and transmission electron microscopy (TEM, Technai G2 Sphera, FEI). Phase identification relied on measured compositions and phase morphology, based on previous experience with the phases [12, 17]. In most cases the phases were uniformly distributed in the solidified melt. When heterogeneity (due to differences in buoyancy) was observed, the phase compositions were measured in areas with high and low precipitate volume fractions. The melt compositions in the respective areas were indistinguishable, indicating that the selective settling of denser phases did not influence the global equilibrium.

Compositions were measured by electron probe microanalysis (EPMA, SX-100, Cameca, Madison, WI) or, for cases with small grain size, energy dispersive spectroscopy in the TEM (TEM-EDS, Oxford, Concord, MA). The TEM-EDS quantification employed fluorite and amorphous $C_{33}M_9A_{13}S_{45}$ standards characterized by ICP-MS. Based on comparison with internal standards, errors are of order 1% and 5% of the measured values for EPMA and TEM-EDS, respectively. For convenience in distinguishing data from the two sources, the EPMA and TEM-EDS results are reported to 0.1 mol% and 1mol% precision, respectively.

3. RESULTS

3.1 Phase Equilibria in Silicate Deposits

In service only a portion of the ingested debris is likely to melt and infiltrate the TBC. The remainder of the adhered material accumulates as a semi-solid deposit on the coating surface (with its own implications for thermo-cyclic durability). The anticipated melting and intrinsic crystallization behavior for $CaO-AlO_{1.5}-SiO_2$ deposits, based on FactSage calculations, is shown in Figure 1(a). The influence of moderate MgO addition (9mol% MgO for $C_{33}M_9A_{13}S_{45}$) is illustrated in Figure 1(b). In both diagrams the range of compositions expected to be completely molten at 1300°C is superimposed on the liquidus projection with darker shading. The deposit compositions that may melt partially (forming liquid compositions around the perimeter of the darker field) are indicated with lighter shading. The equilibria in the regions without shading are below the solidus at 1300°C.

Melting in the CAS system, Figure 1(a), occurs via the eutectic reaction between tridymite (S), anorthite (Ca_2S_2) + pseudo-wollastonite (CS) at $\sim 1185^\circ\text{C}$ or the $\sim 1257^\circ\text{C}$ eutectic involving $\text{Ca}_2\text{S}_2 + \text{CS} + \text{C}_2\text{A}_2\text{S}$ (gehlenite, a melilite end member). At 1300°C the liquid field spans a $\sim 25\text{mol}\%$ change in both SiO_2 and CaO concentration but less than a $10\text{mol}\%$ change in the $\text{AlO}_{1.5}$ content. MgO addition, Figure 1(b), shifts the melilite field and stabilizes diopside (MCS_2), altering the solidus temperatures and increasing the range of $\text{AlO}_{1.5}$ concentrations in the liquid field. However, as illustrated by the overlaid fields in Figure 1(c), the MgO -containing liquid does not extend as far toward the CaO corner.

Based on the calculated equilibria the $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ and $\text{C}_{24}\text{A}_{17}\text{S}_{59}$ deposit compositions are in the liquid fields at 1300°C . $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ is in the CS crystallization field on the $\text{AlO}_{1.5}$ -lean side of the liquid field, and $\text{C}_{15}\text{A}_{15}\text{S}_{70}$ falls beyond the SiO_2 -saturated end of the liquid field. The observed phases for the pure deposits equilibrated at 1300°C , Figure 2 and Table 3, agree with the calculated equilibria. The single-phase melts produced by $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ and $\text{C}_{24}\text{A}_{17}\text{S}_{59}$, Figure 2(a,c), were quenched as glasses. $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ yielded liquid and CaSiO_3 , Figure 2(b), and $\text{C}_{15}\text{A}_{15}\text{S}_{70}$ produced a mixture of liquid and crystalline^f SiO_2 , Figure 2(d). The partitioning between the melt and crystalline phases for $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ and $\text{C}_{15}\text{A}_{15}\text{S}_{70}$, Table 4, is consistent with the melt compositions calculated using the FactSage FTOxid database, Table 2.

3.2 Equilibria with ZrO_2 and 7YSZ

Figure 3 shows the microstructures for ZrO_2 and 7YSZ reacted with the model deposits. The equilibrium phases for each combination are summarized in Table 3. No new phases are formed by interaction with $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ and $\text{C}_{36}\text{A}_{14}\text{S}_{50}$, although the CaSiO_3 present in the pure $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ is now absent. The ZrO_2 grains in Figure 3(a-c) contain up to $0.6\text{ mol}\%$ CaO suggesting that the ZrO_2 dissolves and reprecipitates with a modified composition. Likewise, the dissolution/reprecipitation of 7YSZ in $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ and $\text{C}_{36}\text{A}_{14}\text{S}_{50}$, e.g. Figure 4(a), yields heavily twinned ZrO_2 grains (indicative of the tetragonal to monoclinic transformation on cooling) containing approximately $3\text{ mol}\%$ $\text{YO}_{1.5}$ and $1\text{ mol}\%$ CaO . Therefore, the ZrO_2 phase present in equilibrium at high temperature is identified as tetragonal. The residual melts contained less than $3\text{ mol}\%$ each of dissolved ZrO_2 and $\text{YO}_{1.5}$, Table 4. Compared to the Y:Zr ratio in the YSZ, the relative $\text{YO}_{1.5}$ enrichment in the melt is consistent with the $\text{YO}_{1.5}$ depletion

^f The equiaxed, moderately faceted appearance of the SiO_2 grains suggest that it precipitated as β -cristobalite, rather than the expected tridymite form, while the extensive cracking is indicative of the $\beta \rightarrow \alpha$ transition below the glass transition temperature of the residual melt.

in the reprecipitated ZrO_2 . There was not an apparent correlation between the C(M)AS composition and the ZrO_2 and $\text{YO}_{1.5}$ solubility limits.

Zircon (ZrSiO_4) crystallizes upon reaction between ZrO_2 or 7YSZ and the higher SiO_2 deposits, $\text{C}_{24}\text{A}_{17}\text{S}_{59}$ and $\text{C}_{15}\text{A}_{15}\text{S}_{70}$. The reactions with $\text{C}_{24}\text{A}_{17}\text{S}_{59}$ yield zircon and reprecipitated ZrO_2 , Figures 3(c,g), suggesting that the SiO_2 content to move the system from a phase field containing zircon and t- ZrO_2 to one containing only zircon. The further increase in SiO_2 content from $\text{C}_{24}\text{A}_{17}\text{S}_{59}$ to $\text{C}_{15}\text{A}_{15}\text{S}_{70}$ promotes additional zircon crystallization. Following equilibration of $\text{C}_{15}\text{A}_{15}\text{S}_{70}$ with ZrO_2 or YSZ, zircon is the only ZrO_2 -bearing phase in contact with the melt, Figures 3(d,h). Small particles of unreacted ZrO_2 /7YSZ remain embedded inside the larger zircon grains in these specimens, even after annealing for 200h. The morphology suggests that, once formed, the zircon shell hinders the transport required for further reaction. The zircon in the YSZ specimens contained ~2mol% $\text{YO}_{1.5}$ with a corresponding reduction in the ZrO_2 content, Table 5.

