

Interactions of gadolinium hafnate and zirconate with silicate melts

Andrew R. Ericks,^{*} Collin S. Holgate, Nikita Basilyan, Carlos G. Levi, Frank W. Zok Materials Department, University of California, Santa Barbara

Abstract

Rare earth hafnates and zirconates are candidate materials for thermal and environmental barrier coatings (T/EBC) to protect gas turbine engine components from various environmental threats, including molten silicates derived from ingested mineral debris. This article examines the reactions of $Gd_2Hf_2O_7$ (GHO) and $Gd_2Zr_2O_7$ (GZO) to exemplary acidic and basic silicate melts. Exposure experiments at 1400 °C reveal that both materials react to form mixed layers of apatite and fluorite. These layers largely hinder melt penetration of grain boundaries in GZO for exposures up to 4h. However, extensive intergranular melt penetration occurs into GHO below the reaction layer within 1h for the acidic melt and within 4h for the basic melt. Shorter exposures (1-5 min) of Gd-lean versions of the two compounds, *viz.* $Gd_{0.2}Hf_{0.8}O_{1.9}$ and $Gd_{0.2}Zr_{0.8}O_{1.9}$, are used to probe differences in the dissolution and diffusion rates. While both oxides form fluorite, the HfO₂-based one reacts more slowly than that based on ZrO₂. Analysis of composition profiles across the solid/melt boundary reveals that Hf⁴⁺ diffuses more slowly than Zr⁴⁺ and that the hafnate dissolves more slowly than the zirconate; in both cases dissolution is diffusion-controlled. The implications for the efficacy of reactive crystallization as a silicate mitigation strategy are discussed.

KEYWORDS: CMAS, dissolution, diffusion, hafnate, zirconate

^{*} Corresponding author: aericks@ucsb.edu

1. INTRODUCTION

Implementation of SiC-based composites into hot-section components of gas turbine engines enables higher service temperatures and, in turn, improved fuel efficiency.¹ This strategy, however, hinges on protective coatings that isolate the composites from chemically aggressive environments, including water-vapor generated by combustion and molten silicate deposits derived from mineral debris ingested with the intake air.² While approaches for mitigating water-vapor-mediated volatilization have been identified³, effective strategies to defend against silicate deposits have been more elusive. The deposits span a broad range in compositions⁴ and react with essentially all thermostructural materials of interest.² Management of the kinetics of these interactions is thus critical for mitigating deposit-induced component degradation and for achieving acceptable service lifetimes.⁵

Previous studies on thermal and environmental barrier coatings (T/EBCs) have demonstrated that the effects of silicate deposits are mitigated to some extent when rapid reactions occur at the coating-melt interface. Ideally the reactions lead to formation of kinetically stable crystalline products that hinder further interaction. These products can also reduce the rate of melt penetration into the coatings via intercolumnar gaps of segmented coatings⁶ or inter-splat gaps and grain boundaries of nominally dense coatings.⁷ Otherwise, if the melt penetrates into the coating with concomitant stiffening, large internal residual stresses are generated during subsequent thermal cycling which may accelerate coating spallation.⁸

Rare earth zirconates have proven a promising family of candidate materials for mitigating silicate attack of T/EBCs.^{2, 8, 9} The general behavior is epitomized by Gd₂Z₂O₇ (GZO), which has been used in commercial application for TBCs for over a decade.¹⁰ GZO rapidly reacts with molten silicates to form protective mixed layers of apatite (nominally Ca₂Gd₈Si₆O₂₆) and Gd-lean fluorite.⁶ Evidence from related studies suggests that the effectiveness of GZO in mitigating molten silicate attack decreases at higher temperatures, notably 1500°C, hindering the ability to capitalize on the high temperature capabilities of SiC-based composites.⁹

An alternative group of materials for silicate attack mitigation is based on rare-earth hafnates, for which there is significant work on Yb₄Hf₃O₁₂.^{11, 12} Of particular interest to this study is the comparison between Gd₂Hf₂O₇ (GHO) and GZO. Because the mechanism of interaction between a silicate melt and a coating involves a critical first stage of dissolution, a difference in the nature of reactions may arise from the relative stability of the two pyrochlore compounds. That is, GZO is known to disorder into fluorite at ~1825K, 65% of the fluorite solidus (~2800K);¹³ by comparison, the reported disordering temperature for GHO is ~2710 K,^{*} or 92% of the corresponding solidus (2943 K).¹⁴ These differences have implications for the findings presented later. Additionally, GHO offers a slightly lower CTE than GZO, by ~1 ppm K⁻¹,^{15, 16} thereby reducing the mismatch with the SiC/SiC CMC and by extension the driving force for thermomechanical damage. However, since both GZO and GHO should be amenable to deposition processes that produce segmented microstructures, issues associated with thermal expansion mismatch may become manageable.¹⁷

The current article examines the thermochemical interactions of GHO and GZO with exemplary CMFAS[†] melts, with the goal of elucidating the underlying mechanisms and kinetics. Section 2 provides insight on the relevant phase equilibria, based only on GZO because of the paucity of thermodynamic descriptions for the relevant HfO₂-based phases in CalPhaD. The results illustrate the intended CMFAS mitigation strategy, notably formation of barrier crystalline phases following dissolution of small amounts of GZO into the melt. Section 3 contains descriptions of materials and test methods employed in examining reactions of GHO and GZO with two exemplary CMFAS melts (one acidic, one basic), and reactions of Gd-lean versions of GHO and GZO with a basic (Fe-free) CMAS melt used in prior studies.^{6, 9, 18, 19} The experiments are designed with two goals in mind: (i) to identify the reaction products and their evolution over time and (ii) to examine the kinetics of dissolution and diffusion of the coating materials in the silicate

^{*} There are some conflicting reports about whether GHO disorders or melts congruently at 2710 K.^{49, 50} The discrepancy may be due to differences in the manner in which samples had been cooled from high temperature.¹⁴

[†] CMFAS denotes the oxide constituents in the silicate deposits, <u>CaO</u>, <u>MgO</u>, <u>FeOx</u>, <u>AlO1.5</u>, and <u>SiO2</u>, identified by the first letter of the cation. The total oxygen depends on the state of oxidation of Fe.

melts. Section 4 contains the experimental findings while Section 5 presents a discussion of the interplay between phase equilibria, dissolution, diffusion, and melt saturation.

2. THERMODYNAMIC FOUNDATION

Phase equilibria in the GZO-CMFAS system were calculated to provide a baseline of the terminal state toward which the systems evolve. One specific goal was to determine the amount of GZO that would need to be dissolved in the melt to initiate crystallization of phases beneficial to mitigation, and the amount needed to completely consume the melt through crystallization. Two silicate compositions were selected to inform subsequent experiments: $C_{12}M_6F_6A_{18}S_{58}$ and $C_{29}M_6F_6A_{18}S_{41}$,^{*} with Ca:Si ratios of 0.21 and 0.71, respectively. While comparable thermodynamic descriptions of analogous Hf-based compounds are not yet available, the chemical similarities between Hf⁴⁺ and Zr^{4+ 20, 21} suggest that the two systems should react similarly with silicate melts.

