Molten silicate reactions with plasma sprayed ytterbium silicate coatings

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The reactions between molten calcium aluminum magnesium silicates (CMAS) at 1300 °C and atmospheric plasma spray (APS) deposited environmental barrier coatings on SiC substrates have been investigated. The tri-layer coatings comprised a silicon bond coat protected by a layer of mullite and either Yb2SiO5 (ytterbium monosilicate, YbMS) or Yb2Si2O7 (ytterbium disilicate, YbDS) as the topcoat. The APS deposition process resulted in two-phase top coats; the YbMS coating contained Yb2O3 regions in a matrix of Yb2SiO5 while the YbDS coating contained Yb2Si2O7 in a matrix of Yb2SiO5. Exposure of both coatings to a model CMAS resulted in dissolution of the topcoat accompanied by a rapid rise in the concentration of Yb in the melt, and formation of the same Ca2Yb2(SiO4)2O4 apatite reaction product phase. The thickness of the apatite layer initially varied with (time)1/4, but transitioned to approximately parabolic kinetics after 5–10 h of CMAS exposure. The reaction mechanism on the YbMS layer was consistent with recent observations on Y2SiO5, wherein molten CMAS transport to the undissolved silicate was controlled by diffusion through thin amorphous films at the apatite grain boundaries. The reaction mechanism for the YbDS layer was more complex, and involved preferential reaction with the YbSiO3 rich regions, resulting in a reaction zone that contained CMAS, the apatite reaction compound and undissolved Yb2Si2O7. The coating composition and microstructure significantly influenced the mechanism and rate at which the YbDS top coat was consumed by the reaction.

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1. Introduction

Efforts to increase the combustion temperature of the most advanced gas turbine engines have stimulated interest in the use of ceramic matrix composites (CMCs) with much higher maximum use temperatures than conventional superalloys [1–3]. Since silicon carbide based ceramic matrix composites (CMCs) offer a superior high temperature strength and crack growth resistance compared to most other ceramic candidates [3], they are the currently preferred material for future engines. SiC also has excellent resistance to oxidation at high temperature in dry air owing to the formation of an adherent, thermally grown oxide (TGO) [3]. However, in the moist combustion environment, the SiO2 TGO reacts with water vapor to form gaseous silicon hydroxides such as Si(OH)4, resulting in rapid volatilization under the high gas temperature/pressure/velocity environment within an engine combustor and high pressure turbine [4–6]. Since engine components are normally expected to survive for several thousand hours of operation [7], those made from SiC-based CMCs must be protected from oxidation and volatilization by environmental barrier coating systems (EBCs) [1,3].

While EBCs must be resistant to volatilization by the water vapor present in the combustion environment, they must also be free of pores and cracks to remain effective barriers to the transport of oxygen and water vapor to the SiC surface. Their coefficient of thermal expansion (CTE) must be well matched with the substrate to minimize thermal stresses that can lead to coating cracking or delamination during thermal cycling and thermal shock loading. They must also be able to resist degradation by molten silicates, generically known as CMAS for their major constituents (CaO, MgO, Al2O3, and SiO2), which are deposited on hot coating surfaces during service.

Current generation EBCs use a silicon bond coat applied to the SiC substrate and an outer layer based on a rare earth (RE) silicate, notably one of those based upon Y or Yb. The coating layers are typically applied by atmospheric plasma spray (APS) deposition. While the disilicates (RE2Si2O7) are thermochemically compatible with the thermally grown SiO2 that form on the Si bond coat, and have a CTE reasonably close to that of SiC, they have a substantially higher SiO2 activity (and faster steam volatilization) than their monosilicate counterparts (RE2SiO5) [3,8,9]. However, the monosilicates have a higher CTE than the substrate [10], and if allowed to contact the thermally grown SiO2 on a silicon bond coat, would react to form a disilicate, potentially compromising the adherence of the EBC. In principle, the EBC could be designed to have the disilicate in contact with the SiO2, covered by a thinner layer of monosilicate in contact with the atmosphere. However, a layer of mullite has sometimes been used instead to delay thermochemical interactions between the thermally grown silica on the Si bond coat, and the RE silicate top coat [11].

Environmental barrier coatings are vulnerable to chemical reactions with molten silicates (CMAS) [12–14]. These molten silicates are...
ingested as solid dust particles with the engine intake air and partially or totally melt above a temperature of ~1200 °C [15]. This temperature is first encountered as the particles travel through the combustor, resulting in molten particle impacts with hot component surfaces in this region of the engine, and in the high-pressure turbine. Because EBCs are nominally dense and approximately CTE matched to the substrate, the molten silicate problem is predominantly thermochemical, rather than thermomechanical as in thermal barrier coatings [16,17]. In essence, the EBC is dissolved by the molten glass and may reprecipitate reaction products that are less CTE compatible with the substrate or exhibit a higher tendency for volatilization. Earlier generation barium strontium aluminum silicates (BSAS) based EBCs were found to be highly susceptible to degradation by CMAS [18], not only by dissolution of the EBC, but also by penetration of the glass along grain boundaries well beyond the dissolution front [18].

