Thermochemical Degradation of HfSiO4 by Molten CMAS

Jamesa L. Stokesa,†, Narottam P. Bansala, Valerie L. Wiesnerb

a NASA Glenn Research Center, Cleveland, OH 44135, USA

b NASA Langley Research Center, Hampton, VA 23666, USA

†Corresponding author. Email address: jamesa.l.stokes@nasa.gov Telephone: 1-216-433-5874

**Abstract**

The thermochemical degradation of hafnium silicate (HfSiO4) was investigated with a molten calcium-magnesium-aluminosilicate (CMAS) glass relevant to gas turbine engine applications. Sintered HfSiO4 coupons were fabricated, within which wells were drilled and filled with CMAS glass powder at a loading of ~35 mg/cm2. Samples were heat treated at 1200°C, 1300°C, 1400°C, and 1500°C for 1 hour, 10 hours, and 50 hours. At 1200°C and 1300°C, slow formation of a Ca2HfSi4O12 cyclosilicate phase was observed at the HfSiO4-CMAS interface. At 1300°C and higher, rapid infiltration of CMAS into the material along the grain boundaries was observed. Initial conjecture into CMAS degradation mechanisms of HfSiO4 are presented herein.

**Keywords:** CMAS, HfSiO4, silicate, glass, cyclosilicate, EBC

1. **Introduction**

Ceramic coatings are an enabling technology for the use of advanced structural materials in gas turbine engine hot-section components. Silicon carbide (SiC)-based ceramic matrix composites (CMCs) are a lightweight, high temperature capable alternative to nickel-based superalloys. However, these composites must be protected by environmental barrier coatings (EBC) to prevent water vapor induced oxidation and volatilization in the combustion environment of turbine engines [1,2]. EBCs are multicomponent systems, firstly comprised of a topcoat, which is the main water vapor barrier. Between the topcoat and substrate, Si metal is often used as the bondcoat because of its favorable bonding with SiC. Additionally, the resultant SiO2 thermally grown oxide (TGO) that forms from oxidation of the bondcoat at elevated temperatures can serve as an oxidation barrier. Recent modifications of bondcoat chemistries have taken inspiration from thermal barrier coating (TBC) materials with the goal of lowering oxidation rates by incorporating hafnium oxide (HfO2). Within HfO2-Si composite bondcoats, improved performance was hypothesized due to higher temperature capability by the addition of HfO2. More importantly, SiO2 from the TGO would react with HfO2 to form hafnon (HfSiO4), a line compound in the HfO2-SiO2 system. By its similar CTE (3.6-4.4×10-6/K) [3] to SiC, conjecture followed that the presence of HfSiO4 may reduce strain energy stored by the SiO2 TGO and prevent coating spallation. Studies of HfO2-Si bondcoats have indeed shown that the presence of HfO2 in the bondcoat actually increased Si oxidation rate due to faster oxygen diffusion [4–6]. However, HfSiO4 formation compensated the CTE mismatch occurring from the SiO2 cristobalite high/low displacive phase transformation, resulting in suppressed crack formation [5–7]. With continuing research expected on HfO2-Si bondcoat architectures, it is clear from the literature that HfSiO4 will be a crucial phase for the success of these systems.

For the overall coating to protect the underlying CMC material against the variety of damage mechanisms encountered during engine operation, the individual material components selected for the EBC system must exhibit similar, suitable durability. With increasing operating temperatures of turbine engines, thermochemical damage caused by molten debris (runway dust, desert sand, volcanic ash, etc.) ingested by the engine is particularly problematic, given that the molten deposits, often comprised of calcium-magnesium-aluminosilicates (CMAS), readily dissolve and infiltrate coating microstructures. This behavior was first shown on state-of-the-art TBC topcoat materials, such as 7 wt.% yttria-stabilized ZrO2, for which a dissolution-precipitation mechanism was hypothesized [8]. However, crystallization of these deposits from the reaction with rare earth (RE)-rich zirconates and hafnates (RE2Zr2O7, RE2Hf2O7) has been shown to be potentially beneficial by consuming component oxides of the melt and reducing infiltration primarily through formation of a Ca2RE8(SiO4)6O2 apatite type silicate [9,10]. When attempting to use this mitigation mechanism with silicate-based EBC materials, such reactions consume the coatings even with effective crystallization of apatite [11–13]. Additionally, due to excess silica in the reactions coming from the EBC coating materials themselves, components of the melt are not sufficiently incorporated into crystalline products to mitigate CMAS damage.