The reactions between ZrO_2 and $\text{C}_{24}\text{A}_{17}\text{S}_{59}$ or $\text{C}_{15}\text{A}_{15}\text{S}_{70}$ also promote the crystallization of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), Figure 3(c); this phase was not observed in the equivalent 7YSZ specimens, Figure 3(g).

3.3 Equilibria with $\text{Y}_4\text{Zr}_3\text{O}_{12}$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$

Apatite and one or more ZrO_2 -rich phases are formed by the reactions between each deposit and $\text{Y}_4\text{Zr}_3\text{O}_{12}$ or $\text{Gd}_2\text{Zr}_2\text{O}_7$, Figure 5(a-h). The concentrations of CaO and ZrO_2 in the apatite, Table 6 and Figure 6(a,b), increase with the total CaO content in the initial deposit. The apatite oxygen stoichiometry, an indicator of the nature of defects contributing to the solution behavior, was calculated based on general formula $(\text{RE,Ca,Zr})_{10}(\text{SiO}_4)_6\text{O}_x$. The results, Figure 6(c), are effectively constant with ~26 oxygen atoms per formula unit.

The identity of the ZrO_2 -rich phases varies with both the deposit composition and $\text{REO}_{1.5}$ identity. Reactions between $\text{Y}_4\text{Zr}_3\text{O}_{12}$ and $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$, $\text{C}_{36}\text{A}_{14}\text{S}_{50}$, or $\text{C}_{24}\text{A}_{17}\text{S}_{59}$ yield fluorite containing from 18 mol% to 24 mol% $\text{YO}_{1.5}$ and 2 mol% CaO, Figure 7. The $\text{YO}_{1.5}$ concentration in the fluorite decreases with increasing SiO_2 content in the deposit. $\text{Y}_4\text{Zr}_3\text{O}_{12}$ reacts with $\text{C}_{15}\text{A}_{15}\text{S}_{70}$ to yield a combination of apatite and zircon, the latter containing ~2 mol% $\text{YO}_{1.5}$. The $\text{Gd}_2\text{Zr}_2\text{O}_7$ reaction with $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ yields fluorite, with proportionally more CaO and less $\text{GdO}_{1.5}$ than the equivalent $\text{Y}_4\text{Zr}_3\text{O}_{12}$ specimen. The interaction between $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ produces s apatite and transformable tetragonal ZrO_2 (Figure 4(b)) with <5 mol%

GdO_{1.5}. The C₂₄A₁₇S₅₉ + Gd₂Zr₂O₇ equilibria includes apatite, t-ZrO₂, and zircon while the reaction with C₁₅A₁₅S₇₀ forms apatite and zircon.

The ZrO₂ concentrations in the residual melts, Table 4, were comparable to those measured for reactions with ZrO₂ or 7YSZ. The REO_{1.5} concentration decreases with increasing CaO concentration in the initial deposit, Figure 8; the YO_{1.5} concentrations were slightly higher than the GdO_{1.5} concentrations for each deposit.

3.4 Equilibria with YO_{1.5} and GdO_{1.5}

The diversity of the reaction products and the extent of melt crystallization were greatest for the pure REO_{1.5}. As with the zirconates, apatite was formed with every deposit composition, Figure 9(a-h). However, unlike the ZrO₂-containing systems, the apatite composition (i.e. Ca:RE ratio) was essentially equivalent for all deposits, Table 6 and Figure 6(a).

No residual glass was observed in the equilibrated C₃₃M₉A₁₃S₄₅ + YO_{1.5} specimen. The microstructure contained apatite and large grains of garnet, (Y_{0.63}C_{0.33}M_{0.04})₃(M_{0.6}A_{0.4})₂(S_{0.77}A_{0.23})₃O₁₂, and melilite, Ca₂(A_{0.51}M_{0.63})(A_{0.57}S_{0.73})SiO₇, solid solutions. TEM characterization, Figure 10(a), reveals that garnet is also present between the apatite grains, consistent with previously reported observations of slower growing garnet engulfing the faster growing reaction products [7, 11]. The related C₃₃M₉A₁₃S₄₅ + GdO_{1.5} specimen also contained a large volume of apatite and melilite but not a GdO_{1.5}-bearing garnet. Instead, magnesium aluminate spinel was evident, Figure 9(e). The regions between these crystalline phases were filled with glass, Figure 10(b). The small apatite grains embedded in the melilite and spinel suggests that apatite precipitation precedes the other phases.

Melilite, spinel, and garnet were not observed in the CAS specimens. Reactions between C₃₆A₁₄S₅₀ and YO_{1.5} produced a combination of apatite, anorthite, and silicocarnotite (Ca₃Y₂Si₃O₁₂). The latter phase is known to exist in equilibrium with the liquid phase in the tCaO-SiO₂-YO_{1.5} system [17]. Apatite was the only crystalline phase in the equivalent GdO_{1.5} specimen. C₂₄A₁₇S₅₉ reacts with both YO_{1.5} and GdO_{1.5} to produce apatite and anorthite, Figure 9(c,g) and Figure 10(c). The reaction between YO_{1.5} and C₁₅A₁₅S₇₀ produced a mixture of apatite and yttrium disilicate (Y₂Si₂O₇). The equivalent GdO_{1.5} specimen, Figure 10(d), contained apatite, anorthite, and crystalline SiO₂, but not gadolinium disilicate.

4. DISCUSSION

The reactivity between thermal barrier oxides and silicate deposits is strongly dependent on the initial composition of the latter. Variations are also observed between different $\text{REO}_{1.5}$ (i.e. Y vs. Gd) and with changes in the $\text{REO}_{1.5}$ content of the TBO (i.e. $\text{ZrO}_2 \rightarrow 7\text{YSZ} \rightarrow \text{Y}_4\text{Zr}_3\text{O}_{12} \rightarrow \text{YO}_{1.5}$). The results are discussed in terms of (i) shifts in the residual melt composition following the reactions, (ii) the predominance of various crystalline silicate reaction products and (iii) their solid solution behavior, and (iv) implications for the development of degradation tests and models to aid the design of TBCs that are resistant to degradation by a range of silicate deposit compositions.