Grant et al. [12] showed that CMAS could cause significant recession of yttrium monosilicate (Y2SiO5, YMS). Using fully dense powder coupons and a model CMAS (33CaO–9MgO–13Al2O3–45SiO2) with an incipient melting point of 1233 °C [19], they observed rapid recession (~100 μm in 1 h at 1300 °C), in spite of the formation of a nearly dense Ca2Yb(SiO4)O2 oxyapatite layer at the YMS surface. The continued reaction was enabled by thin amorphous layers at the grain boundaries within the oxyapatite layer, which provided a fast path for diffusion to the YMS-apatite reaction front. They postulated that yttrium disilicate (YDS) coatings might be less effective at mitigating the reaction with CMAS since more YDS cations would be needed (consumed) to form a unit amount of the reaction product. While Ahlborg and Zhu investigated the reactions of hot pressed samples of YbMS and YbDS with CMAS at 1500 °C [13] and noted the formation of Ca2Yb(SiO4)O2 oxyapatite in both systems, they did not investigate the mechanisms or the rates of the reactions.

Thermal spray methods have been developed and recently optimized for depositing EBC systems comprising a silicon bond coat and either ytterbium monosilicate (Yb2SiO5, YbMS) or ytterbium disilicate (Yb2Si2O7, YbDS) top coats [10,20–22]. An interlayer of thermally sprayed mullite was added under the YbMS to prevent interactions with the SiO2 that forms on the silicon bond coat surface. While YbDS is not expected to interact with SiO2, mullite was also added to this system as well because the spray deposited coating was not phase pure. Prior work revealed that stoichiometric YbMS and YbDS powders experience a loss of SiO2 during APS deposition, resulting in YbMS coatings that containing Yb2O3 as a segregate phase, and YbDS coatings that contained Yb2SiO5 [10]. The previous studies [12,13] have examined CMAS reactions using sintered test coupons of nominally phase pure materials. However, since, the EBC systems that will be used in practice are likely to be deposited by a thermal spray method, it is possible that the interaction of CMAS with EBCs could be significantly influenced by the morphology of the spray deposited coating. This investigation therefore seeks to characterize the mechanisms and rate of the reaction between molten CMAS and APS deposited tri-layer EBCs with both YbMS and YbDS top coats.

2. Experiments

Three-layer YbMS/mullite/silicon and YbDS/mullite/silicon EBCs were deposited by APS onto rectangular 2.54 cm × 1.27 cm × 0.32 cm α-SiC substrate coupons obtained from Hexoloy™ (Saint Gobain Ceramics, Niagara Falls, NY). Prior to EBC deposition, the substrates were grit blasted using ~270 μm diameter SiC grit (Black SiC, White Abrasives, Niagara Falls, ON) resulting in an average surface roughness of ~1 μm. The substrates were then ultrasonically cleaned in ethanol to remove surface contamination. The silicon bond coat was deposited using sieved silicon powder with a particle diameter range of 44 to 149 μm obtained from Micron Metals (Bergenfield, NJ). The mullite powder was obtained from Saint Gobain Ceramics (Worcester, MA), and had a particle diameter of 16 to 53 μm. The Yb2SiO5 and Yb2Si2O7 powders were provided by Treibacher Industrie Inc. (Toronto, ON) and had particle diameter distributions of 20 to 50 μm. Powders were identified by the respective manufactures as fully reacted and phase pure, and this was confirmed by X-ray diffraction and SEM examinations of sectioned and polished surfaces.

The coatings were deposited using a Praxair-TAFA UPC 7700 controlled APS system with a SG-100 torch with a model 02083-175 anode, model 02083-120 cathode, and model 03083-112 gas injector. All coating layers were deposited at 1200 °C within a furnace. The detailed deposition setup was identical to that recently described elsewhere [20,21]. The substrate was first heated to the prescribed temperature inside a box furnace containing a small aperture through which the APS plume was introduced. A reducing gas flow within the furnace was used to inhibit oxidation of the SiC substrate and the Si bond coat during its deposition. The flow rate of the reducing gas was 20 slm with a volume ratio of Ar:H2 of 20:1. Immediately after deposition of the Si layer, the reducing gas flow was stopped, and the two subsequent layers were deposited at 1200 °C. The spray parameters for YbMS and YbDS coatings are described elsewhere [10]. Both the YbMS and YbDS coatings had an average thickness of 100 μm with a variation of 36–120 μm for YbMS and 42–126 μm for YbDS. The weight of the deposited topcoats was measured as ~110 mg for YbMS and ~94 mg for YbDS. The mullite and silicon layers were both nominally 75 μm in thickness. Since a variety of metastable phases form during the deposition of tri-layer coatings [22], the “as deposited” samples were annealed at 1300 °C for 20 h in lab air to stabilize their microstructure. All of the molten silicate tests and microstructural characterizations were performed on these “stabilized coating” samples.

The coated samples were subjected to a CMAS test protocol similar to that developed for previous studies of TBC and EBC reactions [12,16,23]. The model CMAS (with the composition 33CaO–9MgO–13Al2O3–45SiO2 (mole percent), or C29MgAl2S2O5) used by Grant et al. [18] was adopted here to enable direct comparison with the YMS studies. The melting range for this CMAS composition was 1233 °C–1249 °C [19]. The CMAS was prepared by ball milling CaO, MgO, Al2O3 and SiO2 powders followed by reaction sintering at 1200 °C for 20 h. The composition of the CMAS after reaction of the powdered constituent oxides has been measured in a scanning electron microscope (SEM) using energy dispersive spectroscopy (EDS), and is shown in Table 2.

