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Molten silicate reactions with plasma sprayed ytterbium silicate coatings

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ARTICLE INFO

ABSTRACT

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 Yb_2SiO_5 (ytterbium monosilicate, YbMS) or $Yb_2Si_2O_7$ (ytterbium disilicate, YbDS) as the topcoat. The APS deposition process resulted in two-phase top coats; the YbMS coating contained Yb_2O_3 regions in a matrix of Yb_2SiO_5 while the YbDS coating contained Yb_2SiO_5 in a matrix of $Yb_2Si_2O_7$. 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 $Ca_2Yb_8(SiO_4)_6O_2$ 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 Y_2SiO_5, 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 $YbSiO_5$ rich regions, resulting in a reaction zone that contained CMAS, the apatite reaction compound and undissolved $Yb_2Si_2O_7$. 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 components 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 SiO_2 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, Al_2O_3, and SiO_2), 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 ($RE_2Si_2O_7$) are thermochemically compatible with the thermally grown SiO_2 that form on the Si bond coat, and have a CTE reasonably close to that of SiC, they have a substantially higher SiO_2 activity (and faster steam volatility) than their monosilicate counterparts (RE_2SiO_5) [3,8,9]. However, the monosilicates have a higher CTE than the substrate [10], and if allowed to contact the thermally grown SiO_2 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 SiO_2, 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 (Y_2SiO_5, YMS). Using fully dense powder coupons and a model CMAS ($33CaO-9MgO-13AlO_{1.5}-45SiO_2$) with an incipient melting point of 1233 °C [19], they observed rapid recession (~100 μm in 100 h at 1300 °C), in spite of the formation of a nearly dense $Ca_2Y_8(SiO_4)_6O_2$ 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 $Ca_2Yb_8(SiO_4)_6O_2$ apatite 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 (Yb_2SiO_5, YbMS) or ytterbium disilicate ($Yb_2Si_2O_7$, YbDS) top coats [10,20–22]. An interlayer of thermally sprayed mullite was added under the YbMS to prevent interactions with the SiO_2 that forms on the silicon bond coat surface. While YbDS is not expected to interact with SiO_2, 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 SiO_2 during APS deposition, resulting in YbMS coatings that containing Yb_2O_3 as a segregate phase, and YbDS coatings that contained Yb_2SiO_5 [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 methods, 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 EBC's 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 Yb_2SiO_5 and $Yb_2Si_2O_7$ 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 manufacturers 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 set up 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:H_2 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 $33CaO-9MgO-13AlO_{1.5}-45SiO_2$ (mole percent), or $C_{33}M_9A1_{13}S_{45}$) 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, Al_2O_3 and SiO_2 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