4.1 Residual Melt Composition

4.1.1 Evolving Melt Composition

The composition of the melt evolves as crystallization proceeds. These changes affect the nature of secondary intrinsic crystallization, discussed in Section 4.2, and the viscosity (η) of the melt. The time to infiltrate a given TBC thickness decreases with the viscosity [13], which itself scales with the degree of connectivity in the SiO_2 network. In this context, reactions that selectively deplete SiO_2 would decrease η , accelerating infiltration, while reactions selectively depleting modifiers (e.g. CaO, MgO) would increase η and retard melt infiltration. The dissolution of ZrO_2 increases η [22] while dissolved $\text{REO}_{1.5}$ decreases η [23].

The changes in the SiO_2 content between the initial and residual melt are most pronounced, Figure 11(a). Except for cases where no new phases were formed (ZrO_2 and 7YSZ interaction with $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ or $\text{C}_{36}\text{A}_{14}\text{S}_{50}$), the SiO_2 concentration in the melt always decreases. The magnitude of the change depends on the specific reactions. No single TBO among those examined offers a clear advantage for all deposits. For instance, the reactions of $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ with the $\text{REO}_{1.5}$ deplete SiO_2 while the $\text{REO}_{1.5}$ reactions with $\text{C}_{24}\text{A}_{17}\text{S}_{59}$ don't significantly change the SiO_2 content. This trend is reversed when the same deposits react with ZrO_2 and 7YSZ.

Apatite precipitation consumes CaO and SiO_2 from the melt and could, in principle, deplete the melt in CaO. However, the Si:Ca ratios in the residual melt decrease, Figure 11(b), indicating CaO enrichment. The initial Si:Ca ratios in $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ and $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ (both ~ 1.4) are less than the corresponding apatite (Si:Ca ≈ 3), leading to progressive CaO enrichment during apatite crystallization. Conversely, the initially CaO-lean deposits form multiple silicates (e.g.,

apatite and zircon) that, when combined, also decrease the Si:Ca ratio. The only exception is $\text{GdO}_{1.5} + \text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ wherein the crystallization of CaO-rich melilite depletes CaO.

Previously described infiltration models [4, 13] indicate that the infiltration time scales linearly with the viscosity. The large changes in melt viscosity are therefore expected to significantly influence the local rate of infiltration in a TBC. Silicate liquid viscosity models [22, 24] enable comparison between the properties of various melts. Unfortunately these models are not optimized for use in systems with the relatively high ZrO_2 and $\text{REO}_{1.5}$ contents observed here. As an approximation, the residual melt viscosities were instead calculated based on the normalized $\text{CaO}+\text{MgO}+\text{AlO}_{1.5}+\text{SiO}_2$ content using the Fluegel [22], and GRD [24] models. Although there were differences in the values obtained from the two models, both showed similar trends. The results obtained from the GRD model are plotted in Figure 11(c). Based on the changes in CMAS content, the viscosity is observed to drop between one and three orders of magnitude cases involving silicate precipitation. The key conclusion is that although crystallization reactions are deemed desirable for their ability to consume the melt and block infiltration channels, the beneficial effect may be partially counteracted if the viscosity of the infiltrating melt progressively decreases.

4.1.2 $\text{REO}_{1.5}$ Solubility in the Melt

The $\text{REO}_{1.5}$ melt saturation limit in equilibrium with apatite decreases with the CaO concentration in the deposit, Figure 8. The $\text{GdO}_{1.5}$ concentrations were consistently lower than $\text{YO}_{1.5}$. The influence of ZrO_2 (c.f. results for the RE-zirconates and pure $\text{REO}_{1.5}$) was negligible. This solubility is determined in part by the influence of the local melt structure on the RE coordination [25, 26]. The increased fraction of non-bridging oxygen (NBO) atoms in the deposits with a high modifier content (e.g. $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$, $\text{C}_{36}\text{A}_{14}\text{S}_{50}$) facilitates a more regular RE^{3+} coordination shell and increased $\text{REO}_{1.5}$ solubility. Additionally, the smaller Y^{3+} should be six-coordinated in the melt while the larger Gd^{3+} would prefer to have a higher coordination state, implying reduced solubility for a given NBO content.

In service, the effect of variations in $\text{REO}_{1.5}$ solubility will be most pronounced in the early stages of interaction between a TBC and a silicate melt. Specifically, the solubility limit determines the fraction of the TBC that must dissolve to saturate the melt and initiate reactive crystallization. Assuming comparable dissolution rates, higher solubility implies a longer interaction time without crystallization allowing more time for the melt to infiltrate. For instance, to initiate apatite crystallization roughly twice the volume of $\text{Y}_4\text{Zr}_3\text{O}_{12}$ must dissolve into

$C_{33}M_9A_{13}S_{45}$ compared to $C_{15}A_{15}S_{70}$. Similarly, the ~50% increase in $YO_{1.5}$ solubility compared to $GdO_{1.5}$ implies that a $GdO_{1.5}$ -containing coating should form apatite more quickly. Unfortunately, the solubility is highest in the deposits that, due to their lower viscosity, would infiltrate most rapidly.

4.2 Reaction Product Predominance

It is desirable for reactions between the melt and TBO to produce phases with fast crystallization kinetics and with morphologies that would effectively seal infiltration pathways. In this context systems that produce apatite with concomitant intrinsic crystallization are preferable to those yielding other crystallization products. The following sections discuss the results in terms of the relative tendency to form various $REO_{1.5}$ -based silicates, the factors contributing to intrinsic crystallization and zircon formation, and the influence of MgO on these crystallization reactions.

4.1.34.2.1 Formation of $REO_{1.5}$ -rich Silicates

Apatite is observed for all deposits upon reaction with the $Y_4Zr_3O_{12}$, $Gd_2Zr_2O_7$, and $REO_{1.5}$. This indicates that apatite is stable in contact with melts covering a wide range of Si:Ca ratios. Secondary effects related to the apatite composition and presence of other reaction products, elaborated below, influence the amount of apatite crystallized for a given fraction of $REO_{1.5}$ in the system.

For $Y_4Zr_3O_{12}$ and $Gd_2Zr_2O_7$, apatite is the only RE-bearing silicate formed. The presence of $REO_{1.5}$ in the reprecipitated ZrO_2 and the melt reduce the amount of apatite formed relative to a scenario where all of the $REO_{1.5}$ precipitates as apatite. Systems with low $REO_{1.5}$ solubility in the melt and those forming zircon or $REO_{1.5}$ -lean tetragonal ZrO_2 instead of the $REO_{1.5}$ -rich fluorite may increase the volume of apatite formed..