Therefore, a concern arises with the use of HfSiO4 in EBC systems, given the drawbacks of utilizing HfO2 as well as silicate-based materials when considering reactions with CMAS. HfO2 on its own offers no protection against CMAS, since, as in TBC systems, the presence of RE2O3 oxides in TBC materials react with CMAS and stabilize the apatite phase. HfO2 is quickly reprecipitated as either monoclinic HfO2 in RE-lean coating chemistries as CMAS ingresses or stabilized fluorites in RE-rich coatings like RE2Hf2O7. While monoclinic HfO2 is stable up to ~1800°C[14], it exhibits an anisotropic CTE. Equally, the much higher CTE of fluorites (compared to SiC-based CMCs) could promote stresses upon thermal cycling at coating interfaces. Thus, the presence of HfO2-rich phases produced by CMAS interactions can be a detriment to coating lifetimes. And as previously stated, excess SiO2 from silicate EBCs results in greater consumption of the coating materials needed to achieve melt saturation. From these findings, it is hypothesized that HfSiO4 will exhibit limited durability against CMAS. However, study of high-temperature stability of hafnon against CMAS has not yet been reported in the literature. The purpose of this paper is to report preliminary results on the high-temperature interactions of HfSiO4 with a CMAS glass composition and initial findings on probable degradation mechanisms.

1. **Materials and Methods**

HfSiO4 powder was obtained from Praxair, Inc. and hot pressed into 5.08 cm × 2.54 cm × 2.5 mm plates at 1500°C for 2 hours in vacuum at 27.6 MPa. The resulting hot-pressed plates were cut into 1.27 cm × 1.27 cm coupons. Cylindrical wells approximately 2.05 mm in diameter and approximately 1.2 mm in depth were drilled into the center of each coupon. The dimensions of the well were chosen so that when filled with CMAS powder, the loading would be ~35 mg/cm2, similar to testing conditions in other EBC studies, which observed that CMAS effectively wets the sides and bottom of the well. Consequently, both well sides and bottom were taken into account when determining the surface area [13,15–17]. A synthetic sand mixture, PTI 11717A, obtained from the Air Force Research Laboratory was melted into CMAS glass and ground to powder with a Fritsch Planetary Mono Mill Pulverisette 6 (Idar-Oberstein, Germany) with zirconia milling media in a zirconia container. A sieve with 297 µm mesh was used to separate the fine from coarse and bulk particles. This CMAS glass was previously characterized for its crystallization kinetics, viscosity and mechanical and thermal properties at high temperatures [18–21]. The final composition of the glass powder [21.85CaO–6.27MgO–6.08AlO1.5–61.25SiO2–4.02Na2O–0.49K2O–0.04FeO1.5 (mol.%)] was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The wells of the HfSiO4 samples were filled with the CMAS glass powder and then heat treated in a furnace in air at 10°C/min to 1200°C, 1300°C, 1400°C or 1500°C for 1 hour, 10 hours, and 50 hours. The specimens were then cooled at a rate of 10°C/min to room temperature. After heat treatment, substrates were mounted in epoxy and sectioned through the well using a slow-speed saw with diamond blade. Specimen cross sections were polished to a 1 µm finish for microstructural and compositional analysis. Polished cross sections of the samples were coated with a thin layer of platinum for electrical conductivity and imaged using scanning electron microscopy (SEM) (Tescan MAIA3 Triglav, Brno, Czech Republic), and compositions of reaction products were determined using energy dispersive spectroscopy (EDS) (Oxford Instruments, Abingdon, United Kingdom). CMAS infiltration depth was measured at ten points around the well from EDS compositional maps and averaged to produce standard deviations for error bars.

1. **Results and Discussion**

The average density of the hot-pressed substrates measured by using the Archimedes technique [22] was found to be ~97% theoretical density of HfSiO4. A micrograph of the starting HfSiO4 microstructure is displayed in Figure 1. The starting microstructure of the as-sintered substrates appeared to have very fine grains with higher levels of local porosity greater than the 3% reported by Archimedes measurements. This localized porosity could likely be due to agglomerates present in the starting powder.

