Slurry Based Coatings on Silicon Based Ceramics

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SLURRY BASED COATINGS ON SILICON BASED CERAMICS

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SLURRY COATING OF SILICON BASED CERAMICS

MURALIDHAR CHALLARAPU

ABSTRACT

Silicon carbide/silicon carbide (SiC/SiC) composites are the leading candidates for advanced high temperature structural components in gas turbine engine application. When SiC surface reacts with O₂, protective SiO₂ scales are formed, which are the basis for the corrosion resistance of SiC. Their main draw back in terms of usage in a gas-turbine engine is the volatilization of the protective silica scale because of the water vapor which is a byproduct of fuel combustion. The purpose of this project was to develop environmental barrier coatings (EBCs) based on ceramic powders to provide resistance to such moisture damage. In this thesis slurry-coating development has been pursued in terms of optimizing the preparation of powder-mixtures, the amount of polyvinyl butyral (PVB) to be added as a binder in the slurry, the degree of powder loading in the slurry, and coat sintering temperatures with different slurry compositions. The α-SiC ceramics were coated by the slurry dip process and sintered at different temperatures; the coated samples were examined under scanning electron microscope. Coated samples were thermally cycled in 96.5% H₂O vapor-balance O₂ flowing gas environment from 1300°C (or 1350°C) to room temperature (RT) for 100 to 300 cycles (1 cycle = 1 h hot temperature and 15 min. RT) to examine the coating stability.
Observations yielded the slurry containing 0.8gm of PVB and 40 gm of powder in 20gm of Ethanol, 0.12 gm of PE gave a good coating surface with no cracks. Presence of the boron oxide (B$_2$O$_3$) in the ceramic powder further reduced the sintering temperature by 15$^\circ$C. Under combustion environment, the mullite/Gd$_2$SiO$_5$ EBCs had a better protection up to 1350$^\circ$C for 100 h exposure. With further exposure to 300 h at 1350$^\circ$C, most of the coating was delaminated from substrate with strong surface cracks. In addition, the interfacial oxidation damage thickness increased with thermal cycling exposure times. At 1350$^\circ$C cycling temperature, the damage thicknesses were about 5 $\mu$m and 10 $\mu$m after 100 h and 300 h, respectively.
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CHAPTER I

INTRODUCTION

For the next generation gas turbine engines and hot structural components in combustion environments silicon based ceramics such as silicon carbide fiber reinforced silicon carbide composites(SiC/SiC) and monolithic $\text{Si}_3\text{N}_4$ ceramics are the ideal candidate materials due to their attractive physical and chemical properties, such as high thermal conductivity, high mechanical strength, maintaining mechanical properties at working temperatures, high thermal shock resistance and low density relative to the current Ni based super alloys[1-3]. Further improvement in the mechanical properties has been carried out by using additives, incorporating toughening mechanisms, and improving processing technologies. However, their high temperature gas-turbine application is still limited because of their very poor oxidation resistance in salt and water vapor containing environment.

In many fossil energy conversion and combustion system environments the applicability of SiC/SiC composites or silicon carbide ceramics (SiC) for the extended services is limited because these suffer from rapid surface recession in gas turbine
combustion environments due to the susceptibility of the silica scale volatilization [4, 5] and corrosion by alkali salts such as Na$_2$SO$_4$ [6-7] and steam at high temperatures. The silica scale which is responsible for high temperature oxidation resistance reacts with the water vapor which is a byproduct of the combustion reactions, and form gaseous silicon hydroxide species [4-6]. Carbon present in the SiC composites accentuates the damage because of the abundant formation of carbon monoxide gas bubbles.

In the presence of compounds like sodium sulphate, sodium carbonate and sodium chloride in condensed or vapor form the oxidation rates of these ceramics increase dramatically as these salts immediately dissolve silicon oxide to form low melting, low viscosity sodium-silicates [8]. Sodium acts as a net-work modifier breaking the corner sharing tetrahedral network structure of [SiO$_4$] and converting the bridging-oxygen ions to non-bridging ions; this reduces the viscosity of the oxide layer and makes it more prone to bubble formation and swelling [9]. Therefore, for the use of this silicon –based ceramics in gas turbine engine applications, development of an effective environmental barrier coating (EBC) is essential which can act as an external barrier to prevent water vapor from accessing the ceramic substrate.