The pure $REO_{1.5}$ systems should produce more apatite crystallization than the zirconates (for a fixed total $REO_{1.5}$ content) by eliminating the undesired precipitation of $REO_{1.5}$ in the fluorite phase. However, the appearance of alternate $YO_{1.5}$ -bearing silicates (garnet, silicocarnotite, and disilicate) limits apatite formation. Based on their morphology, these phases may nucleate and/or grow more slowly than apatite, reducing their relative effectiveness for arresting melt infiltration in a TBC. The absence of these phases in the $GdO_{1.5}$ systems points to a desirable increase in the stability of $GdO_{1.5}$ -apatite relative to $GdO_{1.5}$ - garnet, -silicocarnotite,

and -disilicate. Except for the modest $\text{GdO}_{1.5}$ solubility in the residual melt, all of the $\text{GdO}_{1.5}$ in each system is converted to apatite.

4.1.44.2.2 *Intrinsic crystallization*

There are two notable observations regarding the intrinsic crystallization behavior for the deposits of interest. First, the dissolution of ZrO_2 and/or $\text{YO}_{1.5}$ into the melt can suppress intrinsic crystallization. In other words, TBC dissolution initially expands the liquid field (dark fields in Figure 1). The implication is that compared to the intrinsic crystallization temperature/rate for the initial deposit alone, coating dissolution can retard crystallization as the melt penetrates against a thermal gradient. This effect is most apparent in the ZrO_2 and 7YSZ systems. The CaSiO_3 present in the initial $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ deposit disappears in the mixed systems even through the bulk deposit composition remains unchanged. Additionally, the appearance of anorthite in $\text{C}_{24}\text{A}_{17}\text{S}_{59}/\text{C}_{15}\text{A}_{15}\text{S}_{70}$ ± ZrO_2 but not ± 7YSZ suggests that ZrO_2 and $\text{YO}_{1.5}$ together increase the liquid stability more than ZrO_2 alone.

The changes in the melt composition upon reactive crystallization (e.g., SiO_2 depletion as apatite and zircon precipitate) may promote intrinsic crystallization. With a sufficient proportional reduction in SiO_2 (or coupled $\text{CaO}+\text{SiO}_2$ depletion), the three CAS deposits can shift into the anorthite field while $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ could shift melilite, anorthite, and/or spinel fields (see Figure 1). All three phases were observed in multiple equilibrated mixtures while the fraction of the phases formed was determined by the local equilibria. Due to the influence of intrinsic crystallization on $V_{\text{crys}}/V_{\text{TBO}}$, it is important that efforts to model the melt and reaction behavior consider the likelihood of forming secondary reaction products (i.e. the total phase equilibria).

4.1.54.2.3 *Zircon Crystallization*

Based on mass balance alone, zircon could be a desirable reaction product. It dissolves less $\text{REO}_{1.5}$ than fluorite or t- ZrO_2 , making more $\text{REO}_{1.5}$ available to form apatite, and has a high $V_{\text{crys}}/V_{\text{TBO}}$. However, zircon nucleation is reportedly slow (taking as long as 30 minutes [27], compared to seconds for apatite [2]) and growth of zircon encasing the partially reacted TBO (also observed in EB-PVD TBCs [4, 14]) would hinder further coating-melt interaction. For instance, the formation of zircon over columnar $\text{Gd}_2\text{Zr}_2\text{O}_7$ crystals upon interaction with a SiO_2 -rich deposit would reduce the availability of $\text{GdO}_{1.5}$ for crystallizing apatite.

Zircon precipitates for SiO₂-rich deposits whereas ZrO₂ forms fluorite or t-ZrO₂ in SiO₂-lean melts. The transition in behavior is dictated by the SiO₂ and ZrO₂ activities in the melt. The crystalline SiO₂ in C₁₅A₁₅S₇₀ indicates that the SiO₂ activity is near unity. Therefore it is unsurprising that zircon crystallization is observed for all ZrO₂-containing TBOs. C₂₄A₁₇S₅₉ is closer to the zircon/ZrO₂ transition and provides insight into the role of the ZrO₂ activity, as influenced by the presence of the REO_{1.5}. The reactions with pure ZrO₂ should have the highest driving force for zircon crystallization. For the C₂₄A₁₇S₅₉ + ZrO₂ specimen, the zircon-forming reactions reduce the SiO₂ content in the melt from 59 mol% to 52 mol%. The 2-3 mol% REO_{1.5} in the t-ZrO₂ formed from 7YSZ and Gd₂Zr₂O₇ reduces the ZrO₂ activity and driving force for zircon crystallization, leading to higher SiO₂ concentrations in the residual melt, Table 4 and Figure 11. The absence of zircon in the Y₄Zr₃O₁₂ + C₂₄A₁₇S₅₉ specimen indicates that the ZrO₂ activity is significantly reduced by the 20 mol% solute concentration in the fluorite. The implication is that TBCs containing higher initial REO_{1.5} content (i.e. lower ZrO₂ activity) are less likely to form zircon upon reaction with a silicate deposit.

4.1.64.2.4 Influence of MgO on Crystallization

MgO plays two roles in the phase equilibria. First, MgO increases the variety of reaction products relative to the CAS deposits. It also influences the partitioning of REO_{1.5} between apatite and the reprecipitated ZrO₂ phase. The reactions between the pure REO_{1.5} systems and C₃₃M₉A₁₃S₄₅ produce garnet, melilite, and/or spinel. Each phase contains a significant concentration of MgO and they were not observed in the CAS systems even though the garnet and melilite phase fields exhibit MgO-free end members. Additionally, Gd₂Zr₂O₇ reacts with C₃₃M₉A₁₃S₄₅ to form fluorite with ~15 mol% GdO_{1.5}, whereas the reaction with C₃₆A₁₄S₅₀ forms t-ZrO₂ with only ~5mol% GdO_{1.5}. Given that neither apatite nor fluorite contains appreciable MgO, this behavior presumably stems from changes in the melt chemistry (i.e. constituent activities) upon MgO dissolution. For instance, if MgO reduces the SiO₂ activity the driving force for apatite precipitation would decrease leading to an increase in the equilibrium REO_{1.5} concentration in the melt and reprecipitated fluorite. These influences are important to in-service TBC performance. Given that real-world deposits contain MgO, the present results suggest that model deposit compositions should include at least small fractions of MgO (as well as FeO_x, etc) to accurately capture the relevant melt behaviors.

4.2.4.3 Solid Solution Composition Trends

Several of the reaction products exhibit solid solution behavior allowing their compositions to vary depending on the local chemical conditions. The $V_{\text{crys}}/V_{\text{TBO}}$ for a given reaction sequence is impacted by these composition variations. The following sections discuss the composition trends in (i) apatite, (ii) reprecipitated ZrO_2 , and (iii) zircon. In addition to the implications for TBC reactions with molten silicates, the results provide new insight into the solution behavior of these phases.