The CMAS testing consisted of cold-pressing pre-reacted CMAS powder into a pellet ~5 mm in diameter with a mass of ~30–35 mg. The pellet was placed on the surface of the coated samples at ambient temperature, and then heated in air at a rate of 10 °C/min to 1300 °C. The samples were held at this temperature for varying times followed by furnace cooling at a rate of 10 °C/min to ambient temperature. The specimens were then sectioned, mounted in epoxy and polished, using a 0.5 μm diameter diamond suspension for the final step. Backscattered electron (BSE) images and the compositions of various phases were obtained using a scanning electron microscope (FEI Quanta 650 FEG) equipped with Bruker QUANTAX 400 energy dispersive X-ray spectrometer (EDS). Transmission electron microscopy (TEM) specimens were prepared from the areas of interest by a “lift-out” technique using a FEI Helios 600 dual-beam FIB microscope. The TEM samples were examined in a JEOL 2000FX 200 keV transmission electron microscope.

3. Results

3.1. Coating microstructure

Fig. 1 shows the BSE images of the as-deposited and annealed tri-layer coatings with YbMS, Fig. 1(a) and (c), and YbDS, Fig. 1(b) and (d), top coats. The top coats of both coating systems were nearly pore free. However, the YbMS layer contained periodic channel cracks with a spacing of ~200 μm, while the YbDS coatings contained only small microcracks in regions of lighter contrast (higher Yb concentration), Fig. 1(d). The YbMS channel cracking has been previously shown to
arise because its coefficient of thermal expansion (~7.4 ppm/°C) is higher than that of the SiC substrate (4.5–5.5 ppm/°C) [22]. Stabilization annealing at 1300 °C enables creep relaxation of the coating stresses and the development of a large biaxial tensile stress in the YbMS layer upon cooling. The resulting stored elastic strain energy then provides a driving force for the formation of (coating layer penetrating) channel cracks.

Fig. 1. SEM images (in BSE mode) of annealed tri-layer coatings with (a) ytterbium monosilicate and (b) ytterbium disilicate top coats. The structure of the ytterbium monosilicate layer is shown in (c) and that of the ytterbium disilicate layer in (d). The black box regions identified as A and B mark positions where FIB lift-out lamellae were extracted for subsequent transmission electron microscopy.

Fig. 2. (a) Bright field TEM image of an annealed YbMS coating (area A shown in Fig. 1) and (b) image of particles taken at high magnification. The SAED patterns of the monoclinic YbMS matrix for the region shown in (a) along the [011], and [155] zone axes are shown in (c) and (d). (e) Shows the SAED pattern of a cubic Yb2O3 particle along its [210] zone axis.
The nominal CTE of the YbDS layer (~4.5 ppm/°C) [24] was much better matched to the substrate, and resulted in the development of a small compressive stress in the coating after cooling [25], with no channel cracking.

When imaged in BSE mode, Fig. 1(b) and (d), the YbMS and YbDS layers were seen to contain banded regions of lighter contrast that were depleted in low atomic number elements (Si and O). Previous studies on APS deposited coatings [20,21] indicated that the banded morphology was created by droplet spreading during deposition of the coating. The phases formed within the light and darker contrast regions of both coatings were investigated by TEM. The black box areas in Fig. 1(c), (d) mark the location of the FIB lamella extracted for TEM. A bright field image of area A in the YbMS coating is shown in Fig. 2(a). Second phase segregates can be clearly seen in the banded zone. The compositions of the segregates (of darker contrast) and the matrix (lighter gray) have been listed in Table 1. The results indicate that the second phase particles have a composition close to Yb₂O₃, while the matrix is very close to Yb₂SiO₅. Selected area electron diffraction (SAED) patterns from the matrix are shown in Fig. 2(c) and (d). The indexed diffraction patterns indicate that the matrix has a monoclinic structure while the particle is the cubic phase of Yb₂O₃.

3.2. YbMS–CMAS reaction

The evolution of the CMAS/YbMS reaction with increasing exposure time is shown in Fig. 4. All of the samples exhibited channel cracks upon cooling from 1300 °C with many of the cracks extending through the solidified CMAS. The CMAS had melted and spread over the coating surface as the samples were heated to 1300 °C which was well above the CMAS melting range of ~1233–1249 °C [19]. A thin and continuous layer of reaction product between the melt and the YbMS was observed even for exposure times at 1300 °C as short as 1 min, Fig. 4(a). A FIB milling and lift-out operation was performed on the YbMS reaction layer formed after the YbMS was exposed to CMAS for 24 h at 1300 °C, Fig. 5(a). A bright field image of a reaction product grain is shown in Fig. 5(b). The SAED patterns of the reaction phase are shown in Fig. 5(c) and (d), and correspond to the [001, 021] zone axes of a hexagonal apatite phase similar to that found in YMS [12]. The lattice parameters of the apatite phase were measured at locations marked with crosses are presented in Table 1. The results indicate that the matrix has a Yb:Si atomic ratio of ~1:1 while that of the particles was approximately 2:1. This is consistent with YbMS segregation from a SiO₂ depleted YbDS melt during deposition. The SAED patterns of the segregate confirm this finding. Fig. 3(c) and (d) correspond to the [11T] and [01T] zone axes of the monoclinic Yb₂SiO₅ phase, respectively. The microcracks present in the lighter contrast region are therefore consistent with local shrinkage due to the higher CTE of YbMS.