A picture containing text, nature

Description automatically generated

**Figure 1.** BSE micrograph of sintered HfSiO4 microstructure.

No phase contrast was observed in SEM analyses that suggested phase impurity of the hot-pressed samples. Trace SiO2 or HfO2 could potentially be present in the sample if there was slight variation in the line compound composition during synthesis, although further in-depth analyses would be needed to confirm the presence of these free oxides in the as-densified materials. Because all of the HfSiO4 substrates were processed similarly, if trace amounts of HfO2 or SiO2 were present, the effects on the thermochemical interactions would be likely similar across the times and temperatures utilized in this study. Back scattered electron (BSE) images of the HfSiO4 wells after CMAS exposure for 1 hour are displayed in Figure 2.

A picture containing graphical user interface

Description automatically generated

**Figure 2.** BSE micrographs of HfSiO4:CMAS samples heat treated at a) 1200°C, 1 hour; 10 hours (inset) b) 1300°C, 1 hour; 10 hours (inset) c) 1400°C, 1 hour and d) 1500°C, 1 hour.

In the specimen heat treated at 1200°C, changes in the amount of CMAS content in the wells were not readily observable. However, a thin reaction layer (~15 µm) was observed at the HfSiO4-CMAS interface that seemed to increase in thickness with increasing exposure duration to ~70 µm a shown in Figures 3(a)-(c). At 1300°C and higher exposures, the amount of CMAS glass remaining in the wells decreased as a function of increased reaction temperature and time from ~15 µm to ~41 µm after 1 hour and 50 hours, respectively. In the 1300°C, 1 hour specimen (Figure 1(b)), HfSiO4 clusters appeared to become detached from the HfSiO4 surface and suspended within the residual CMAS. By 10 hours of exposure, the remaining CMAS in the well had pooled at the corners, and a reaction zone with similar morphology to the 1200°C samples at the same exposure time was present. A comparable interaction region was also present in the 1300°C, 50 hour specimen, even though no residual CMAS was observed in the well. Exposure at 1400°C resulted in observable changes in HfSiO4 grain morphology such that a thin layer of CMAS remained on the HfSiO4 surface after 1 hour, and CMAS was observed between HfSiO4 grains, which seemed to exhibit Oswald ripening at this temperature (Figure 2(c)). HfSiO4 grains appeared to further coarsen after the 1500°C, 1 hour exposure as evidenced by the larger grains seen in Figure 2(d), where no CMAS glass remained in the well. Large voids of varying sizes greater than 50 µm in diameter were observed concentrated around the well surface. These large voids did not appear to contain CMAS glass, as all of the remaining silicate was seen between HfSiO4 grains.

Figure 3 displays high magnification micrographs of the interaction regions after 1200°C and 1300°C CMAS exposures. Figure 3(a) and Figure 3(b) display the interaction regions of the 1200°C, 1 hour and 1200°C, 10 hour samples, respectively. As evident in the figure, there seemed to be an increase in thickness of this reaction layer with increasing time of exposure. At 1200°C, 50 hours, the thickness of this layer appeared to be approximately four times thicker than that of the 1200°C, 1 hour specimen. Precipitates were also observed in the residual CMAS melt in the well after 50 hours as shown in Figure 3(c). EDS analysis suggested that these precipitates that appeared to crystallize from the melt had a nominal composition approximating CaMgSi2O6, the mineral phase diopside. The presence of diopside could be indicative of the crystallization of the CMAS melt itself at 1200°C accompanying the growth of this interaction region. Diopside has been reported to form from CMAS crystallization in previous studies [18,23]at higher temperatures and may correlate with the formation of diopside observed in this work.

Map

Description automatically generated

**Figure 3.** Higher magnificationBSE micrographs of HfSiO4:CMAS interaction zones at a) 1200°C, 1 hour, b) 1200°C, 10 hours, c) 1200°C, 50 hour, d) 1300°C, 10 hours, and e) 1300°C, 50 hours. Cy = cyclosilicate, Di = diopside

Below the residual CMAS melt within the interaction region, the difference in contrast showed another distinct phase that tended to be located around clusters of HfSiO4 at the HfSiO4--CMAS melt interface (Figure 3). As previously mentioned, this phase appeared to be present in specimens after all durations at 1200°C (Figures 3(a)-(c)) and 10 hours and 50 hours at 1300°C (Figure 3(d) and Figure 3(e), respectively). The nominal composition of this phase was determined to be Ca2HfSi4O12, which is a cyclosilicate in the *P21/m* space group [24], based on compositional analyses by EDS in the 1200°C and 1300°C samples listed in Table 1.