Calculations were undertaken using the Thermo-Calc (TC) TCOX10.1 database.^{22, 23} Two types of calculations were performed, using a temperature of 1400 °C[†] and a total pressure of 10^5 Pa. In the first, a pseudo-ternary section of the phase diagram was constructed using the TC Console Mode, prescribing one total mole of cations and an O₂ activity of 0.21. In the second, point equilibrium calculations were performed by progressively adding GZO to one of the two exemplary CMFAS silicates, continually adjusting the CMFAS:GZO ratio to maintain one mole of cations total. To minimize the potential for reduction of iron, 0.01 moles of atomic O was also added to the systems. The phase fractions and compositions were calculated using TC-Python.²⁴ In all cases the O activity after equilibration in the two types of calculations was essentially the same (~ 10^{-7}).

^{*} Unless noted otherwise, all reported compositions and concentration ratios are in mole percent of oxide formulae based on a single cation.

[†] At both 1300 °C and 1400 °C HfO₂ is monoclinic while ZrO₂ is tetragonal. The difference is not critical for the present discussion.

2.1. Isothermal equilibrium at 1400°C

The pseudo-ternary section for the GZO-CMFAS system at 1400 °C is shown in **Figure 1**. One corner of the diagram represents GZO (specifically $Gd_{0.5}Zr_{0.5}O_{1.75}$) while the opposite side represents an isopleth of a series of CMFAS compositions with constant $M_{0.06}F_{0.06}A_{0.18}$, or (MFA)_{0.3}, the balance ranging from S_{0.7} to C_{0.7} at the ends of the isopleth. The shading distinguishes fields that contain liquid, liquid and apatite, and apatite without liquid; other phases, when present, are not labeled. Specifically, the onset of apatite formation is denoted by the transition from blue to purple fields while complete melt consumption is denoted by the transition from blue to purple fields while complete melt consumption is denoted by the transition from purple to pink fields. The two circles along the CMFAS isopleth denote the compositions of the two exemplary CMFAS. The tie lines connecting these circles to the $Gd_{0.5}Zr_{0.5}O_{1.75}$ corner indicate the reaction paths with changing CMFAS:GZO ratio.

All compositions along the CMFAS isopleth in **Figure 1** are predominantly molten at 1400 °C prior to GZO addition, with liquid present as a single phase in the approximate range $0.06 \le \text{Ca:Si} \le 1$ ($0.035 \le \text{Ca} \le 0.35$). Outside this range the liquid is in equilibrium with crystallization phases, e.g. trydimite at the highest SiO₂ contents. For a wide range of initial melt Ca:Si ratios, new crystalline phases begin to form after addition of only small amounts of GZO (~5%). Notably, apatite forms as a primary crystalline phase in the range $0.56 \le \text{Ca:Si} \le 1$, usually followed by fluorite, and after formation of primary tetragonal zirconia (Z) between Ca:Si~0.28 and Ca:Si~0.56. The minimum amount of GZO required to initiate crystallization is relatively insensitive to the initial Ca:Si ratio up to ~1.63, beyond which apatite should form directly from the melt. The fraction of GZO needed to completely consume the melt⁴ is ~0.6 for Ca:Si ≤ 0.2 , which decreases slightly to 0.55 for 0.21 \le Ca:Si ≤ 0.71 , and then goes down to ~0.24 for Ca:Si ~ 1.63 . Interestingly, the smallest amount of GZO needed to eliminate the melt is ~0.15, but it does not involve the formation of apatite, as revealed by the point on the white phase field closest to the CMFAS isopleth at Ca:Si ~ 2.1 .

2.2. Phase evolution with Gd pyrochlore addition

Figure 2 shows the *predicted* evolution and composition of the equilibrium phases as GZO is added to the two exemplary silicates. For the more acidic CMFAS (Ca:Si \approx 0.21), zircon forms first, followed shortly by apatite at GZO \approx 0.05 (**Figure 2a**). Because GZO donates equal amounts of ZrO₂ and GdO_{1.5} to the melt, the relatively early zircon formation implies that the melt saturates in ZrO₂ before reaching the GdO_{1.5} content needed for apatite formation. Both zircon and apatite deplete SiO₂ from the melt (**Figure 2b**), gradually decreasing the driving force to form zircon and leading to the emergence of *t*-ZrO₂ (plateau in SiO₂ concentration in **Figure 2b**). At GZO \approx 0.15, zircon begins to be less stable, and eventually disappears (GZO \approx 0.33), as *t*-ZrO₂ becomes the preferred (and only) ZrO₂-rich phase (**Figure 2a**). At yet later stages, the melt becomes slightly enriched in AlO_{1.5} and FeO_{1.5} but not MgO, since apatite is predicted to incorporate up to ~8% MgO based on the existing database (**Figure 2c**).

For the more basic CMFAS (Ca:Si \approx 0.71), apatite should form first, followed shortly by fluorite (**Figure 1** and **2e**). The apatite depletes the melt of SiO₂ and also incorporates more CaO than that found for the reaction with the lower Ca:Si CMFAS (**Figure 2g**). The apatite also contains some Zr⁴⁺ by charge-coupled substitution with Ca²⁺ and Mg²⁺ for Gd³⁺.^{2, 6, 9} Finally, the fluorite is predicted to incorporate ~13% GdO_{1.5} and ~3% CaO (**Figure 2h**).

The key inference from this analysis is that reactions of GZO with the two exemplary silicates should yield one GdO_{1.5}-rich phase and one ZrO₂-rich phase, both starting to form after dissolution of only small amounts of GZO. *Total* melt consumption would require substantial addition of GZO and thus would not be a viable mitigation strategy. However, formation of continuous layers of reaction products that isolate the pristine GZO from the melt could slow down recession of EBCs and/or melt penetration into TBCs, provided crystallization is sufficiently rapid. A corollary of the predicted phase evolution is that the melt changes in composition as more oxide is added, so the equilibrium established early may not be sustainable as the melt evolves, and thus the crystallized phases may partially re-dissolve and reprecipitate to adjust their compositions accordingly.

3. EXPERIMENTAL METHODS

3.1. Overview

Two types of experiments were performed. One was aimed to identify the *reaction products and their evolution* upon contact of GZO or GHO with one of the two exemplary CMFAS. These experiments were conducted by laying thin disks of the silicate material onto cylindrical compacts of GHO or GZO, heating the assemblages to 1400 °C and holding for a prescribed time (10, 60, or 240 min), rapidly cooling the samples in flowing air, and sectioning and characterizing the reacted interfaces and surrounding regions.