![Fig. 3](image-url)

Fig. 3 shows bright-field TEM images of the annealed YbDS coating collected from the two-phase region corresponding to area B in Fig. 1(d). A magnified view of one of the second phase particles is shown in Fig. 3(b). The EDS compositions of the particle and the matrix (measured at locations marked with crosses) are presented in Table 1. The results indicate that the matrix has a Yb:Si atomic ratio of ~1:1 while that of the particles was approximately 2:1. This is consistent with YbMS segregation from a SiO₂ depleted YbDS melt during deposition. The SAED patterns of the segregate confirm this finding. Fig. 3(c) and (d) correspond to the [11T] and [01T] zone axes of the monoclinic Yb₂SiO₅ phase, respectively. The microcracks present in the lighter contrast region are therefore consistent with local shrinkage due to the higher CTE of YbMS.
of the CMAS melt for different infiltration times have been included in Fig. 4(a), (d) and (f). They indicate that the CMAS melt contained approximately 7.5 mol% YbO1.5 and remained at this concentration as the exposure time was increased, up to the 250 h experimental limit. This is consistent with the dissolution of approximately 10 μm (~11 mg) of the Yb2SiO5 coating in the original volume of CMAS melt.

Determination of the rate at which the apatite formed was complicated by the presence of residual CMAS within the crystalline phases. However, its difference in average atomic number contrast enabled the area fraction of the apatite to be determined. This was then divided by the width of the image to determine an “equivalent” thickness of the reaction product layer. This “equivalent” thickness, which is an indirect measure of the YbMS surface recession rate, was found to increase over time, Fig. 6. For exposure times of <10 h, the thickness data could be fitted by a power law of the form; h(t) = kt^n where h is the equivalent thickness (in μm), n = 0.26 (–1/4) is the power law exponent, t is the time (hours) and k is a rate constant with units of μm(hour)^1/4. Data for samples subjected to more prolonged exposures could also be fitted to a power law, but with an exponent ~1/2, and a slightly different (parabolic) rate constant, Fig. 6.

Chemical composition profiles within the reaction layer were obtained from EDS line scans normal to the substrate surface, Fig. 7. The CMAS reaction depth was clearly differentiated by the contrast difference between the apatite and the unreacted YbMS in BSE imaging. The Ca, Mg and Al concentrations dropped below the level of EDS detection in the unreacted region of the YbMS coating, indicating that solid state (including grain boundary) diffusion of these elements in the almost fully dense coating was negligible at 1300 °C. The average compositions of the CMAS melt located in pockets between the apatite grains, as well as in the residual CMAS well above the reaction zone, have been measured and are summarized in Table 2, along with the initial composition and that estimated after saturation with Yb. It is noted that Ca in the CMAS melt was depleted as the reaction time increased, and was accompanied by an increase in concentration of the non-reacting Al, while the Si concentration slightly decreased but then increased abnormally following a 250 h exposure time. The amount of YbO1.5 in the pockets within the reaction zone was ~5–6 mol%; slightly less than that in the CMAS melt (~7.5 mol% YbO1.5), consistent with local depletion of Yb³⁺ cations dissolved in the CMAS. This composition difference has also been observed in the CMAS interaction with yttrium monosilicate [12], where it was argued that additional crystallization upon cooling resulted in the local depletion of the rare earth element near the reaction front.

Higher resolution SEM images of the interface between the YbMS and growing apatite are shown in Fig. 8. A thin, denser (less CMAS entrained) layer of reaction product is evident at the interface with the YbMS in this figure. Fingers of unreacted YbMS were observed intruding into the apatite layer (typically well away from its grain boundaries), for distances up to ~3 μm from the macroscopic recession front, Fig. 8(d), (e) and (f). This was consistent with a gradual diffusion of reactants from the grain boundary to the grain interior. The denser layer of apatite transitioned into a thicker layer of large, elongated crystals interpenetrated by residual CMAS. The width of these crystals, and the volume fraction of CMAS between them, increased with distance above the interface. Bright field TEM images of the interfacial region, Fig. 9(a) and (b) reveal gaps between the grains of apatite penetrated by a thin layer of amorphous material, which arguably provided pathways for continued transport of reactants from the bulk melt to the interface with the YbMS and byproduct transport in the opposite direction. The thickness of the denser reaction layer followed a power law dependence on time with an exponent of ~1/4, similar to that seen during the initial stages of the reaction, Fig. 6.

The width of the apatite grains in the plane of this dense layer also exhibited a two-stage power law behavior, Fig. 10, with an earlier period of slower coarsening (n ~ 0.08) followed by a faster evolution (n ~ 0.21). Examination of the cross sections of coatings exposed to CMAS for 250 h revealed the presence of occasional regions of full tri-

Fig. 4. SEM images showing the formation of a reaction layer during YbMS coating exposure to CMAS at 1300 °C for (a) 1 min, (b) 1 h, (c) 4 h, (d) 24 h, (e) 100 h and (f) 250 h.
layer coating penetration by the CMAS. This appeared to occur at locations where the initial YbMS coating was thinner, e.g. Fig. 11(a). In some areas, the CMAS had fully penetrated the YbMS, mullite and silico- con layers and vigorously reacted with the SiC substrate resulting in the formation of large voids presumably associated with CO release during reaction of CMAS with the SiC substrate.

3.3. YbDS CMAS reaction

The evolution of the ytterbium disilicate coating to a similar molten CMAS exposure at 1300 °C can be seen as a function of exposure time in

Fig. 6. The equivalent reaction layer thickness plotted as a function of reaction time at 1300 °C for both ytterbium monosilicate and disilicate coatings under the assumption that the reaction layer is densely packed.

Fig. 7. EDS composition profile analysis of the coating after exposure of YbMS to CMAS for 100 h at 1300 °C.