**Table 1.** EDS analysis (mol %) of cyclosilicate phase identified in Figure 3 for samples heat treated at 1200°C and 1300°C for various times.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | 1200°C | | | 1300°C | |
|  | 1 hour | 10 hours | 50 hours | 10 hours | 50 hours |
| CaO | 23.9±0.2 | 24.0±0.2 | 25.2±0.1 | 24.5±0.2 | 23.7±0.1 |
| MgO | ---- | ---- | ---- | ---- | ---- |
| AlO1.5 | 0.8±0.1 | 0.5±0.03 | 0.70±0.32 | 0.5±0.1 | 0.4±0.1 |
| SiO2 | 61.1±0.6 | 61.2±0.3 | 61.6±0.8 | 61.4±0.6 | 62.6±0.2 |
| Na2O | 0.5±0.1 | 0.4±0.0 | 0.3±0.1 | 0.2±0.1 | 0.2±0.1 |
| K2O | ---- | ---- | ---- | ---- | ---- |
| FeO1.5 | ---- | ---- | ---- | ---- | ---- |
| HfO2 | 13.7±0.9 | 13.9±0.3 | 12.2±0.0 | 13.4±0.4 | 13.1±0.1 |

The authors note that the composition measured does not exactly match the stoichiometry of the Ca2HfSi4O12 phase, though given that the same analyses show little to no presence of other oxides in the system in the measured phase, the authors conclude that this discrepancy is likely the product of the semi-quantitative nature of the measurement technique. Furthermore, cyclosilicates have been previously observed to form in other EBC candidate materials, including rare earth silicates, after exposure to molten CMAS at or below 1300°C after various durations [15,23,25–27]. In an earlier study involving the reaction between Ca2Y8(SiO4)6O2 apatite and the CMAS glass composition utilized in this study, a cyclosilicate phase was observed at temperatures at or below 1300°C in CMAS exposures [22]. In the current study, the cyclosilicate phase was not observed after CMAS exposures at 1400°C or 1500°C, correlating well with previous observations of this structure in other CMAS investigations as a probable result of thermodynamic instability of this material at higher temperatures as previously reported [15,23,25–27]. Of note, the cyclosilicate phase was not observed to crystallize at 1300°C after 1 hour, but did appear after 10 hours of exposure at this temperature and 1200°C after all durations observed in this study. At 1300°C, one would likely expect faster crystallization due to more rapid dissolution of the starting material into the melt.

EDS analysis of the residual CMAS across the samples indicated that the amount of HfO2 present in the residual CMAS was miniscule, but increased slightly with increasing temperature (~0.6 mol% at 1200°C to ~2.3 mol% at 1400°C). The low amount of HfO2 in the melt could be the result of low solubility of HfO2 in the CMAS melt. In TBC interactions with CMAS compositions, ZrO2- and HfO2-based materials have been reported to be dissolved by molten CMAS with ZrO2 and HfO2 reprecipitating from the melt. However, no HfO2 precipitates were readily observed within the residual melt of any samples in this study by EDS analysis. The composition of the grains in all of the samples was consistent with HfSiO4. ~2.0 mol% CaO and ~1.5 mol% AlO1.5 solubility was detected in HfSiO4 in CMAS-reacted regions. HfO2 was not readily observed as a separate precipitated phase in any of the samples, possibly indicating that HfSiO4 was not dissolved as molten CMAS infiltrated the EBC material at elevated temperatures. In addition to the low amount of HfO2 detected in the residual CMAS glass in the well, limited dissolution was also indicated by the morphology of the grains in these regions, which were more angular in shape. This result contrasted with the globular HfO2-rich precipitates often observed in CMAS interactions with HfO2-based coating materials [28,29]. Thus, a dissolution-precipitation mechanism was likely not the mechanism by which CMAS interacted with HfSiO4 during exposure. Based on the presence of residual CMAS glass between grains, molten silicates likely infiltrated the HfSiO4 substrate by ingress along grain boundaries. Silicate EBC materials that do not possess a high propensity for reaction-crystallization with CMAS have exhibited similar behavior to HfSiO4 shown here[17,23,26,30]. This mechanism of infiltration is probable in HfSiO4, as the large voids observed in the 1500°C samples, hypothesized to be caused by a swelling of the material attributed to CMAS grain boundary penetration, has been documented in investigations of other EBC materials [16,30]. Additionally, due to the localized porosity in the as-sintered substrate materials, capillary infiltration of these porous regions may have also contributed to the CMAS ingress into the substrates in addition to penetration along grain boundaries. Further study of HfSiO4 with starting microstructures more relevant to an actual EBC system will aid in determining the dominant infiltration mechanism.