The second set of experiments was designed to examine the *kinetics of dissolution and diffusion* of the coating material constituents into the melt during the early stages of interaction. Based on previous experience, these processes are studied most effectively by delaying the onset of crystallization of reaction products so that the intrinsic concentration profiles at the dissolution front can be measured and thus the dissolution and diffusion rates can be ascertained. To this end, the exposure temperature in the second set of experiments was reduced from 1400 °C to 1300 °C, and the Gd content of the putative coating materials was reduced from 50% to 20%, i.e. $Gd_{0.5}Zr_{0.5}O_{1.75}$ (GZO) and $Gd_{0.5}Hf_{0.5}O_{1.75}$ (GHO) were substituted for $Gd_{0.2}Zr_{0.8}O_{1.9}$ and $Gd_{0.2}Hf_{0.8}O_{1.9}$, respectively. Both changes delay the onset of crystallization.²⁵

In order to minimize melt flow and convection and to properly capture the intrinsic dissolution and diffusion processes, the second set of experiments required a different set-up from the first. Here an assembly made from graphite crucibles and graphite tubes was employed, as described elsewhere.¹⁸ Since graphite can reduce FeO_x, the silicate composition selected for this part of the study was Fe-free (i.e. CMAS rather than CMFAS). Additionally, these experiments were restricted to a single silicate, with a Ca:Si ratio close to that of the basic melt used in the first set. This modified silicate also facilitated direct comparison with previous studies on the dissolution and diffusion kinetics of yttria-stabilized zirconia and hafnia.^{18,19}

3.2. Coating material compacts

Dense compacts of the coating materials were made by sintering cold-pressed powders. GZO powder (Praxair Surface Technologies) was supplied by GE Global Research. Powders of the other three materials $(Gd_{0.2}Zr_{0.8}O_{1.9}, Gd_{0.5}Hf_{0.5}O_{1.75}, and Gd_{0.2}Hf_{0.8}O_{1.9})$ were synthesized in-house by reverse co-precipitation using precursors of gadolinium nitrate-hydrate, zirconium dinitrate-oxide-hydrate, and hafnium chloride $(all \ge 99.9\% purity, Alfa Aesar, Ward Hill, MA)$. The compounds were dissolved in ethanol, mixed in the proper proportions, and then co-precipitated by gradual slow addition to an ammonium hydroxide bath following previously established procedures.²⁶ The precipitated product was washed, dried, and calcined at 1000°C, thereby yielding uniformly-mixed single phase oxide powder.

Powders were then ball-milled down to ~1 μ m using 5 mm and 1 mm YSZ media in YSZ containers (TOSOH USA, Inc., Grove City, OH), compressed into 10 mm-diameter cylindrical pellets using a hydraulic press (Carver Inc., Wabash, IN), and sintered in air at 1600 °C for 48 h. The relative densities of the sintered compacts, determined using a modified Archimedes method (ASTM C373),²⁷ were at least 97%. Electron probe micro-analysis (EPMA, Cameca SX-100) on the four types of consolidated compacts revealed that the compositions were within ±2% of their target values. In preparation for subsequent silicate exposure tests, one surface of each compact was polished to a 1- μ m finish using SiC paper and diamond suspensions.

The phase constitutions of the sintered compacts were determined using X-ray diffraction (XRD; monochromatic Cu-K_{α} radiation; Panalytical Empyrean, Westborough, MA). Both the GHO and GZO compacts with 50% GdO_{1.5} are ordered cubic pyrochlores; their XRD scans exhibit the expected low intensity superlattice reflections (**Figure 3**). Those with 20% GdO_{1.5} are disordered cubic fluorites; their XRD scans lack the low intensity superlattice reflections. Comparisons of scans for the 20% GdO_{1.5} and the 50% GdO_{1.5} reveal an inverse relationship between GdO_{1.5} content and diffraction angle, as reported in an earlier study.²⁸ That is, decreasing the GdO_{1.5} content from 50% to 20% shifts the (222) pyrochlore/(111) fluorite peak from ~29° to ~30°, consistent with a shrinkage of the unit cell with reduced Gd content.

3.3. CM(F)AS compositions and preparation

Synthetic silicate deposits were prepared from the corresponding individual constituent oxides: CaO (99.95%), MgO (99.95%), Fe₂O₃ (99.99%), Al₂O₃ (99.97%), and SiO₂ (99.99%) (all from Alfa Aesar, Ward Hill, MA). Two silicate compositions were selected for the first set of experiments: $C_{12}M_6F_6A_{18}S_{58}$ and $C_{29}M_6F_6A_{18}S_{41}$ (as described in Section 2). These selections were based on known competing effects of the oxides on deposit thermophysical properties and on thermochemical reactions with prototypical coating materials.^{2, 4} Properties of the two silicates are listed in Table 1.^{29, 30}

To prepare thin CMFAS disks, oxide powders were calcined, mixed in the appropriate proportions, and ball-milled in ethanol. The resulting slurries were dried, ground using a mortar and pestle, and heated for 24 h at ~40 C° below their respective solidi to promote reaction between the constituents.³¹ The prereacted powders were pressed into 6 mm-diameter pellets, sintered at 1100 °C for 12 h, and then mechanically thinned to yield a nominal areal density of 18 mg cm⁻² (as in previous studies).^{7, 32, 33}

The CMAS composition is identical to that used in earlier work $(C_{33}M_9A_{13}S_{45})^{19,18}$ and has a Ca:Si ratio (0.73), close to that of the basic CMFAS used in the first set of experiments (0.71). Additionally, being Fe-free it can be used with graphite crucibles. The CMAS powder was prepared in the same way as the CMFAS powders but then converted to amorphous form to ensure homogeneity of the melt composition. To achieve this, it was placed in a graphite crucible under gettered Ar, heated to a fully molten state at 1400 °C, held for 4 h, quenched to form a glass, and then ground into a powder (~200 mesh, <74 µm). Properties of this CMAS are listed in **Table 1**.

3.4. Silicate exposure tests

For the first type of experiment a CMFAS disk was placed onto a polished surface of a sintered compact (either GZO or GHO) and the pair placed on Pt foil within a covered alumina crucible. The assemblage was heated at 10 °C min⁻¹ to 1400 °C, held at temperature for 10, 60, or 240 min, and then quenched in flowing air (\sim 30 °C s⁻¹).

The procedure for the second type of experiment was the same as that used in previous studies to make analogous measurements of dissolution and diffusion rates.^{18, 19} A polished compact was placed at the bottom of a graphite crucible and a hollow graphite tube was placed on top of the compact. Amorphous CMAS powder was packed into the hollow tube. The assemblage was inserted into a pre-heated horizontal tube furnace equipped with a high-purity alumina tube (Coorstek, Golden, CO). The insertion was performed in two stages: first to a location at 715 °C and held (to preheat the sample, remaining below the glass transition temperature), and then to the hot zone, at 1300 °C. After a prescribed amount of time (1-5 min), the sample was rapidly extracted from the furnace and quenched in flowing air; the temperature fell below the glass transition within ~20 s. This procedure and test fixture have been shown previously to minimize convection otherwise caused by melt spreading in the first type of experiment.¹⁷ Such convection can perturb the concentration profiles and lead to anomalously high dissolution rates.