1.1 Environmental Barrier Coatings:

The current state-of-the-art-EBC derive their water-vapor resistance from low silica activity glass-ceramic formulation based on mullite and BSAS (1-xBaO-xSrO-AL2O3-2SiO2, 0<=x<=1). These EBCs were developed for SiC/SiC composites under NASA High Speed Research-Enabling Propulsion Materials (NASA-EPM) program [10]. These EBC exhibited superb crack resistance due to reduced tensile
stress resulting from the low coefficient of thermal expansion (CTE) and low modulus of BSAS. Adding BSAS second phase in the mullite coating also significantly reduced the tensile stress, resulting in the far superior crack resistance compared to the unmodified mullite coating. The second generation EBCs consists of three layers: a silicon bond coat, a mullite or a mullite + BSAS intermediate coat, and a BSAS top coat.

These second generation EBCs have been scaled up and applied on SiC/SiC CMC combustor liners used in three solar Turbine (San Diego, CA) Centaur 50s gas Turbines engines under the DOE Ceramic Stationary Gas Turbines (CSGT) program [11, 12]. The combined operation of the three engines has resulted in the accumulation of over 24,000 h without failure (1250°C maximum combustor liner temperatures). An engine used by Texaco in Bakersfield, CA successfully completed a 14,000 h field test.

The higher operating temperature resulted in emission consistently below 15 ppmv nitrogen oxide and below 10 ppmv carbon monoxide throughout, roughly reducing the NO and CO loads on the environment by factors of about 2 and 5 respectively [4]. However, the second generation plasma-sprayed mullite layer EBCs provided adequate protection only up to about 1300°C. Their high temperature limitation arises from BSAS-silica chemical reaction and volatility of BSAS [10]. A projection based on a silica volatility model [6] in conjunction with BSAS volatility data from high steam low velocity environments indicates a BSAS recession of 70 microns after 1000 h at 1400°C, 6 atm pressure, and 24m/s gas velocity [10]. In reality gas turbines operate at significantly high pressures and gas velocities which increase the projected recession to much higher levels.
Research has been conducted for identifying a new top coat for replacement of current BSAS so as to overcome the higher temperature limitations arising from BSAS-silica chemical reaction and volatility of BSAS. The research is carried out to identify EBC with high temperature capability and chemical/mechanical compatibility with mullite or mullite+BSAS intermediate coat at higher operating temperatures [4]. Higher temperature EBC based on rare earth silicates (RE$_2$SiO$_5$ and RE$_2$Si$_2$O$_5$; RE = rare earth elements) were developed under NASA with the support of Ultra Efficient Engine Technology (UEET) program [4]. These third generation EBCs have low volatility in water vapor, high chemical stability and low thermal conductivity compared to the second generation BSAS-based EBCs.

1.2 Plasma Spraying Vs Slurry Based Dip Coating Processes:

EBC deposition is mainly carried out commercially by plasma spraying. There are three major limitations of the plasma spraying process.

(i) It is a line-of-sight process which is very difficult and time consuming for depositing coatings on complex shaped components, such as turbine vanes and blades.

(ii) The plasma spraying of EBC requires EBC to be sprayed into a high temperature furnace with the component placed inside the furnace to improve the phase stability of mullite, further limiting its process flexibility.

(iii) The plasma spraying of EBC degrades the fracture strength of ceramic components because it requires some sort of surface roughening (pitting) of the substrate in order to provide mechanical bonding of the coating to the substrate.
In this research it was decided to investigate slurry based coating for \(\alpha\)-SiC (Hexaloy) substrates. \(\alpha\)-SiC can be considered as the model material for SiC/SiC composites, a candidate material in gas turbine engine applications. This process has many potential advantages as compared with plasma-spraying. It is less expensive and it is a non-line of sight which can be easily used for coating complex shaped components. It gives flexibility in terms of being able to select the ceramic composition of the mixtures to be used for EBC. It is expected to achieve chemical bonding between the coating and the interface hence which is better than the simple mechanical bonding of the plasma spray coatings. Since surface roughening is not required it is also not expected to degrade the substrate fracture toughness. In addition, we expect to be able to incorporate nano-micro texture by a judicious use of slurry constituents and sintering conditions in order to improve fracture resistance of the slurry-based EBC.