Thermodynamic assessment of the CaO-HfO2-SiO2 system has not been carried out to the best of the authors’ knowledge, although assessment of the similar CaO-ZrO2-SiO2 system can give some insight into how the cyclosilicate Ca2ZrSi4O12 forms. Researchers report that the Gibbs free energy reaction [31–33] that results in Ca2ZrSi4O12 is as follows:

(1)

with the cyclosilicate forming as a product of CaO and SiO2 interactions with zircon (ZrSiO4). On the CaO-ZrO2-SiO2 ternary, cyclosilicate is a stable phase on the 1300°C isotherm but is no longer present on the 1600°C isotherm, possibly also pointing to thermodynamic stability being a key factor in the formation of this phase at certain temperatures. Applying this reaction to the current system suggests that complete dissociation of HfSiO4 to HfO2 and SiO2 into the melt did not occur to form cyclosilicate, but rather the CaO and SiO2 likely must react with HfSiO4 to form Ca2HfSi4O12. Similar results into the formation of this phase have been reported by Holgate et al., in which CMAS reactivity with HfO2 was investigated.[27] The presence of cyclosilicate was confirmed to crystallize only after a layer of HfSiO4 formed on the surface of HfO2in reactions with acidic CMAS melts (i.e., Ca:Si<0.44). In more basic CMAS melts, HfO2 did not exhibit reactive crystallization of HfSiO4 or any other phase, further supporting the current observations that the formation of cyclosilicate only occurs in the presence of HfSiO4 with acidic CMAS compositions. A likely explanation of the lack of cyclosilicate after 1 hour of exposure at 1300°C is that infiltration of CMAS into HfSiO4 may be happening more rapidly than the reactions of the melt with HfSiO4 needed for crystallization of the cyclosilicate to occur. At 1300°C, 1 hour, due to infiltration via grain boundaries, detachment of grains and migration of them into the melt was observed (Figure 2(b)). Based on the presence of clusters of HfSiO4 remaining in the cyclosilicate layers in both 1200°C and 1300°C samples (Figure 3), it is hypothesized that these clusters may have been the initial nucleation point for cyclosilicate to form. Because Ca2HfSi4O12 forms directly from HfSiO4, the greater amount of surface area of HfSiO4 clusters in contact with CMAS could have driven the thermodynamic equilibria for cyclosilicate crystallization. This mechanism of crystallization from detached HfSiO­4 clusters may also explain why Ca2HfSi4O12 forms in discontinuous layers and clusters remain as it grows in thickness up to 50 hours (Figure 3). In the case of cyclosilicate formation, this reaction consumes both SiO2 and CaO from CMAS. Crystallization of phases from the melt could be beneficial in consuming SiO2 and modifiers, as well as reducing melt volume. However, because this phase has only been observed at temperatures of 1300°C and lower, crystallization of this phase as a possible mitigation technique may not be viable at higher temperatures relevant to operation of gas turbine engines containing CMC components. Moreover, its sluggish formation compared to its infiltration around HfSiO4 grains means that even if it were to form at higher temperatures, its crystallization would not be rapid enough to halt CMAS ingress.

The rapid infiltration of molten CMAS into HfSiO4 coupon is demonstrated by exemplary EDS maps showing distribution of CaO as a function of time at 1300°C displayed in Figure 4.

Graphical user interface, timeline

Description automatically generated

**Figure 4.** EDS maps of CaO distribution in samples heat treated at 1300°C for a) 1 hour, b) 10 hours, and c) 50 hours. The white dashed lines mark the depth of infiltration.

Distinct halos of CaO spread outward from all sides of the original HfSiO4:CMAS well interface, indicative of the diffusion of the molten silicate into the material. Similar maps were taken for all other samples, and from these results, average infiltration depths were determined and plotted in Figure 5. Because no CMAS ingress was detected at 1200°C, up to 50 hours, no data points for 1200°C are shown. As expected, the infiltration of CMAS into HfSiO4 appeared to proceed more quickly with increasing temperature, such that the infiltration depth at 1300°C, 50 hours was roughly equal to the exposure at 1500°C after only 1 hour.