Recall that the lighter contrast elongated regions in the top coat correspond to a YbMS segregate. No mud cracking of the YbDS top coat was observed even though cracks had formed in the CMAS above the top coat on cooling. These CMAS cracks resulted from the substantial CTE difference between CMAS and the rest of the system. Even though the vertical cracks entered the YbDS layer with an elastic modulus (170 GPa) identical to that of the YbMS [20], they were quickly arrested since this layer was under a state of weak biaxial compression [20,21].

1 The driving for vertical crack extension is the tensile elastic strain energy (proportional to the elastic modulus and the difference in CTE of the coating and substrate), and is resisted by the fracture toughness of the region in which fracture occurs.
As in the YbMS case, a reaction product layer was formed between the CMAS and the YbDS coating. Its morphology was much more irregular and less columnar than that seen on the YbMS surface, as can be inferred from a comparison of Figs. 4 and 8. The reaction product was again interpenetrated by CMAS.

A bright field TEM image of the reaction interface between YbDS and CMAS is shown in Fig. 13. The chemical composition of the darker grains was determined by EDS, and is summarized in Table 3. The YbDS/CMAS reaction product had approximately the same composition as that of the YbMS/CMAS system (Table 3). The SAED patterns of the dark grains were indexed to the [021] and [210] zone axes of hexagonal oxyapatite with a nominal composition of Ca$_2$Yb$_8$(SiO$_4$)$_6$O$_2$.

An effective reaction layer thickness was calculated by image analysis, and is compared with the corresponding YbMS coating data in Fig. 6. The dependence of the equivalent apatite thickness upon exposure time for YbDS was similar to that of YbMS and could be fitted by a power law with an exponent of 0.27 (-1/4) for exposure times of less than 4 h and -1/2 thereafter. However, the net apatite thickness for the YbDS coating was slightly less than that of YbMS at the longer exposure times. EDS line scan analyses of samples subjected to different CMAS reaction times, Fig. 12(b), indicate that the CMAS melt above the reaction zone again contained approximately 7.5 mol% YbO$_{1.5}$. The average compositions of the CMAS melt located in pockets between the apatite grains, and in the CMAS reservoir well above the reaction zone were also measured by EDS, and are summarized in Table 4. As with the YbMS case, the Ca concentration in the CMAS melt decreased as the reaction time increased, but in the YbDS case it was accompanied by a noticeable increase in the Si concentration. The Yb content within the CMAS pockets between apatite crystals above the dense layer was again less than that in the CMAS reservoir. Note that the evolving MgO concentration in the melt was slightly lower for YbDS than YbMS, although the changes in both cases are relatively small compared to the variation in the AlO$_{1.5}$ content.

The morphology of the reaction product between CMAS and YbDS can be seen in the SEM images of samples subjected to CMAS exposures of 1 and 100 h, Fig. 14(a) and (b). The morphology was quite different to that formed on YbMS, Fig. 7. In the YbMS reaction case, a planar interface was formed between the growing columnar apatite and the YbMS layer. However, in the YbDS case, the apatite did not have a columnar

![Fig. 8](image-url)

**Fig. 8.** SEM images of cross sections normal to the ytterbium monosilicate/reaction product interface after reaction for 24 h (a, c), 100 h (b, e) and 250 h (c, f) at 1300 °C.
morphology, and nothing resembling a planar interface at the micro- or meso-grain scale could be identified. Instead, the apatite within the coating adopted an approximately equiaxed, blocky morphology (see left center of Fig. 14(b)), with the apatite crystals embedded in solidified CMAS. The reaction had intruded into the interior of the coating by reacting preferentially with the surface connected YbMS segregates. These intrusions then left peninsulas of less reacted YbDS between them. Prolonged exposure of the coating to molten CMAS, Fig. 14(b) resulted in the formation of a thin layer of reaction product on the coating surface. The ac-

The reaction with YbMS began rapidly, as seen in Fig. 4(a). A YbMS coating exposed to CMAS for as little as one minute resulted in the formation of a thin layer of reaction product on the coating surface. The accompanying Yb concentration data, Table 2, shows that the CMAS above this reaction product contained ~7.5 mol% YbO1.5 and this concentration did not increase significantly over time. The inference is that the Yb supersaturation in the CMAS melt needed to form apatite was developed in the time required to ramp up the temperature from that for the onset of CMAS melting (~1233 °C) to the prescribed hold temperature (1300 °C), ~7 min. Note that the dissolution of sufficient YbMS to saturate the melt would dilute the concentrations of all other oxides, including SiO2 since YbMS has a lower Si content than the original melt.

4. Discussion

The reactions between molten CMAS and APS deposited EBCs with either a YbMS or YbDS top coat have been investigated by interrupted isothermal testing at 1300 °C using a model CMAS that was fully molten above 1250 °C. No evidence of CMAS penetration along the grain boundaries was found in either of the ytterbium silicates investigated here; an observation at variance with similar experiments conducted upon the BSAS system [18]. The reaction between YbMS and CMAS was generally consistent with observations on the analogous yttrium monosilicate (YMS) system [12]. In essence, both reactions lead to the initially rapid dissolution of the monosilicate and the precipitation of apatite with a composition close to the nominal stoichiometry Ca2(RE)8(SiO4)6O2 (RE = Y or Yb). The microstructural features of the reaction front are remarkably similar in the two silicates, notwithstanding the difference in their initial morphology. This comprised a dense assemblage of equiaxed grains for the consolidated YMS [12] and a typical APS splat microstructure for the YbMS, Fig. 1(a) and (c), with a small (10–15%) volume fraction of Yb2O3 second phase and limited porosity.