4.2.14.3.1 Apatite

The apatite crystal structure and crystal chemistry have been discussed at length in the context of interactions between TBC and molten silicates [6-8, 17, 28]. The structure (with general formula $\text{M}^{\text{I}}_4\text{M}^{\text{II}}_6(\text{SiO}_4)_6\text{X}_2$) contains seven-fold and nine-fold coordinated cation sites, M^{I} and M^{II} , respectively, and anion sites, X, distinct from the oxygen in the silica tetrahedra. Ca is believed to reside only on the M^{I} sites, RE may sit on either the M^{I} or M^{II} sites, and oxygen atoms occupy the X sites. Minor ZrO_2 solubility is generally observed in apatite formed by reactions in TBCs [6, 8, 29]. Variations in the Ca:RE ratio are accommodated by introducing vacancies on the X site (CaO-rich) or the cation sites ($\text{REO}_{1.5}$ -rich), as elaborated below. These coupled substitutions produce a notional stability range between $\text{Ca}_4\text{RE}_6(\text{SiO}_4)_6\text{O}$ and $\text{RE}_{9.33}(\text{SiO}_4)_6\text{O}_2$. Alternately, oxygen interstitials could yield $\text{RE}_{10}(\text{SiO}_4)_6\text{O}_3$ [30], although there is less evidence for this mechanism in the literature.

In the CaO-SiO₂-REO_{1.5} systems neither the YO_{1.5}- nor GdO_{1.5}-based apatite is stable over the entire range allowed by the crystal chemistry. The YO_{1.5}- and GdO_{1.5}-bearing apatites are stable from $\text{Ca}_{2.5}\text{Y}_{7.5}(\text{SiO}_4)_6\text{O}_{1.75}$ to $\text{Ca}_{0.5}\text{Y}_9(\text{SiO}_4)_6\text{O}_2$ [17] and $\text{Ca}_{2.75}\text{Gd}_{7.25}(\text{SiO}_4)_6\text{O}_{1.625}$ to $\text{Gd}_{9.33}(\text{SiO}_4)_6\text{O}_2$, respectively. In the ternary equilibria there appears to be a strong preference for the $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ stoichiometry (i.e. the composition without structural defects).

The apatite formed by reactions with the pure REO_{1.5}, Table 6 and Figure 6(a), is near the nominal $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ stoichiometry indicating that deposits with Si:Ca ratios between 1.4 and 4.7 do not influence the Si:Ca ratio in the apatite. Conversely, in systems containing ZrO_2 , the CaO content in the apatite increases with the CaO concentration in the deposit. $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{Y}_4\text{Zr}_3\text{O}_{12}$ react with $\text{C}_{15}\text{A}_{15}\text{S}_{70}$ to produce $\text{Ca}_2\text{RE}_8(\text{SiO}_4)_6\text{O}_2$ while apatite formed by reactions with $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ contains 50% more CaO. The latter CaO concentration is above the CaO saturation limit for apatite in the CaO-SiO₂-REO_{1.5} ternaries and is likely facilitated by coupled,

charge neutral substitution of $\text{Ca}^{2+}:\text{Y}^{3+}$ and $\text{Zr}^{4+}:\text{Y}^{3+}$ in the apatite structure, consistent with the trends in Figure 6.

The implication is that apatite-forming reaction consume more CaO from the melt (per mole of $\text{REO}_{1.5}$) if $\text{REO}_{1.5}$ is supplied by the dissolution of a RE zirconate than a ZrO_2 -free coating (e.g., pure $\text{REO}_{1.5}$, silicates, aluminates). This result illustrates the delicate balance between various factors influencing the overall reaction mass balance.

4.2.24.3.2 *Reprecipitated ZrO_2*

The $\text{REO}_{1.5}$ solubility in fluorite or t- ZrO_2 (i.e the $\Delta\text{REO}_{1.5}$ between the TBO and reprecipitated ZrO_2 phase) has previously been identified as a key indicator of the effectiveness of reactive crystallization to consume silicate melts [7, 11, 12]. Reactions with a small $\Delta\text{REO}_{1.5}$ will produce less apatite than those with a larger $\Delta\text{REO}_{1.5}$. The equilibrium $\text{REO}_{1.5}$ concentration in the reprecipitated phase is a manifestation of (i) the relative driving force for apatite crystallization in a given system, which increases with RE^{3+} size [31], (ii) the stability of the fluorite phase (inversely related to RE^{3+} size [32]), and (iii) the $\text{REO}_{1.5}$ solubility in the melt (decreasing with increasing RE^{3+} size, discussed above). Based on these factors, $\Delta\text{REO}_{1.5}$ increases with the RE^{3+} size (c.f. Yb, Y, and Gd data for $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ in Figure 7).

This study extends the prior understanding by determining the influence of the melt composition on the $\Delta\text{REO}_{1.5}$ trends for the zirconates. For each deposit, the $\Delta\text{GdO}_{1.5}$ for $\text{Gd}_2\text{Zr}_2\text{O}_7$ is larger than the $\Delta\text{YO}_{1.5}$ for $\text{Y}_4\text{Zr}_3\text{O}_{12}$, confirming that the RE^{3+} cation size trend extends to a range of melts. Additionally, the $\text{REO}_{1.5}$ concentration in the ZrO_2 phase is inversely proportional to the SiO_2 content in the melt ($\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45} \rightarrow \text{C}_{36}\text{A}_{14}\text{S}_{50} \rightarrow \text{C}_{24}\text{A}_{17}\text{S}_{59}$), Figure 8. For $\text{GdO}_{1.5}$, the larger jump between $\text{C}_{33}\text{M}_9\text{A}_{13}\text{S}_{45}$ and $\text{C}_{36}\text{A}_{14}\text{S}_{50}$ corresponds to the transition from fluorite to t- ZrO_2 [33]. Coupled with the differences in silicate reaction product predominance, coatings based on $\text{GdO}_{1.5}$ offer improved melt crystallization efficiently than $\text{YO}_{1.5}$; the efficiency increases with the SiO_2 content in the deposit.

4.2.34.3.3 *$\text{REO}_{1.5}$ Solubility in ZrSiO_4*

The zircon formed by reaction with 7YSZ, $\text{Y}_4\text{Zr}_3\text{O}_{12}$, or $\text{Gd}_2\text{Zr}_2\text{O}_7$ contained between 1 and 3 mol% $\text{REO}_{1.5}$, Table 5. This solubility is notable because it could influence on the phase evolution pathway. It was previously suggested that following YSZ exposure to volcanic-type deposits, zircon crystallizes once YSZ dissolves in the melt [14] and that the $\text{YO}_{1.5}$ remains dissolved in the melt. However, the $\text{YO}_{1.5}$ solubility observed in the present study accounts for

over sixty percent of the $\text{YO}_{1.5}$ in 7YSZ. Therefore, kinetic hindrances associated with the selective removal of $\text{YO}_{1.5}$ are less likely to play a role in zircon.