Chart, line chart

Description automatically generated

**Figure 5.** Estimated CMAS infiltration plots as a function of time at 1300°C, 1400°C, 1500°C.

Prior analyses indicated that the viscosity of this CMAS glass at 1200°C (96.6 Pa·s) is more than an order of magnitude higher than at 1500°C (3.73 Pa·s) [19,21], showing a decrease as a function of increasing temperature, which could explain the more rapid flow and subsequent infiltration at higher temperatures. After 1400°C, 50 hours and 1500°C, 10 hours, molten CMAS appeared to penetrate the full thickness of the HfSiO4 coupon from the bottom of the drilled well to the bottom of the coupon, a distance of ~1.4 mm, much thicker than typical bondcoat thicknesses of ~50-100 µm. Although in application HfSiO4 has not comprised the entirety of starting bondcoat architectures, it can be estimated based on current results that molten CMAS can infiltrate a ~100 µm layer of monolithic HfSiO4 in ~15 minutes at 1300°C and ~6 minutes at 1500°C. CMAS compositions with greater modifier content would likely have lower viscosities, meaning that other such glasses could cause greater amounts of damage via infiltration of grain boundaries in less time than estimated here. Of equal concern would be the generation of voids within the bondcoat due to CMAS ingress, as the presence of defects can weaken the EBC-substrate interface and promote coating spallation. Further investigation of HfSiO4 within HfO2-Si bondcoats with CMAS coupled with more quantitative characterization techniques is needed to fully elucidate the thermodynamic stability of these bondcoat architectures with molten silicates in EBC systems.

1. **Conclusions**

The current study has presented important findings in the durability of HfSiO4, an important phase in HfO2-Si bondcoat chemistries, against CMAS infiltration. The results here suggested the lack of durability of HfSiO4 against thermochemical degradation by molten silicates. While thermodynamic equilibria may favor the extrinsic crystallization of Ca2HfSi4O12 cyclosilicate, such behavior would likely be negated at higher temperatures due to the rapid infiltration around HfSiO4 grains. Although this behavior is not desirable for coating applications, the results presented here, along with further quantitative analysis, will be useful in subsequent optimization of EBC bondcoats and in the development of future EBC materials for next-generation gas turbine engines.

**Acknowledgements**

Thanks are due to Dr. Paul Angel and Mr. Douglas Doza for melting the synthetic sand into glass. This work was supported by the Transformational Tools and Technologies (TTT) Project under the NASA Transformative Aeronautics Concept Program.

**References**

[1] E.J. Opila, J.L. Smialek, R.C. Robinson, D.S. Fox, N.S. Jacobson, SiC Recession Caused by SiO2 Scale Volatility under Combustion Conditions: II, Thermodynamics and Gaseous-Diffusion Model, J. Am. Ceram. Soc. 82 (1999) 1826–1834. https://doi.org/10.1111/j.1151-2916.1999.tb02004.x.

[2] K.N. Lee, Environmental Barrier Coatings for SiCf/SiC, in: N.P. Bansal, J. Lamon (Eds.), Ceram. Matrix Compos. Mater. Model. Technol., John Wiley and Sons, Inc., Hoboken, NJ, 2014: pp. 430–451. https://doi.org/10.1002/9781118832998.ch15.

[3] Z. Ding, M. Ridley, J. Deijkers, N. Liu, M.S. Bin Hoque, J. Gaskins, M. Zebarjadi, P.E. Hopkins, H. Wadley, E. Opila, K. Esfarjani, The thermal and mechanical properties of hafnium orthosilicate: Experiments and first-principles calculations, Materialia. 12 (2020) 100793. https://doi.org/10.1016/j.mtla.2020.100793.

[4] B.J. Harder, Oxidation performance of Si-HfO2 environmental barrier coating bond coats deposited via plasma spray-physical vapor deposition, Surf. Coatings Technol. 384 (2020) 125311. https://doi.org/10.1016/j.surfcoat.2019.125311.

[5] R. Anton, V. Leisner, P. Watermeyer, M. Engstler, U. Schulz, Hafnia-doped silicon bond coats manufactured by PVD for SiC/SiC CMCs, Acta Mater. 183 (2020) 471–483. https://doi.org/10.1016/j.actamat.2019.10.050.

[6] J.A. Deijkers, H.N.G. Wadley, Hafnium silicate formation during oxidation of a permeable silicon + HfO2 powder composite system, Acta Mater. 201 (2020) 448–461. https://doi.org/10.1016/j.actamat.2020.10.019.