The reaction with YbMS began rapidly, as seen in Fig. 4(a). A YbMS coating exposed to CMAS for as little as one minute resulted in the formation of a thin layer of reaction product on the coating surface. The accompanying Yb concentration data, Table 2, shows that the CMAS above this reaction product contained ~7.5 mol% YbO1.5 and this concentration did not increase significantly over time. The inference is that the Yb supersaturation in the CMAS melt needed to form apatite was developed in the time required to ramp up the temperature from that for the onset of CMAS melting (~1233 °C) to the prescribed hold temperature (1300 °C), ~7 min. Note that the dissolution of sufficient YbMS to saturate the melt would dilute the concentrations of all other oxides, including SiO2 since YbMS has a lower Si content than the original melt (Table 2).

It is evident from Fig. 4 that the overall thickness of the reaction layer increased with exposure time, with concomitant recession of the YbMS surface. Note, however, that the reaction layer was only dense at the interface with the YbMS, Fig. 8. The growing apatite crystallites, initially with an average (in-plane) width of ~400 nm, were interpenetrated by a network of thin amorphous films at the grain boundaries, Fig. 9(a), which enabled the transport of Ca and Si to the reaction front as schematically depicted in Fig. 15(a). The upper part of the reaction layer, however, was more substantially interpenetrated by CMAS, and some of the apatite grains appear weakly connected with the main reaction layer, analogous to observations of the reaction with YMS [12]. Compositional analysis of the CMAS pockets within the reaction layer revealed an YbO1.5 concentration of ~5.5 mol%; slightly lower than that of the bulk CMAS layer, but again essentially constant over time. Table 2. This lower concentration is consistent with the formation of additional apatite upon cooling, which locally depletes the Yb3+ concentration.
Table 2 also shows an initially rapid decline in the Ca concentration of the CMAS melt consistent with the growth kinetics of the Ca rich apatite reaction product. The initially faster loss of Ca was consistent with the time necessary to form a continuous apatite layer, and the shorter grain boundary diffusion distances through the nearly dense layer while it was relatively thin, Fig. 6. It is notable that while the Ca concentration in the CMAS melt declined with exposure time, the CMAS SiO₂ concentration decreased more slowly before rising rapidly after 250 h of exposure. These trends are the result of the net reaction between YbMS and the CMAS composition utilized here, which, omitting oxygen, can be written as:

\[
6\text{Ca}_{0.33}\text{Mg}_{0.67}\text{Al}_{0.09}\text{Si}_{0.45} + 4\text{Yb}_2\text{Si} \rightarrow \text{Ca}_2\text{Yb}_8\text{Si}_6 + 2\text{Mg}_{0.26}\text{Al}_{0.39}\text{Si}_{0.35}/C_{138} \left(1\right)
\]

where the term in brackets represents the oxides not involved in the reaction and therefore rejected back into the melt. The formation of a molecular unit of apatite required the provision of two Ca²⁺ ions and two (SiO₄)⁴⁻ anions from the melt, with the other four (SiO₄)⁴⁻ anions supplied by the YbMS. Because the Ca:Si ratio was < 1, one can readily show that the removal of an equal number of moles of CaO and SiO₂ from the melt would lead to a faster reduction of CaO concentration than that of SiO₂. While this is in qualitative agreement with the data of Table 2, it cannot account for the nearly constant SiO₂ concentration. One might further argue that because the total volume of melt is being reduced, some of the Yb³⁺ originally dissolved to saturate the melt would have to reprecipitate as apatite with the concomitant amounts of Ca and Si, but that would result in slightly larger changes in the CaO and SiO₂ concentrations. Moreover, the reaction of the ~15 vol.% Yb₂O₃ second phase to form apatite should have consumed Si at a relatively faster rate than Ca, as shown by the following reaction:

\[
13.33\text{Ca}_{0.33}\text{Mg}_{0.67}\text{Al}_{0.09}\text{Si}_{0.45} + 8\text{Yb}_2\text{Si} \rightarrow \text{Ca}_2\text{Yb}_8\text{Si}_6 + 5.33\text{Ca}_{0.45}\text{Mg}_{0.21}\text{Al}_{0.32}/C_{138} \left(2\right)
\]

This would produce an increase in the Ca content and a substantial decrease in SiO₂, again inconsistent with the nearly constant concentration of the latter observed in the CMAS over time. Moreover, reaction (1) also shows that the concentrations of Mg and Al should increase over time, which is in agreement with the trend for Al but not for Mg. One possible explanation for these trends is that the melt began to gain access to the mullite underlayer at locally thinner regions the YbMS top coat. The ensuing dissolution then contributes only SiO₂ and AlO₁.₅ to the melt, compensating for the consumption of SiO₂ to form apatite and raising the Al concentration. Indeed, after the longest time, the reaction was seen to have locally consumed the entire YbMS layer and CMAS had become in contact with the mullite and even the Si underlayers, Fig. 11(a), consistent with the noticeable increases in the SiO₂ and AlO₁.₅ between 100 h and 200 h, Table 2. In principle, CMAS might also reach the mullite layer via penetration through YbMS channel cracks. However, there was no visual evidence of significant penetration by this mechanism for these isothermal (non-cyclic) tests.