The solubility of $\text{REO}_{1.5}$ in zircon has been studied extensively due to its importance in geochronology [34]. Natural zircons contain low concentrations of $\text{REO}_{1.5}$ and P_2O_5 consistent with coupled $\text{P}^{5+}:\text{Si}^{4+}$ and $\text{RE}^{3+}:\text{Zr}^{4+}$ substitutions to maintain charge neutrality. However, the absence of phosphorus in this study suggests that another mechanism facilitates the $\text{RE}^{3+}:\text{Zr}^{4+}$ substitution. The zircon structure is composed of SiO_4 tetrahedra and ZrO_8 dodecahedra alternating along the c-axis; each oxygen is bonded to Si. Unlike the apatite structure, there are no ‘ionic’ oxygen sites. Oxygen vacancies are therefore unlikely due to the associated vacancy energies and relative instability of the SiO_3^{2-} group [35]. Likewise, Si vacancies or cation interstitials are unfavorable due to the associated strains in the structures. Nonetheless, other groups have reported $\text{REO}_{1.5}$ solubility in zircon without adding phosphorous for charge compensation [35, 36]. The leading hypothesis is that, in the absence of P, selective protonation of oxygen in the nominally anhydrous ZrSiO_4 occurs in conjunction with the $\text{REO}_{1.5}$ solubility. Limited substitution of $\text{AlO}_{1.5}$ for SiO_2 may also contribute to the observed non-stoichiometry.

4.34.4 Implications for *developing CMAS degradation models*

Due to the systematic changes in reactivity illustrated by this study, it is important to consider a variety of deposit compositions when evaluating TBC performance. Notably, none of the TBOs tested exhibits optimal behavior over the entire range of deposit compositions. Demonstrating that a coating material/architecture is resistant to degradation by a single synthetic sand, dust, or ash composition is likely insufficient to guarantee performance. However, the wide variety of ‘representative’ compositions makes it impractical to experimentally investigate all potential interactions with a menu of candidate coating compositions.

Instead, the problem is better viewed in the context of a broader modeling framework to elucidate the influence of deposit composition variations, including the role minor deposit constituents, on the anticipated performance of a TBC system. The complete framework would couple thermodynamic and kinetics descriptions of the infiltration and reaction dynamics with thin-film mechanics models. Ideally, existing melt infiltration models [4, 13] could be combined with phase equilibrium insights and descriptions of the crystallization kinetics to determine the time dependent infiltration depth. The reaction layer thickness could then be fed into mechanics models describing TBC cracking and delamination under thermo-cyclic stresses [2, 4, 37, 38] to

determine the likelihood of failure for a given TBC architecture exposed to an arbitrary silicate deposit.

The key element of this framework is a thermodynamic database capable of predicting the wide variety of intrinsic and reactive crystallization products observed upon CMAS-TBC interaction. Owing to their basis in slag chemistry, existing databases (e.g., FactSage FToxid [20] or Thermo-Calc SLAG4) effectively capture the melting and crystallization behavior of the deposits but not the interaction with TBCs. The Thermo-Calc TCOX6 database [39] covers some TBC constituents (i.e. Y and Zr) but does not include adequate descriptions of all potential reaction products. Based on the results of this study, the existing databases should be extended to capture (i) the differences in the solubility of various $\text{REO}_{1.5}$ in the silicate melt, (ii) the relative stability and multi-component solid solution behavior of $\text{REO}_{1.5}$ -bearing silicates including apatite and garnet, (iii) the $\text{REO}_{1.5}$ partitioning between fluorite and crystalline silicates, and (iv) the transition between ZrO_2 precipitation and zircon crystallization for systems containing various $\text{REO}_{1.5}$. To support these efforts, additional experimental phase equilibrium and thermochemistry data on key ternary subsystems (e.g., SiO_2 - $\text{REO}_{1.5}$ - ZrO_2) and multicomponent melts and reaction products (e.g. C(M,F)AS+RE+Zr including quaternary and quinary phases) is needed.

5. CONCLUSIONS

The overarching conclusion is that the reactions between candidate thermal barrier oxides and molten silicates are strongly influenced by the composition of the deposit, the ratio of ZrO_2 : $\text{REO}_{1.5}$ in the TBO, and the identity of the $\text{REO}_{1.5}$. The results make it clear that the underlying multi-component phase equilibria must be considered when developing and evaluating mitigation strategies. Key conclusions include:

- Reactive crystallization depletes SiO_2 from the residual melt. CaO, MgO, and $\text{AlO}_{1.5}$ are enriched, even when CaO-bearing apatite is formed. Due to changes in viscosity, composition evolution is expected to accelerate infiltration into a porous TBC.
- The higher equilibrium $\text{YO}_{1.5}$ solubility in both the residual melt and reprecipitated fluorite reduces the efficacy of crystallization reactions for $\text{YO}_{1.5}$ - compared to $\text{GdO}_{1.5}$ -based TBCs.
- Apatite and zircon are the predominant silicate reaction products. Apatite was observed as an equilibrium reaction product for over the entire range of deposit Si:Ca ratios

studied. Zircon only forms for SiO₂-rich deposits; the minimum SiO₂ content to precipitate zircon is influenced by the REO_{1.5} content in the system. YO_{1.5} is more likely than GdO_{1.5} to partition into other crystalline silicates including yttrium disilicate, garnet, and silicocarnotite.

- Coupled Ca²⁺:RE³⁺ and Zr⁴⁺:RE³⁺ substitutions allow apatite precipitation to capture more CaO from the melt in systems containing ZrO₂. This effect is most pronounced for deposits initially containing a high CaO concentration.
- The addition of MgO increased the variety of reactive and intrinsic crystallization products. The effect was more pronounced in systems with little or no residual melt.

Ongoing efforts focus on integrating these findings into thermodynamic databases that, as part of a framework with kinetic and mechanics models, will improve the capability to predict TBC performance.