3.5. Post-exposure characterization

Following silicate exposure, samples were mounted in epoxy, sectioned along their diametral plane, and polished to a 0.25-µm finish. Microstructures were then characterized using scanning electron microscopy (SEM) in secondary and backscattered electron imaging (BSEI) modes (Fisher Scientific, Apreo C). In select cases, lamellae were extracted using a focused ion beam (FEI, Helios Dualbeam Nanolab 600) and analyzed in a scanning transmission electron microscope (STEM, ThermoFisher, Talos G2 200X). Three types of data were collected: selected area diffraction patterns (SADP); bright field (BF), dark field (DF) and high angle annular dark field (HAADF) images; and standardless energy-dispersive x-ray spectra (EDS, ChemiSTEM silicon drift detectors and Velox software³⁴).

Additionally, for the second set of tests, concentration profiles of the dissolved Gd³⁺, Hf⁴⁺, and Zr⁴⁺ were measured using electron probe micro-analysis (EPMA, Cameca SX-100), following previously reported procedures.¹⁸ Diffusivities and dissolution rates were obtained by fitting the concentration profiles to a crystal dissolution and diffusion model described in earlier publications.^{18, 19, 35} The model accounts for the effects of recession of the dissolving solid by calculating an equivalent melt growth rate. The key

parameters resulting from the analysis are the effective binary diffusion coefficients, D_i ; the initial intrinsic melt growth rate, u_0 ; the undersaturation of species *i* at the interface, relative to the concentration needed to initiate crystallization of a specific reaction product; and the time-dependent oxide recession distances, L(t). The latter was determined by integrating the concentration profiles for the dissolving species and then converting the results to the equivalent amount of solid oxide.

4. EXPERIMENTAL RESULTS AND ANALYSIS

To provide context for the more complex interactions between the two pyrochlores and CMFAS melts, the results on the experiments with Fe-free CMAS melt and the Gd-lean oxides are presented first.

4.1. Interaction of Gd-lean fluorites with CMAS

Short exposures of the Gd-lean HfO₂- and ZrO₂-based fluorites lead to differing rates of dissolution, diffusion, and reprecipitation. On the Zr-based fluorite surface, new fluorite grains appear after 1 min exposure and almost completely cover the surface after 3 min (**Figure 4**). On the Hf-based surfaces, in contrast, new grains are sparse even after 3 min. In both cases a thin amorphous layer resides between the original fluorite substrate and the reprecipitated grains, reminiscent of the behavior observed in the dissolution/reprecipitation of fluorite in $Y_{0.2}$ Zr_{0.8}O_{1.9}.¹⁸

SADPs taken at adjacent locations across the interface between pre-existing and new grains indicate that the product phase for both parent oxides is fluorite and that it grows with a preferred orientation relationship with the substrate, despite the presence of the thin amorphous layer along most of the interface. The reprecipitated fluorites differ in composition from their respective parent material but are similar in the two systems: $Hf_{0.89}Ca_{0.07}Gd_{0.04}O_{1.91}$ and $Zr_{0.87}Ca_{0.06}Gd_{0.07}O_{1.91}$. These compositions are in line with those of stabilized cubic fluorites at $1300^{\circ}C$.^{14, 36–38} Apatite does not form in either case, consistent with previous experience in similarly dilute systems, presumably because the Gd^{3+} content in the dissolving oxide is insufficient to trigger apatite formation. Concentration profiles through the boundary layers show that Zr^{4+} diffuses more quickly than Hf⁴⁺ (**Figure 5a,b**). After 2 min exposures (while the dissolution front is not yet significantly covered with the reprecipitated product), the diffusivities are 2.0±0.04 µm²s⁻¹ for Hf⁴⁺ and 4.1±0.1 µm²s⁻¹ for Zr⁴⁺ (**Figure 6**). Differences in Gd³⁺ diffusivities in the two systems are less pronounced: 4.6±0.1 µm²s⁻¹ for the Hf-fluorite and 5.6±0.3 µm²s⁻¹ for the Zr-fluorite. The plateaux in interface concentrations in **Figure 5** further suggest that the solubility of Hf⁴⁺ in the melt (~4.3%) is slightly higher for than that for Zr⁴⁺ (~3.3%). Additionally, the ratios of Gd:Hf and Gd:Zr at the interface after 1 min, when reprecipitation is minimal, are 0.16 and 0.24, respectively, compared with the expected value of 0.25 from the stoichiometry of the dissolved oxide. The inference is that, in the Hf-based system, the concentration of Gd³⁺ in the boundary layer is diluted by excess Hf⁴⁺, a consequence of the slower diffusion of Hf⁴⁺.

Recession of both fluorite phases reveals an approximately parabolic scaling with time, suggesting that the rate of dissolution is diffusion-controlled (**Figure 7**). More importantly, the Hf-based fluorite recedes more slowly than that based on Zr.

4.2. Reactions of GZO and GHO with CMFAS

At the macroscopic level the behaviors of the two melts on the pyrochlore substrates are similar. That is, the melts spread rapidly and cover most of the pellet surfaces within 10 min. Using low magnification SEM images of cross-sections in regions where the pellets had not yet been covered with melt, contact angles were measured and found to fall within a rather narrow range of $8.4\pm0.9^{\circ}$. While these values are approximate, they suggest that both surfaces are substantially wetted by both melts.

The reaction zones after 10 min exposures also exhibit similar features (**Figure 8**). Each comprises: (i) a thin (ca. 2-5 μ m) compact layer directly above the substrate; (ii) a 25-30 μ m-thick "mushy" zone of crystalline products interpenetrated by residual melt; and (iii) the bulk melt. Details of the compact layers and neighboring parts of the "mushy" zones are shown in the TEM images and EDS maps in **Figure 9**. The compact layers apparently form by direct reaction; they comprise mixtures of apatite and fluorite that grow cooperatively to produce aligned structures. This is best illustrated for the basic CMFAS/GHO reactions in **Figure 9.** Image analysis of the micrographs in **Figure 9(c,d)** (using ImageJ³⁹) indicates that approximately equal amounts of apatite (~55vol%) and fluorite (~45 vol%) form in the high Ca:Si melt upon reaction with both the Hf- and Zr-based fluorites. Pockets of aligned apatite/fluorite grains are also produced through reactions with the acidic CMFAS, although the structure is not quite as well developed as those formed in the basic CMFAS.