[7] J.A. Deijkers, H.N.G. Wadley, A duplex bond coat approach to environmental barrier coating systems, Acta Mater. (2021) 117167. https://doi.org/10.1016/j.actamat.2021.117167.

[8] S. Krämer, J. Yang, C.G. Levi, C.A. Johnson, Thermochemical interaction of thermal barrier coatings with molten CaO-MgO-Al 2O 3-SiO 2 (CMAS) deposits, J. Am. Ceram. Soc. 89 (2006) 3167–3175. https://doi.org/10.1111/j.1551-2916.2006.01209.x.

[9] S. Krämer, J. Yang, C.G. Levi, Infiltration-inhibiting reaction of gadolinium zirconate thermal barrier coatings with CMAS melts, J. Am. Ceram. Soc. 91 (2008) 576–583. https://doi.org/10.1111/j.1551-2916.2007.02175.x.

[10] J.M. Drexler, K. Shinoda, A.L. Ortiz, D. Li, A.L. Vasiliev, A.D. Gledhill, S. Sampath, N.P. Padture, Air-plasma-sprayed thermal barrier coatings that are resistant to high-temperature attack by glassy deposits, Acta Mater. 58 (2010) 6835–6844. https://doi.org/10.1016/j.actamat.2010.09.013.

[11] K.M. Grant, S. Krämer, J.P.A. Löfvander, C.G. Levi, CMAS degradation of environmental barrier coatings, Surf. Coatings Technol. 202 (2007) 653–657. https://doi.org/10.1016/j.surfcoat.2007.06.045.

[12] D.L. Poerschke, J.H. Shaw, N. Verma, F.W. Zok, C.G. Levi, Interaction of yttrium disilicate environmental barrier coatings with calcium-magnesium-iron alumino-silicate melts, Acta Mater. 145 (2018) 451–461. https://doi.org/10.1016/j.actamat.2017.12.004.

[13] V.L. Wiesner, B.J. Harder, N.P. Bansal, High-temperature interactions of desert sand CMAS glass with yttrium disilicate environmental barrier coating material, Ceram. Int. 44 (2018) 22738–22743. https://doi.org/10.1016/j.ceramint.2018.09.058.

[14] D. Shin, R. Arróyave, Z.-K. Liu, Thermodynamic modeling of the Hf–Si–O system, Calphad. 30 (2006) 375–386. https://doi.org/10.1016/j.calphad.2006.08.006.

[15] J. Sleeper, A. Garg, V.L. Wiesner, N.P. Bansal, Thermochemical interactions between CMAS and Ca2Y8(SiO4)6O2 apatite environmental barrier coating material, J. Eur. Ceram. Soc. 39 (2019) 5380–5390. https://doi.org/10.1016/j.jeurceramsoc.2019.08.040.

[16] V.L. Wiesner, D. Scales, N.S. Johnson, B.J. Harder, A. Garg, N.P. Bansal, Calcium–magnesium aluminosilicate (CMAS) interactions with ytterbium silicate environmental barrier coating material at elevated temperatures, Ceram. Int. 46 (2020) 16733–16742. https://doi.org/10.1016/j.ceramint.2020.03.249.

[17] F. Stolzenburg, M.T. Johnson, K.N. Lee, N.S. Jacobson, K.T. Faber, The interaction of calcium – magnesium – aluminosilicate with ytterbium silicate environmental barrier materials, Surf. Coat. Technol. 284 (2015) 44–50. https://doi.org/10.1016/j.surfcoat.2015.08.069.

[18] V.L. Wiesner, N.P. Bansal, Crystallization kinetics of calcium – magnesium aluminosilicate (CMAS) glass, Surf. Coat. Technol. 259 (2014) 608–615. https://doi.org/10.1016/j.surfcoat.2014.10.023.

[19] V.L. Wiesner, U.K. Vempati, N.P. Bansal, High temperature viscosity of calcium-magnesium-aluminosilicate glass from synthetic sand, Scr. Mater. 124 (2016) 189–192. https://doi.org/10.1016/j.scriptamat.2016.07.020.

[20] V.L. Wiesner, N.P. Bansal, Mechanical and thermal properties of calcium–magnesium aluminosilicate (CMAS) glass, J. Eur. Ceram. Soc. 35 (2015) 2907–2914. https://doi.org/10.1016/j.jeurceramsoc.2015.03.032.