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TABLES

Table 1: Reaction Product Identities

Type	Name	Abbreviation	Nominal Formula
Reprecipitation	Fluorite	F	(Zr,RE,Ca)O _{1.x}
	Tetragonal ZrO ₂	Z	(Zr,RE,Ca)O _{1.x}
Reactive Crystallization	Zircon	ZS	ZrSiO ₄
	Apatite	Ap	(Ca,RE) ₄ (RE,Zr) ₆ (SiO ₄) ₆ O ₂
	Garnet	Gar	(Ca,RE,Zr) ₃ (Mg,Al) ₂ (Si,Al) ₃ O ₁₂
	Yttrium Disilicate	YDS	Y ₂ Si ₂ O ₇
	Silicocarnotite	SC	Ca ₃ RE ₂ Si ₃ O ₁₂
Intrinsic Crystallization	Anorthite	An	CaAl ₂ Si ₂ O ₈
	Diopside	Di	CaMgSi ₂ O ₆
	Cristobalite, Tridymite	SiO ₂	SiO ₂
	(Pseudo-)wollastonite	CS	CaSiO ₃
	Melilite	Mel	(Ca) ₂ (Al,Mg)(Al,Si)SiO ₇
	Spinel	Sp	MgAl ₂ O ₇

Table 2: Synthetic Silicate Deposits

Composition (mol%)	Si:Ca Ratio	T _{IM} (Exp.) [16]	T _s (Calc)	T _L (Calc)	1300°C Eq. (Calc)
C ₃₃ M ₉ A ₁₃ S ₄₅	1.4	1233°C	1229°C	1258°C	Liquid
C ₃₆ A ₁₄ S ₅₀	1.4	1140°C	1184°C	1363°C	Liq + CS (Liq = C _{33.7} A _{16.3} S ₅₀)
C ₂₄ A ₁₇ S ₅₉	2.5	1125°C	1184°C	1184°C	Liquid
C ₁₅ A ₁₅ S ₇₀	4.7	1140°C	1184°C	1479°C	Liq + SiO ₂ + An* (Liq = C _{18.8} A _{18.1} S _{63.1})

* Calculated anorthite fraction is less than 1%.

Table 3: Observed Equilibrium phases at 1300°C

TBO	C ₃₃ M ₉ A ₁₃ S ₄₅	C ₃₆ A ₁₄ S ₅₀	C ₂₄ A ₁₇ S ₅₉	C ₁₅ A ₁₅ S ₇₀
--	Liq	Liq + CS	Liq	Liq + SiO ₂
ZrO ₂	Liq + Z	Liq + Z	Liq + tZ + ZS + An	Liq + An + ZS*
7YSZ	Liq + Z	Liq + Z	Liq + tZ + ZS	Liq + ZS*
Y ₄ Zr ₃ O ₁₂	Liq + F + Ap	Liq + F + Ap	Liq + F + Ap	Liq + Ap + ZS*
Gd ₂ Zr ₂ O ₇	Liq + F + Ap	Liq + tZ + Ap	Liq + tZ + Ap + ZS	Liq + Ap + ZS + An
YO _{1.5}	Ap + Mel + Gar	Liq + Ap + SC + An	Liq + Ap + An	Liq + Ap + YDS*
GdO _{1.5}	Liq+Ap+Mel+Sp	Liq + Ap	Liq + Ap + An	Liq + Ap + An+SiO ₂

* These specimens were annealed for 200h instead of 50h. In some cases ZrO₂ grains still remain trapped inside the ZS grains. They persist in local equilibrium with the ZS but are not included in reporting the global equilibrium.

Table 4: Measured Glass Compositions (mol%)*

System		CaO	MgO	AlO _{1.5}	SiO ₂	REO _{1.5}	ZrO ₂
TBO	Syn. Deposit						
--	C ₃₃ M ₉ A ₁₃ S ₄₅	31.9	9.3	13.9	44.7	--	--
	C ₃₆ A ₁₄ S ₅₀	30.8	--	19.0	49.6	--	--
	C ₂₄ A ₁₇ S ₅₉	23.4	--	17.1	59.4	--	--
	C ₁₅ A ₁₅ S ₇₀	17.2	--	18.1	64.7	--	--
ZrO ₂	C ₃₃ M ₉ A ₁₃ S ₄₅	31.4	9.0	13.6	44.3	--	1.6
	C ₃₆ A ₁₄ S ₅₀	33.9	--	14.7	48.8	--	2.3
	C ₂₄ A ₁₇ S ₅₉	31.7	--	13.9	51.4	--	2.5
	C ₁₅ A ₁₅ S ₇₀	22.0	--	17.3	59.6	--	1.0
7YSZ	C ₃₃ M ₉ A ₁₃ S ₄₅	31.0	9.1	13.4	43.2	1.6	1.7
	C ₃₆ A ₁₄ S ₅₀	33.3	--	14.4	48.0	2.0	2.3
	C ₂₄ A ₁₇ S ₅₉	25.5	--	18.7	52.0	1.9	2.0
	C ₁₅ A ₁₅ S ₇₀	18.9	--	20.0	58.1	1.7	1.3
Y ₄ Zr ₃ O ₁₂	C ₃₃ M ₉ A ₁₃ S ₄₅	30.9	10.4	16.0	38.8	2.8	1.1
	C ₃₆ A ₁₄ S ₅₀	33.7	--	18.4	46.8	2.3	1.6
	C ₂₄ A ₁₇ S ₅₉	21.5	--	18.7	53.6	4.3	2.0
	C ₁₅ A ₁₅ S ₇₀	15.5	--	18.1	59.4	5.2	1.7
Gd ₂ Zr ₂ O ₇	C ₃₃ M ₉ A ₁₃ S ₄₅	30.3	10.4	16.1	39.9	1.9	1.4
	C ₃₆ A ₁₄ S ₅₀	33	--	19	44	2	2
	C ₂₄ A ₁₇ S ₅₉	24.3	--	18.5	51.6	3.3	2.4
	C ₁₅ A ₁₅ S ₇₀	14.3	--	18.9	62.0	3.8	1.0
YO _{1.5}	C ₃₃ M ₉ A ₁₃ S ₄₅	No Glass					
	C ₃₆ A ₁₄ S ₅₀	35.9	--	22.8	38.4	2.8	--
	C ₂₄ A ₁₇ S ₅₉	25	--	13	58	4	--
	C ₁₅ A ₁₅ S ₇₀	15.4	--	20.7	59.2	4.7	--
GdO _{1.5}	C ₃₃ M ₉ A ₁₃ S ₄₅	18	16	23	41	2	--
	C ₃₆ A ₁₄ S ₅₀	36	--	20	41	2	--
	C ₂₄ A ₁₇ S ₅₉	22	--	19	57	3	--
	C ₁₅ A ₁₅ S ₇₀	28	--	12	55	4	--

* Values reported to 0.1 mol% and 1 mol% precision measured by EPMA and TEM-EDS, respectively.

Table 5: Measured ZrSiO₄ Compositions (mol%)*

System	SiO ₂	ZrO ₂	REO _{1.5}	ZrO ₂ +REO _{1.5}
C ₂₄ A ₁₇ S ₅₉ + ZrO ₂	49.8	49.8	--	49.8
C ₂₄ A ₁₇ S ₅₉ + 7YSZ	49.8	48.1	1.8	49.9
C ₁₅ A ₁₅ S ₇₀ + 7YSZ	49.1	48.1	2.2	50.3
C ₁₅ A ₁₅ S ₇₀ + Y ₄ Zr ₃ O ₁₂	49.4	47.9	2.4	50.3
C ₂₄ A ₁₇ S ₅₉ + Gd ₂ Zr ₂ O ₇	49.5	48.8	1.5	50.3
C ₁₅ A ₁₅ S ₇₀ + Gd ₂ Zr ₂ O ₇	49.7	47.6	2.7	50.3

* Total measured CaO + AlO_{1.5}, not tabulated here, was 0.1 mol% to 0.3 mol%.