The two phases in the mushy zone (identified via TEM EDS) are fluorite and apatite (**Figure 9**). The fluorite grains are globular and are predominant in the reactions with the acidic melt. The apatite crystals are generally acicular and appear to grow out of the compact reaction layer directly above the substrate. Compositions of these phases at various locations, marked in **Figure 9**, are given in **Table 2**. In general, the Ca content of the apatite is somewhat lower when growing from the acidic melt, although the crystallites are smaller so the signal might be mixed in some cases with that of surrounding phases. A useful composition metric is the ratio of ionically-bonded cations to covalently-bonded Si; for apatite with the nominal stoichiometry, $Ca_2Gd_8(SiO_4)_6O_2$, this ratio is $10/6\approx 1.67$; the measured range of values presented in **Table 2** (1.59-1.86) agrees reasonably well with the expected range (1.55-1.67). Similarly, the ratio of O to cation content in the fluorite reflects the vacancy concentration and the degree of stabilization of the Hf⁴⁺ or Zr⁴⁺ solid solutions.⁴⁰ The values in **Table 2** suggest that the vacancy content of the fluorite phase ranges from 4.5 to 8.5%, which in most cases would be sufficient to stabilize fluorite.⁴¹

After 10 min exposures, grain boundary penetration by the melt is not evident at most interfaces; the arrow in **Figure 9**(a) points to one of the few GHO grains that had been undercut over a short distance by melt. The grains are separated at this location by fluorite and a small amount of melt over a distance of only \sim 1 µm from the bottom of the compact reaction layer. Although a few boundaries in the GZO exposed to the acidic melt exhibit some contrast, e.g. **Figure 9**(b), careful examination did not conclusively reveal other phases or indicate separation of grains.

Concentrations of the dissolved species (obtained by TEM EDS) in the two melts after 10 min exposures differ from one another (**Figure 10**). For both GHO and GZO, the concentrations of $GdO_{1.5}$ are

9-10% in the low Ca:Si melt (Figure 10a) and only 2-3% in the high Ca:Si melt (Figure 10b). By comparison, the predicted equilibrium solubility of $GdO_{1.5}$ from GZO in both melt types is 1-3% (Figure 2b,f). The measured concentrations of the two metal cations differ by a factor of about two: 2.7-3.5% HfO₂ vs. 1.0-1.5% ZrO₂. The dissolution process also leads to reductions in the local melt Ca:Si ratios, from an initial value of 0.21 to 0.16 and to 0.15 in reactions of the acidic melt with GHO and GZO, respectively, and from 0.71 to 0.55 and to 0.60 in reactions of the basic melt with GHO and GZO, respectively (Figure 10). The latter values differ from those predicted from a mass balance, as discussed later.

Following 1h exposures to the low Ca:Si melt, the reaction layers with GHO and GZO begin to show more substantive differences in morphology. The compact layer of fine crystallites on GZO essentially doubles in thickness (**Figure 8f**). However, no such layer is evident for GHO (**Figure 8**e), as the melt fills larger pockets between apatite and fluorite in a 125 μ m-thick layer, as shown in **Figure 11**(a). Moreover, the acidic melt penetrates the GHO grain boundaries over 200 μ m (EDS/EPMA), well below the locations marked in **Figure 11**(a). Below the lowest point where apatite is present, the Hf-rich phase transitions from fluorite with ~40 % GdO_{1.5} to GHO with ~50 % GdO_{1.5} (EDS, **Figure 11(a)**). Below the ~125 μ m-thick layer containing apatite, partially dissolved GHO grains ~60 μ m below the lower boundary of the reaction layer in **Figure 11(a)** are shown in **Figure 11(d)**; here, the grains are rounded and contain small amounts of melt at the boundaries and triple junctions.

TEM images of lamellae extracted from the top and bottom of the apatite-containing region in the GHO compact exposed to the acidic melt (marked in **Figure 11**(a)) are displayed in Figure 11(b) and (c). Near the top, apatite is abundant and mixed with fluorite and melt; near the bottom, the amount of apatite is much lower. The CaO concentrations in the melt at these locations are 8-9% and ~1%, respectively. The inference is that the melt near the bottom may no longer supply the CaO necessary to form apatite. In contrast, the melt near the pristine GZO is relatively CaO-rich, based on EDS measurements of a TEM lamellae extracted from the reaction layer orthogonal to the direction of melt penetration, as marked in **Figure 8**(f). The phase morphology and the EDS maps are shown in **Figure 12**. The green highlights

correspond to the Al signal; since Al is essentially insoluble in the crystals, its presence indicates the presence of melt. Here, the concentration of CaO in the melt is ~8-10 %, thereby facilitating growth of both fluorite and CaO-containing apatite.

Thickening of the reaction zones on both GHO and GZO implies that the melt continues to feed the reaction via transport along boundaries between previously-formed fluorite and apatite grains, e.g. **Figure 11(b,c)** and **Figure 12**. After 4 h exposures to the acidic melt, the melt penetration depth in the GHO exceeds 500 µm while that in GZO is essentially nil—**Figure 8(o,p)**.

The melt-penetrated region in GHO consists of an outer band of apatite and fluorite entrained in glass with fluorite content increasing towards the reaction front, followed by a region comprising apatite, fluorite, GHO, melt, and fine particles of an Al-, Fe-, Gd-, Hf-, Mg-bearing phase—**Figure 8(j)**. (The fine particles were too small for SEM EDS point analysis but were spatially discernable in EDS maps. While not critical to the present study, previous studies⁸ suggest that these particles are probably garnet or spinel.) The reaction zones of apatite and fluorite continue to thicken without appreciable penetration below the main reaction front—**Figure 8(k,l)**.

5. DISCUSSION

In all cases GHO and GZO react with CMFAS deposits to produce compact reaction layers initially comprising columnar arrays of alternating apatite/fluorite grains with very thin intervening layers of melt. The apatite and fluorite grains gradually coarsen over time behind the advancing compact reaction layer while incorporating a concomitantly larger amount of melt. Moreover, the volume fraction of apatite relative to fluorite decreases from the reaction front to the outer mushy zone. The implication is that the permeability of the reaction layer increases with distance behind the reaction front. While the morphology of the reaction layers in the two systems is similar after short exposures (10 min), substantial differences are evident at longer times (\geq 1 h). Most notably, with GHO, the melt penetrates along grain boundaries far ahead of the reaction front; such penetration does not occur with GZO. The underpinnings of these findings are discussed next.

5.1. Evolution of phases and compositions

The experimental findings on GZO deviate somewhat from those predicted by the thermodynamic calculations, in part due to kinetic effects. Experimentally, reactions of GZO with both the acidic and the basic melts result in formation of fluorite and apatite (without other crystalline phases) for exposure durations up to 4 h. The equilibrium calculations for the *acidic* melt, on the other hand, predict that ZrSiO₄ (zircon) should form first, at a molar concentration of GZO of 0.01 (or, equivalently, 0.5% GdO_{1.5}), followed by apatite at ~0.035 GZO (1.8% GdO_{1.5}) (**Figure 2(a)**). With further additions of GZO, apatite and zircon would progressively deplete the melt of SiO₂ until zircon becomes destabilized and *t*-ZrO₂ begins to form. While zircon was not observed experimentally in the current experiments, zircon and apatite *have* been observed together in previous long-term equilibrium experiments (1300°C/50h) involving GZO and acidic ternary melts (CAS) with Ca:Si ratios in the range 0.21 - 0.4.⁹ The absence of zircon in the current study suggests its crystallization is kinetically delayed.