[21] V.L. Wiesner, U.K. Vempati, N.P. Bansal, Corrigendum to “High temperature viscosity of calcium-magnesium-aluminosilicate glass from synthetic sand” [Scripta Mater. 124 (2016) 189–192](S1359646216303219)(10.1016/j.scriptamat.2016.07.020), Scr. Mater. 130 (2017) 298. https://doi.org/10.1016/j.scriptamat.2016.12.007.

[22] ASTM C373-88(2006) - Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired White Ware Products, in: ASTM Annu. B. Stand., ASTM International, West Conshohocken, PA, 2006. https://doi.org/10.1520/C0373-88R06.

[23] J.L. Stokes, B.J. Harder, V.L. Wiesner, D.E. Wolfe, High-Temperature thermochemical interactions of molten silicates with Yb2Si2O7 and Y2Si2O7 environmental barrier coating materials, J. Eur. Ceram. Soc. 39 (2019) 5059–5067. https://doi.org/10.1016/j.jeurceramsoc.2019.06.051.

[24] K. Du, X.-Q. Song, Z.-Y. Zou, J. Fan, W.-Z. Lu, W. Lei, Improved microwave dielectric properties of novel low-permittivity Sn-doped Ca2HfSi4O12 ceramics, Mater. Res. Bull. 129 (2020) 110887. https://doi.org/10.1016/j.materresbull.2020.110887.

[25] F. Perrudin, M.H. Vidal-Sétif, C. Rio, C. Petitjean, P.J. Panteix, M. Vilasi, Influence of rare earth oxides on kinetics and reaction mechanisms in CMAS silicate melts, J. Eur. Ceram. Soc. 39 (2019) 4223–4232. https://doi.org/10.1016/j.jeurceramsoc.2019.06.036.

[26] V.L. Wiesner, B.J. Harder, A. Garg, N.P. Bansal, Molten calcium–magnesium–aluminosilicate interactions with ytterbium disilicate environmental barrier coating, J. Mater. Res. 35 (2020) 2346–2357. https://doi.org/10.1557/jmr.2020.211.

[27] C.S. Holgate, Y. Yang, C.G. Levi, Reactive crystallization in HfO2 exposed to molten silicates, J. Eur. Ceram. Soc. 41 (2021) 5686–5695. https://doi.org/10.1016/j.jeurceramsoc.2021.03.025.

[28] D.L. Poerschke, G.G.E. Seward, C.G. Levi, Influence of Yb:Hf Ratio on Ytterbium Hafnate/Molten Silicate (CMAS) Reactivity, J. Am. Ceram. Soc. 99 (2016) 651–659. https://doi.org/10.1111/jace.13964.

[29] D.L. Poerschke, C.G. Levi, Effects of cation substitution and temperature on the interaction between thermal barrier oxides and molten CMAS, J. Eur. Ceram. Soc. 35 (2015) 681–691. https://doi.org/10.1016/j.jeurceramsoc.2014.09.006.

[30] L.R. Turcer, A.R. Krause, H.F. Garces, L. Zhang, N.P. Padture, Environmental-Barrier Coating Ceramics for Resistance Against Attack by Molten Calcia-Magnesia-Aluminosilicate (CMAS) Glass: Part II, β-Yb 2 Si 2 O 7 and β-Sc 2 Si 2 O 7, J. Eur. Ceram. Soc. (2018). https://doi.org/10.1016/j.jeurceramsoc.2018.03.010.

[31] S.Y. Kwon, W.-Y. Kim, P. Hudon, I.-H. Jung, Thermodynamic modeling of the CaO-SiO2-ZrO2 system coupled with key phase diagram experiments, J. Eur. Ceram. Soc. 37 (2017) 1095–1104. https://doi.org/10.1016/j.jeurceramsoc.2016.10.011.

[32] K.T. Jacob, Y. Waseda, High-Temperature Stability of Ca2ZrSi4O12, J. Am. Ceram. Soc. 77 (1994) 3033–3035. https://doi.org/10.1111/j.1151-2916.1994.tb04543.x.

[33] S. Colin, B. Dupre, G. Venturini, B. Malaman, C. Gleitzer, Crystal Structure and Infrared Spectrum of the Cyclosilicate Ca2ZrSi4O12, J. Solid State Chem. 102 (1993) 242–249. https://doi.org/10.1006/jssc.1993.1028.