Table 6: Measured Apatite Compositions (mol%)*

System		CaO+	SiO ₂	REO _{1.5}	ZrO ₂	O per
TBO	Syn. Deposit	MgO				Formula
Y ₄ Zr ₃ O ₁₂	C ₃₃ M ₉ A ₁₃ S ₄₅	16.8	38.3	42.1	2.8	25.9
	C ₃₆ A ₁₄ S ₅₀	18.8	38.3	38.0	4.9	25.9
	C ₂₄ A ₁₇ S ₅₉	15.5	39.6	41.5	3.4	26.2
	C ₁₅ A ₁₅ S ₇₀	13.7	38.6	46.7	0.9	26.1
Gd ₂ Zr ₂ O ₇	C ₃₃ M ₉ A ₁₃ S ₄₅	17.5	37.4	40.9	4.2	25.9
	C ₃₆ A ₁₄ S ₅₀	19	38	36	7	26.1
	C ₂₄ A ₁₇ S ₅₉	16	38	42	4	26.1
	C ₁₅ A ₁₅ S ₇₀	13	38	48	1	26.1
YO _{1.5}	C ₃₃ M ₉ A ₁₃ S ₄₅	13	38	49	--	26.0
	C ₃₆ A ₁₄ S ₅₀	13	38	49	--	26.0
	C ₂₄ A ₁₇ S ₅₉	13	38	49	--	26.0
	C ₁₅ A ₁₅ S ₇₀	13	38	49	--	26.0
GdO _{1.5}	C ₃₃ M ₉ A ₁₃ S ₄₅	12	39	49	--	26.1
	C ₃₆ A ₁₄ S ₅₀	13	39	48	--	26.0
	C ₂₄ A ₁₇ S ₅₉	12	39	49	--	26.1
	C ₁₅ A ₁₅ S ₇₀	12	38	50	--	26.1

* AlO_{1.5} was not observed in apatite. MgO concentrations were below 1 mol% and are included with CaO where applicable.

FIGURES

Figure 1: Calculated phase equilibria for the (a) CaO-AlO_{1.5}-SiO₂ system and (b) section at 9 mol% MgO in CaO-MgO-AlO_{1.5}-SiO₂ system. The liquid field at 1300°C (dark shading), phase fields containing liquid (light shading), and synthetic deposit compositions for this study are superimposed on the projected liquidus surface. The relevant eutectic compositions and temperatures are labeled. The effect of MgO addition on the shape and extent of the liquid field is highlighted in (c).

Figure 2: BS-SEM micrographs of the synthetic silicate deposit microstructure following equilibration at 1300°C. Numbers in brackets indicate the CaO:SiO₂ ratio for the overall deposit composition.

Figure 3: BS-SEM micrographs showing the equilibrated microstructures of mixtures of synthetic silicate deposits with ZrO₂ and 7YSZ. The figure is arranged in order of increasing SiO₂ fraction from top to bottom. Crystalline phases labeled according to Table 1; the dark gray matrix in each micrograph is glass. The contrast of the inset in (d) adjusted to distinguish anorthite and glass. TEM analysis of (f) shown in Figure 4(a).

Figure 4: BF-TEM micrographs showing the structures of C₃₆A₁₄S₅₀ equilibrated with (a) 7YSZ or (b) Gd₂Zr₂O₇. The twinned microstructure of the ZrO₂ grains indicates the tetragonal to monoclinic transformation upon cooling.

Figure 5: BS-SEM micrographs comparing the Y₄Zr₃O₁₂ and Gd₂Zr₂O₇ reactivity with synthetic silicate deposits at 1300°C, arranged with increasing SiO₂ content from top to bottom. Apatite is observed for every combination. ZrO₂-based reaction products include (a-c,e) fluorite, (d,g,h) ZrSiO₄, and (f,g) t-ZrO₂. The dark gray matrix in each micrograph is glass; TEM analysis of (f) shown in Figure 4(b).

Figure 6: The equilibrium (a) CaO and (b) ZrO₂ concentration in apatite increases with the CaO concentration in the melt for systems containing ZrO₂ while those without ZrO₂ exhibit constant CaO content. The incorporation of ZrO₂ into the apatite enables the increased CaO content without incorporating oxygen vacancies leading to (c) constant oxygen content for all scenarios tested. The shaded bands are based on a linear fit to each data set.

Figure 7: Compositions of fluorite and tetragonal ZrO₂ phases illustrating the influence of both REO_{1.5} identity and deposit composition on the equilibrium reaction products. The data for equivalent experiments using YbO_{1.5}-HfO₂ TBOs was reported previously [12].

Figure 8: The equilibrium REO_{1.5} concentrations in the residual melt varies as a function of both the reacted TBO and the initial melt composition. Concentrations for all oxides but 7YSZ correspond to REO_{1.5} saturation limit with respect to apatite precipitation.

Figure 9: BS-SEM micrographs comparing YO_{1.5} and GdO_{1.5} reactivity with synthetic silicate deposits at 1300°C, arranged with increasing SiO₂ content from top to bottom. Apatite is observed for every combination. The dark gray matrix in each micrograph except (a) is glass. The contrast in the insets is adjusted to distinguish between the darker phases. TEM characterization revealing additional detail of (a, e, g, h) is shown in Figure 10.

Figure 10: BF-TEM micrographs showing additional detail of YO_{1.5} and GdO_{1.5} in equilibrium with various silicate deposits. Note the absence of a residual amorphous phase in (a).

Figure 11: The change (a) SiO₂ concentration, (b) Si:Ca ratio, and (c) calculated viscosity[24] of the residual melt is a function of the deposit composition and the crystallization products. As discussed in the text, compositions in (a) and (c) are normalized to SiO₂ + CaO + MgO + AlO_{1.5}. The solid and dotted horizontal lines represent the initial bulk silicate deposit and the initial liquid compositions, respectively. Error bars for the measurements are smaller than the symbols.

Figure 1

(a) CaO-AlO_{1.5}-SiO₂
(mol%)

(b) CAS + 9 mol% MgO
(mol% / 0.91)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

(a) CaO Concentration in Apatite

(b) ZrO_2 Concentration in Apatite

(c) Calculated Oxygen Atoms per Apatite Formula Unit

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

(a) SiO₂ Concentration in Residual Melt

(b) Molar Si:Ca Ratio in Residual Melt

(c) Calculated Viscosity of Residual Melt (excl. Zr, Y, Gd)