While apatite, like zircon, is an orthosilicate with a relatively large unit cell, it forms readily, unlike zircon. One possible explanation is that apatite has a significant solubility for many of the cations present (**Figure 2**c) whereas zircon does not. Additionally, both fluorite and t-ZrO₂ can more readily accommodate some of the dissolved cations and thus supersede the formation of zircon. Finally, zircon formation requires ordering during crystallization, which further constrains the kinetics of the transformation, as discussed by Holgate *et al.*¹⁹

Differences between predictions from the thermodynamic calculations and experimental observations are less pronounced in the reaction of GZO with the basic melt. The calculations predict that apatite forms first, at 0.022 GZO (1.1 %GdO_{1.5}), followed by fluorite solid solution at 0.04 GZO (2 %GdO_{1.5}) (Figure 2(e). This result is qualitatively consistent with the observed apatite and fluorite in the current experiments, although the current experiments cannot distinguish the crystallization sequence. However earlier work on very short exposures (\leq 30 s) of GZO to the CMAS used here (Ca:Si=0.73) have demonstrated that fluorite forms first upon dissolution, followed soon thereafter by apatite.⁸ The observation is attributed to the role

of the higher diffusivity of Gd^{3+} relative to Zr^{4+} in the transport of the dissolving cations away from the dissolution front. In essence, each mole of dissolving GZO releases half a mole each of Gd^{3+} and Zr^{4+} . The former is preferentially partitioned to apatite and the latter to fluorite. Since the concentration of Zr^{4+} builds up faster in the boundary layer next to the dissolution front, formation of fluorite is favored over apatite. This hypothesis is supported by the observations in **Figure 4** and the concentration profiles in **Figure 5**. Here the Zr^{4+} concentration in the boundary layer builds to the saturation level within 1-2 min whereas that for Gd^{3+} continues to increase (albeit gradually) over time, not reaching a plateau at the level needed for apatite formation. Additionally, the buildup of Gd^{3+} at the GHO interface is lower than that in GZO owing to the greater dilution of Gd^{3+} by the excess Hf^{4+} , which is relatively slow in diffusing away from the dissolution front (**Figure 5**).

In principle the Gd^{3+} concentration might eventually reach a level sufficient to form apatite, although the thermodynamic calculations for the Gd-lean fluorite (not shown) indicate that the requisite $GdO_{1.5}$ concentration is ~2.1%, well above the measured levels (ca 1%). The $GdO_{1.5}$ concentration may not reach this level if there is a suitably-large sink for the dissolving Gd^{3+} , as in the current experiments and the Gd^{3+} can diffuse sufficiently quickly away from the interface. It is also possible that the thermodynamic predictions underestimate the onset of apatite for the system, as discussed in separate studies.⁴² The implication is that the database may need to be refined for low GZO additions.

5.2. Diffusion considerations

Differences in diffusivities of the various cations in the melt can affect the onset and sequence of crystallization. Diffusion through silicate melts involves transport through channels bound by non-bridging oxygens within the glass network.³⁵ One useful indicator of the ion-melt interactions is the ionic field strength, F_s :

$$F_s = \frac{Z}{(R_c + R_a)^2} \tag{1}$$

where *Z* is the cation charge, and R_c and R_a are the cation and anion radii, respectively⁴⁴. The effective radii are dependent on the ionic coordination numbers which, for this exercise, are taken as 6 for Gd³⁺, Hf⁴⁺, Zr⁴⁺, and O^{2-,43} The calculated and ranked cationic field strengths are: Gd³⁺ (~0.55) < Zr⁴⁺ (~0.89) < Hf⁴⁺ (~0.90). These values are in line with the differences in the diffusivity between Gd³⁺ and those of the transition metals, but does not capture the approximate factor of two difference in diffusivities between Hf⁴⁺ and Zr⁴⁺. However, the latter are in reasonable agreement with those generally in the literature,⁴⁵ and those in recent investigations by Holgate et al.^{18, 19, 25} on the basic CMAS melt used here.

5.3. Mechanistic insights

The mechanism of interfacial reaction is best illustrated by the microstructures obtained following short (10 min) exposures of GHO and GZO to the basic melt (**Figure 9**). Previous studies have shown that, with the right concentration of rare earth in the hafnate or zirconate and a moderate ratio of melt to T/EBC oxide, reactions with basic CMAS lead to the formation of both apatite and fluorite within a few seconds at temperatures as low as 1150°C.⁸ The two phases grow cooperatively as the melt consumes the T/EBC oxide. Cooperative growth is manifested in the alternating columnar morphology of phases seen in **Figure 9**. Additionally, evidence from the current and prior studies^{6, 46} suggests that a thin layer of melt resides at the interface at which GZO/GHO is being dissolved and that this melt layer can be redistributed laterally to enable concurrent growth of the two phases. This process is reminiscent of the classical mechanism for eutectic growth.

Additional insights into phase fractions and phase compositions are gleaned from examinations of the pertinent mass balances associated with the reactions. The approximate^{*} mass balance equations corresponding to the reactions of GZO with the basic and acidic melts (neglecting oxygen) are as follows:

$$Gd_{0.5}Zr_{0.5} + 0.485Ca_{0.42}Si_{0.58} \rightarrow 0.75Ca_{0.125}Gd_{0.5}Si_{0.375} + 0.625 Zr_{0.8}Gd_{0.2} + 0.11Ca_{melt}$$
(2)

^{*} The Ca:Si ratio of the melts is consistent with their composition, neglecting the Mg, Fe and Al since they are not captured significantly in the crystalline reaction products. The M⁴⁺ content of the apatite and the Ca²⁺ content of the fluorite are neglected based on their comparatively small values in **Table 2**.

$$Gd_{0.5}Zr_{0.5} + 0.55 Ca_{0.17}Si_{0.83} \rightarrow 0.75Ca_{0.125}Gd_{0.5}Si_{0.375} + 0.625 Zr_{0.8}Gd_{0.2} + 0.18Si_{melt}$$
(3)

Assuming an estimated molar volume for both phases of ~20-21 cm³ per mole of cations,⁶ the resulting calculated apatite:fluorite molar ratio of 1.2 is essentially the same as the measured volume ratio of 55:45. A corollary of the mass balance equations is that, when the Ca:Si ratio in the initial melt is greater than that in stoichiometric apatite (1/3) – as it is in the current basic melt – the Ca:Si ratio should *increase* as the reaction proceeds; conversely, in the acidic melt, the ratio should *decrease*. However, composition measurements through the bulk of the mushy zone (above the compact reaction layer) indicate that the Ca:Si ratios in *both* melt types are lower between the coarsening material near the reaction front than in their respective parent melts. Coupled with the observation that most of the mushy zone contains more fluorite than apatite, the results suggest that the coarsening process leads to a change in the underlying dissolution/reprecipitation process, wherein the fraction of apatite gradually decreases while that of fluorite increases. Because apatite releases more SiO₂ than CaO as it dissolves and fluorite captures only CaO (not SiO₂), the composition of the acidic melt should evolve as predicted by Equation (3). The composition of the basic melt, however, would be counteracted by the additional SiO₂ produced as apatite coarsens.