The thickness of the equivalent reaction layer (after subtracting the entrained glass phase) exhibited a power law time dependence with an exponent that evolved from ~1/4 during the early exposure to ~1/2 after longer exposure times, Fig. 6. This is consistent with the hypothesis that the overall volume of apatite was growing at a rate controlled by

![Fig. 11. SEM BSE mode images of (a) YbMS and (b) YbDS tri-layer samples exposed to CMAS for 250 h at 1300 °C showing eventual penetration of the coatings by CMAS. Note the large pores in (a) and anorthite (CaAl₂Si₂O₈) platelets precipitated in the CMAS melt in (b).](image-url)
The YbDS coatings were eventually breached locally by dissolution into the CMAS melt, as shown by comparing the Si content of the original CMAS and the residue, with an increase in the amount of residue added to the melt relative to reaction (1). The inference is that Ca\(^{2+}\) must still be diffusively transported to the reaction front through the glassy phase, but there is no need for drawing SiO\(_2\) from the melt to form apatite. Instead, the excess SiO\(_2\) released by the reaction could be used to feed the reaction with the YbMS second phase according to reaction (1), reducing the need for net exchange of SiO\(_2\) with the bulk melt. The Si contents listed in Table 4, however, are significantly higher than expected from the initial dissolution of YbDS to saturate the melt.

A salient finding of this work is that the CMAS reaction with YbDS progressed by a different mechanism than that between CMAS and YbMS, as schematically illustrated in Fig. 15(b). The molten CMAS preferentially reacted with regions containing a high fraction of YbMS segregates as noted in Fig. 1(b) and (d). This resulted in the deep intrusion of the reaction front into the topcoat and left the YbDS regions of the coating to react more slowly. The mechanism of reaction was influenced by the presence of YbMS as a second phase within YbDS, as well as by the as-deposited coating morphology.

Notwithstanding the differences in mechanism, the results in Fig. 6 suggest that the evolution of the reaction layer on YbDS follows a similar power law time dependence but with a slightly smaller rate constant than that of YbMS. The rationale is that the process is still controlled by diffusion through the glass network, but the increase in diffusional area is counteracted by the enrichment of SiO\(_2\) of the region between the growing apatite grains and the dissolving YbDS/YbMS coating.

The YbDS coatings were eventually breached locally by dissolution into CMAS after exposure at 1300 °C for 250 h, as were those for YbMS, Fig. 11(a). This occurred at locally thinner (~40–50 μm thick) regions of the YbDS coating whose thickness was sometimes similar to the equivalent reaction layer thickness after exposure for 250 h. Once penetration reached the mullite layer, the local enrichment in Al promoted the formation of anorthite (Ca\(_6\)Al\(_2\)Si\(_2\)O\(_{18}\)) platelets, Fig. 14(a). The dissolution rate apparently increased enabling the melt to reach the bond coat. Further attack is likely to involve oxidation of the Si bond coat by diffusion of oxygen through the local CMAS pool and its subsequent dissolution into the CMAS, with potential for eventually reaching the SiC substrate. The consequences of subsequent oxidation of the SiC are better represented in Fig. 11(a), where a large bubble resulted from the evolution of CO during the reaction.

5. Conclusions

It has been shown that molten CMAS poses a serious threat to the durability of EBC systems based on Yb silicates. Both YbMS and YbDS diffusion [28]. It therefore appears that both diffusion kinetics and apparently the progressive depletion of Ca from the CMAS contributed to the gradual slowing of the reaction with time.

The YbDS coatings also initially reacted rapidly with molten CMAS at 1300 °C to form apatite of very similar composition as that for YbMS, Table 3, albeit with a coarser morphology and without an evident dense layer at the interface, Fig. 14. Indeed, there was no well-defined near-planar reaction front formed on the YbDS coatings as seen for YbMS in Fig. 8. The reaction of CMAS with YbDS to form apatite reaction product can occur without any contribution of Si from the melt, as shown by the following reaction:

\[
6\text{Ca}_{0.33}\text{Mg}_{0.67}\text{Al}_{0.13}\text{Si}_{0.45} + 4\text{Yb}_2\text{Si}_2 \rightarrow \text{Ca}_2\text{Yb}_8\text{Si}_6 + 6[\text{Mg}_{0.05}\text{Al}_{0.13}\text{Si}_{6.78}].
\]

The reaction now involves a net release of SiO\(_2\) from the YbDS into the CMAS melt, as shown by comparing the Si content of the original CMAS and the residue, with an increase in the amount of residue added to the melt relative to reaction (1). The inference is that Ca\(^{2+}\) must still be diffusively transported to the reaction front through the glassy phase, but there is no need for drawing SiO\(_2\) from the melt to form apatite. Instead, the excess SiO\(_2\) released by the reaction could be used to feed the reaction with the YbMS second phase according to reaction (1), reducing the need for net exchange of SiO\(_2\) with the bulk melt. The Si contents listed in Table 4, however, are significantly higher than expected from the initial dissolution of YbDS to saturate the melt.

A salient finding of this work is that the CMAS reaction with YbDS progressed by a different mechanism to that between CMAS and YbMS, as schematically illustrated in Fig. 15(b). The molten CMAS preferentially reacted with regions containing a high fraction of YbMS segregates as noted in Fig. 1(b) and (d). This resulted in the deep intrusion of the reaction front into the topcoat and left the YbDS regions of the coating to react more slowly. The mechanism of reaction was influenced by the presence of YbMS as a second phase within YbDS, as well as by the as-deposited coating morphology.

Notwithstanding the differences in mechanism, the results in Fig. 6 suggest that the evolution of the reaction layer on YbDS follows a similar power law time dependence but with a slightly smaller rate constant than that of YbMS. The rationale is that the process is still controlled by diffusion through the glass network, but the increase in diffusional area is counteracted by the enrichment in SiO\(_2\) of the region between the growing apatite grains and the dissolving YbDS/YbMS coating.