A notable feature of the cooperative growth mechanism is the presence of thin intergranular melt films through which diffusion of reactive species (Ca, Si) sustains the reaction with the underlying GZO/GHO. This process facilitates not only continued growth of the product phases but also the counterdiffusion of excess CaO or SiO₂ produced at the reaction site. While the dense compact layer of columnar phases evident at short times continues to grow with time, it does not seem to increase in thickness to the extent corresponding to apparent recession of the original T/EBC (**Figure 8**(a-d)). The melt behind the reaction front promotes grain coarsening and increased grain separation at the interphase boundaries, as inferred from **Figure 8**(a,e) and **Figure 11**(a). As the grains coarsen, their separation distances increase, as evident in the microstructures above the compact layer in **Figure 9**(a-d). Both phases coarsen significantly and anisotropically, with the fluorite columns becoming more globular and the apatite grains wider and more acicular. The implication is that the coarsening particles push their neighbors away at contact points,^{33, 47} widening the channels available for melt transport. This feature is evident in the cross section parallel to the growth front shown in **Figure 12**. It is also evident that the relative amounts of fluorite and apatite change with distance away from the compact layer, as noted earlier, with fluorite becoming more prominent near the bulk melt, especially for GHO (**Figure 8**(i, m)). The implication is that the composition of the interpenetrating melt changes through its thickness, where the cooperative growth mechanism at the original reaction interface offers no advantage and may also influence the relative stability of the fluorite and apatite phases as they coarsen.

5.4. Grain boundary penetration

A key difference in behaviors relates to melt penetration ahead of the main reaction front, especially at longer exposure times. Notably, melt penetration occurs in GHO well ahead of the reaction front, especially with acidic melts, but not in GZO. The difference cannot be attributed to substantive differences in how compact the reaction layers are, since even for GZO there are melt-filled channels (ca. 50-100 nm) between crystalline grains in the reaction layer near the GZO surface (**Figure 12**). Current understanding of grain boundary penetration suggests the mechanism involves preferential dissolution at the junctions of grain boundaries with the solid/liquid interface, where the atoms/ions have higher free energy⁴⁸, followed by reprecipitation of the reaction products³³. If reprecititation is sufficiently rapid, the grain boundary may effectively remain "sealed" and thus prevent further penetration (analogously to the mitigation mechanism for segmented thermal barrier coatings)⁶. While wetting is also needed for continued penetration, it is unlikely to be a major contributor to the differences in behaviors of GZO and GHO, especially because the spreading behavior of the melts on the bulk surfaces of GZO and GHO are quite similar.

Dissolution in reaction couples represented by **Figure 4** and **5** is controlled by detachment of the zirconate or hafnate molecules from the oxide surface in contact with the melt followed by diffusion of the dissolved species away from the detachment sites. The diffusivities of the pertinent species are ranked approximately in the order $D_{Hf} < D_{Zr} < D_{Gd/GHO} \le D_{Gd/GZO}$ (**Figure 6**). Given that the current measurements indicate dissolution is generally rate-limited by diffusion, crystal dissolution rates in GHO should be lower

than those in GZO, consistent with the experimental observations (**Figure 7**). However, given the short length scales in the reaction layers, diffusion should be fast during cooperative growth, and so any differences in the detachment rates between GHO and GZO could also contribute. As noted earlier, the higher disordering temperature of GHO could indicate that it detaches more slowly than GZO. Thus, selecting coating materials with fast diffusion and detachment rates should still be prioritized for CMFASresistant coatings.

6. CONCLUSIONS

During short exposures to molten silicates at 1400°C, GHO and GZO form compact reaction layers comprising columnar, aligned fluorite and apatite grains through a cooperative growth mechanism. During longer exposures the layer thicknesses increase and the grains behind the reaction layer coarsen. Coarsening involves dissolution and re-precipitation of the crystalline phases in an anisotropic fashion. Because of compatibility constraints at the boundaries and the low flow stress of the intervening melt, anisotropic growth causes the grains to push each other apart, thereby widening the channels for further melt ingress. The rates of these processes are influenced by the initial melt composition as well as the evolution of composition over time and across the thickness of the reaction layer as the reactions proceed.

While the reaction layer with GZO does not prevent ingress of the melt *to* the reaction front, the melt does not penetrate appreciably *beyond* this front. Evidently the rate of dissolution and crystallization at the reaction front is sufficiently fast to consume much of the incoming melt and to prevent it from penetrating further (at least over the time scales considered here). In contrast, melt penetration through the reaction layer with GHO is followed by further penetration into the underlying GHO, to a depth of several hundred μ m beyond the reaction front. This process is driven by a combination of dissolution and wetting. In this case the rate of dissolution and crystallization at the reaction front is insufficient to arrest further melt penetration. Differences in the kinetics of these processes in the two systems are likely due to the higher stability temperature of GHO relative to GZO as well as the lower diffusivity of Hf⁴⁺ relative to Zr⁴⁺ within

the melts. The key implication is that zirconates may offer advantages over hafnates in T/EBC applications where CMFAS resistance is essential.

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7. TABLES

	$C_{12}M_6F_6A_{18}S_{58}^a$	$C_{29}M_6F_6A_{18}S_{41}{}^a$	$C_{33}M_9A_{13}S_{45}{}^a$
Ca:Si	0.21	0.71	0.73
Si:O	0.34	0.27	0.30
Solidus (°C)	1185	1219	1225
Liquidus (°C)	1264	1286	1257
Glass CTE (°C) b	5.59	8.94	8.81
Melt viscosity (Pa·s) ^c	51	0.23	5.2
$T_g (^{\circ}C)^c$	990°	941°	966°, 764 ^d

Table 1 . Sincate deposit properties	Table 1.	Silicate	deposit	properties
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^a Compositions in terms of single cation formulae where C=CaO, M=MgO, F=FeO_x, A=AlO_{1.5}, and S=SiO₂.

^b Based on model from Fluegel *et al.*²⁹

[°] Based on Giordano model.³⁰ Viscosities for CMFAS compositions are at 1400°C and for CMAS at 1300°C.

^d Based on differential scanning calorimetry.³¹

Table 2. TEM EDS measurements	s of apatite (Ap)	and fluorite (Fl), corresp	ponding to Figure 9
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	Acidic Melt (Ca:Si=0.2 1)						Basic Melt (Ca:Si=0.71)									
	Pt.	Pha	Ca	Gd	M^{4+}	Si	Σ _I :Si	$O:\Sigma_F$	Pt.	Pha	Ca	Gd	M^{4+}	Si	Σ_I/Si	$O:\Sigma_F$
	1	Ap	10	44	9	37	1.70	-	13	Ар	19	40	6	35	1.86	-
	2	Ap	10	45	9	36	1.78	-	14	Ap	16	41	5	38	1.63	-
OF	3	Ap	11	48	4	37	1.70	-	15	Ap	14	43	5	39	1.59	-
GF	4	Fl	1	18	81	-	-	1.90	16	Fl	3	19	78	-	-	1.88
	5	Fl	0	19	81	-	-	1.91	17	Fl	4	20	76	-	-	1.86
	6	F1	1	24	75	-	-	1.87	18	Fl	4	23	73	-	-	1.85
GZO	7	Ap	12	49	3	36	1.78	-	19	Ap	19	42	5	36	1.83	-
	8	Ap	12	50	2	36	1.78	-	20	Ap	16	44	3	36	1.75	-
	9	Ap	12	50	2	36	1.78	-	21	Ap	15	46	3	36	1.78	-
	10	F1	0	19	81	-	-	1.91	22	Fl	3	18	79	-		1.88
	11	Fl	0	19	81	-	-	1.91	23	Fl	3	19	78	-		1.88
	12	Fl	1	23	76	-	-	1.88	24	Fl	3	28	69	-		1.83

Notes: M^{4+} refers to the measured concentrations of Hf for GHO or of Zr for GZO in the apatite phase. Σ_I :Si is the ratio of ionically bonded cations to number of Si in the apatite formulae. $O:\Sigma_F$ is the ratio of O to all cations in the fluorite formulae.

8. FIGURES



Figure 1. Pseudo-ternary section of the septenary CMFAS-GZO system at 1400°C (with constant MgO, FeO_x, and AlO_{1.5} concentrations along the CaO-SiO₂ isopleth). Apatite forms in all fields next to the GZO corner at all Ca:Si ratios, but from the melt only for Ca:Si<1.63, the latter indicated by the diamond marker. Apatite forms as a primary phase only for Ca:Si ratios crossing the boundary between the L and L+Ap fields, corresponding to $0.56 \le Ca:Si \le 1$. The dashed black lines bound liquid miscibility gaps although no liquid phase separation was observed in any of the experiments.



Figure 2. Calculated reaction pathways for the tielines in Figure 1 show that (a-d) progressive addition of GZO to the low Ca:Si CMFAS melt should initially yield zircon and apatite and that (e-h) addition of GZO to the high Ca:Si CMFAS melt should yield apatite and fluorite. Evolution of the (b,f) melt composition, (c,g) apatite composition, and (d,h) fluorite or tetragonal ZrO_2 (Z) solid solutions with GZO addition. Note that zircon in (a) is eventually destabilized and superseded by Z by the consumption of SiO₂ at higher levels of GZO.



Figure 3. XRD patterns for the pyrochlores with 50% $GdO_{1.5}$ and the corresponding fluorite phases with 20% $GdO_{1.5}$. The intensity is plotted on a logarithmic scale to enhance the smaller ordering reflections associated with the pyrochlore phase.



Figure 4. BSEI micrographs showing progressive reactions of (a-e) $Gd_{0.2}Hf_{0.8}O_{1.9}$ and (f-j) $Gd_{0.2}Zr_{0.8}O_{1.79}$ with $C_{33}M_9A_{13}S_{45}$ at 1300°C. The boundaries between parent and product fluorites contain very thin layers of glass. Plume-like precipitate grains in (h,i,j) derive their shapes from local changes in melt densities.



Figure 5. Concentration profiles within the diffusion boundary layer for the dissolution of (a) Hf^{4+} and (c) Gd^{3+} from $Gd_{0.2}Hf_{0.8}O_{1.9}$, and of (b) Zr^{4+} and (d) Gd^{3+} from $Gd_{0.2}Zr_{0.8}O_{1.9}$ into the $C_{33}M_9A_{13}S_{45}$ melt. (e,f) The solid-melt interface concentrations rapidly evolve toward their respective saturation values for Hf^{4+} and Zr^{4+} , and more slowly for Gd^{3+} .



Figure 6. Inferred diffusivities following exposures of $Gd_{0.2}Hf_{0.8}O_{1.9}$ and $Gd_{0.2}Zr_{0.8}O_{1.9}$ to $C_{33}M_9A_{13}S_{45}$ at 1300 °C.



Figure 7. Surface recession distance of $Gd_{0.2}Zr_{0.8}O_{1.9}$ and $Gd_{0.2}Hf_{0.8}O_{1.9}$ follows a parabolic dependence on time, suggesting that dissolution is diffusion-controlled. $Gd_{0.2}Hf_{0.8}O_{1.9}$ recedes slightly more slowly than $Gd_{0.2}Zr_{0.8}O_{1.9}$.



Figure 8. BSEI of GHO and GZO compacts following exposure to low and high Ca:Si CMFAS deposits show that, after 10 min (a-d), the product phases comprise mostly fluorite (Fl) with some apatite (Ap) near the base of the layers. After 1h, the low Ca:Si melt penetrates the GHO grain boundaries to a depth >300 μ m (e), and to a lesser extent in (f,g,h). After 4h, both types of melts penetrate the GHO grain boundaries (i,j,m,n) while the products of the GZO 4h CMFAS reaction (k.l,o,p) appear to hinder melt penetration.



Figure 9. (a-d) HAADF images (depicted extraction sites in Figure 4(a-d)) show apatite and fluorite on the surfaces of the dissolving GHO and GZO compacts following 10 min exposure to the CMFAS melts. (e-h) EDS maps with accompanying markers show points from which the data in Table 2 were taken. The reaction products richest in GdO_{1.5} are nearest the dissolving GHO and GZO surfaces.



Figure 10. Measured melt compositions (TEM EDS) following 10 minute exposure to (a) the acidic melt and (b) the basic melt. (Measurement errors are those reported by the Velox software.)



Figure 11. Micrographs of GHO following 1 h exposure to the low Ca:Si CMFAS deposit. (a) The melt reacts with GHO to form a band (ca. 125 μ m thick) of apatite and fluorite. (b,c) HAADF images show the topmost (b) and bottommost (c) apatite grains in the reaction layer. The middle EDS marker in (a) denotes the transition from fluorite to undissolved GHO. (d) A region ~60 μ m below the lower boundary of the reaction layer in (a) shows melt in the partially dissolved GHO grain boundaries and triple junctions.



Figure 12. (a) HAADF and (b) EDS map of the reaction layer formed following a 1h exposure of GZO to the low Ca:Si CMFAS (exemplary extraction site shown in **Figure 8f**). The lamella is in the transverse orientation, i.e. with viewing direction parallel to melt penetration direction. The layer comprises a network of apatite and fluorite with pockets of intergranular melt.