The YbDS coatings were eventually breached locally by dissolution into CMAS after exposure at 1300 °C for 250 h, as were those for YbMS, Fig. 11(a). This occurred at locally thinner (~40–50 μm thick) regions of the YbDS coating whose thickness was sometimes similar to the equivalent reaction layer thickness after exposure for 250 h. Once penetration reached the mullite layer, the local enrichment in Al promoted the formation of anorthite (Ca\(_6\)Al\(_2\)Si\(_2\)O\(_{18}\)) platelets, Fig. 14(a). The dissolution rate apparently increased enabling the melt to reach the bond coat. Further attack is likely to involve oxidation of the Si bond coat by diffusion of oxygen through the local CMAS pool and its subsequent dissolution into the CMAS, with potential for eventually reaching the SiC substrate. The consequences of subsequent oxidation of the SiC are better represented in Fig. 11(a), where a large bubble resulted from the evolution of CO during the reaction.

5. Conclusions

It has been shown that molten CMAS poses a serious threat to the durability of EBC systems based on Yb silicates. Both YbMS and YbDS
were dissolved by molten CMAS and precipitated the same apatite phase. The overarching mechanism was dissolution of the silicate and reprecipitation as apatite, with some important differences in reaction morphology between YbMS and YbDS. The net thickness of reaction product followed a power law dependence on time for both coatings, with an exponent of $-1/4$ at shorter times that evolves toward $-1/2$ as the time increased. In both cases, the reaction was arguably controlled by diffusion of Ca and Si through the glass network interpenetrating the apatite product close to the dissolving silicate. However, the reaction front with YbMS involved a nearly dense layer of columnar apatite crystals with thin amorphous films at the grain boundaries, which is consistent with a rate controlled by diffusion through the grain boundaries of this dense layer. The change in power law exponent is attributed to coarsening of the apatite grains with an accompanying

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**Table 3**

The chemical compositions of the apatite for Yb monosilicate and disilicate coatings reacted with CMAS.

<table>
<thead>
<tr>
<th>Composition (mole%)</th>
<th>CaO</th>
<th>YbO$_{1.5}$</th>
<th>SiO$_2$</th>
<th>MgO</th>
<th>AlO$_{1.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YbMS apatite</td>
<td>12.5</td>
<td>47.9</td>
<td>37.7</td>
<td>1.9</td>
<td>0</td>
</tr>
<tr>
<td>YbDS apatite</td>
<td>12.4</td>
<td>47.0</td>
<td>38.5</td>
<td>2.1</td>
<td>0</td>
</tr>
</tbody>
</table>

---

**Table 4**

The compositions (mole%) of the CMAS melt near the reaction layer and bulk CMAS (columns in gray) for YbDS EBC system after different reaction times.

<table>
<thead>
<tr>
<th>CMAS</th>
<th>CaO</th>
<th>MgO</th>
<th>AlO$_{1.5}$</th>
<th>SiO$_2$</th>
<th>YbO$_{1.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>36.2</td>
<td>6.0</td>
<td>11.8</td>
<td>46.0</td>
<td>0</td>
</tr>
<tr>
<td>Saturated</td>
<td>30.8</td>
<td>5.1</td>
<td>10.0</td>
<td>46.6</td>
<td>7.5</td>
</tr>
<tr>
<td>1 min</td>
<td>29.3</td>
<td>28.4</td>
<td>6.2</td>
<td>8.9</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>27.4</td>
<td>26.9</td>
<td>5.5</td>
<td>10.7</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>25.5</td>
<td>25.2</td>
<td>5.4</td>
<td>11.7</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>24.6</td>
<td>24.2</td>
<td>5.5</td>
<td>13.3</td>
<td>11.5</td>
</tr>
<tr>
<td>100 h</td>
<td>24.6</td>
<td>24.2</td>
<td>5.5</td>
<td>11.4</td>
<td>51.5</td>
</tr>
<tr>
<td>200 h</td>
<td>24.4</td>
<td>23.8</td>
<td>5.6</td>
<td>11.0</td>
<td>51.8</td>
</tr>
</tbody>
</table>

---

**Fig. 13.** (a) Shows a bright field TEM image of the reaction product between YbDS and CMAS. TEM EDS analysis and the SAED patterns of the [021] (b) and [210] (c) zone axes from the reaction product particle are similar to the reaction product between YbMS and CMAS.

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**Fig. 14.** BSE images of the YbDS top coat after exposure to CMAS at 1300 °C for (a) 1 h and (b) 100 h. Note that the apatite phases first penetrated the coating in SiO depleted (lighter contrast YbMS rich) regions and became intermixed with unreacted YbDS particles in the coating.
The presence of Yb$_2$O$_3$ as a minor phase within the YbMS top coat appears to have less influence on the reaction process than the presence of YbMS dispersed within the YbDS layer. The latter seems to provide a preferential path for penetration of the CMAS through reaction with the YbMS, presumably because of the SiO$_2$ enriched glass around the dissolving YbDS grains. It is clear that in situations where the reaction rate is not controlled by the availability of silicate deposits, the reaction between CMAS and tri-layer EBC’s with nominally 100 μm thick YbMS or YbDS top coats is sufficiently aggressive at 1300 °C to seriously imperil the desired 5000 to 10,000 h operational life of SiC composite components.

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References


Fig. 15. Schematics of the envisaged reaction mechanisms between CMAS and (a) YbMS and (b) YbDS APS coatings.