1.3. Mullite/Gadolinium-silicate EBCs:

Mullite (3Al\(_2\)O\(_3\)-2SiO\(_2\)) is used as bond coat to provide adherence to \(\alpha\)-SiC substrate and also in more complex aluminosilicates as top coat in EBCs to provide insulation and protection from water vapor. Mullite was selected because of its low coefficient of thermal expansion (5-6 X 10\(^{-6}\) K\(^{-1}\), vs. 4-5 X 10\(^{-6}\) K\(^{-1}\) for SiC), and chemical stability with SiC. Mullite having a silica activity of 0.3-0.4 is fairly stable in molten salts, and thus it is expected to provide excellent protection from molten salt corrosion.

Gadolinium silicate (Gd\(_2\)SiO\(_5\)) was selected as an additive to the mullite because of its expected advantage in terms of enhancing the sintering kinetics and thus
allowing a denser coating to be obtained at lower temperatures or shorter sintering times. It also has a very good coefficient of thermal expansion match with mullite. A good dense coating for mullite alone is obtained only at nearly 1500°C where as with low quantities of Gd$_2$SiO$_5$ addition, a good deposition of dense coating is obtained after sintering at lower temperatures (1350°C). Addition of B$_2$O$_3$ is also expected to still lower the melting point phases, thus enhancing the sintering kinetics further. The mullite/Gd$_2$SiO$_5$ microstructure of our EBC coating has brick and mortar type structure, where the lower melting point constituent is expected to act as a mortar which bonds the mullite bricks together in a composite form and provides resistance to fracture and crack propagation.

1.4 Binder and Dispersant:

For good slurry based coating, a good control of slurry viscosity is very important. A high viscosity of the slurry is likely to cause surface cracks and thick uneven coating, and very low viscosity slurry may not give adequate coverage. Several factors determine the slurry viscosity, such as, concentration of binder used, ceramic powder particle size and its distribution, particle loading of the slurry, and the nature of particle dispersant. Fine ceramic particles have greater tendency to agglomerate in the slurry due to their larger specific surface area. A proper amount of dispersant gives well dispersed and stable slurries of fine particles. In an earlier investigation, polyvinyl butyrate (PVB) was used as the binder, 3 wt% of the solvent ethanol and phosphate ester (PE) a suitable dispersant material for metallic and ceramic powders [13].
1.5 Mechanical alloying:

Experiments conducted at Cleveland State University (CSU) by Dr R. Sivakumar and Dr. S. N. Tewari, revealed that high energy planetary impact milling of the starting ceramic powder materials yielded much finer particles with active surface. In addition, a molecular level mixing of starting materials was obtained after mechanical alloying process. This results in a considerable enhancement of particle sintering during high temperature annealing of the coating, as compared with that formed by using as blended powders. Planetary milling or Mechanical alloying for 30 minutes using zirconia vial and zirconia carbide balls was used for this purpose.

![Surface morphologies of the sintered samples using as-blended 88wt% mullite and 12wt% Gd$_2$SiO$_5$ powders.](image)

Figure 1. Surface morphologies of the sintered samples using as-blended 88wt% mullite and 12wt% Gd$_2$SiO$_5$ powders.
Figure 1 (a) and (b) show the SEM micro-structure of the sintered α-SiC coupons samples with the slurry prepared using the raw materials 88wt% mullite and 12wt% Gd$_2$SiO$_5$ after blending and sintered at 1350°C and 1400°C temperatures, respectively. From the figures, it is seen that there is no change in the surface morphology and the densification with increase in temperatures. Figure 2 (a) and (b) show the SEM micro-structure of coated α-SiC coupons with the slurry prepared using mechanically alloyed 88/12: mullite/ Gd$_2$SiO$_5$ powders after sintering at 1350°C and 1400°C. Comparing figures 1 and 2, it is revealed that the mechanically alloyed powders yielded a much denser coating as compared with as blended powders.
CHAPTER II

EXPERIMENTAL PROCEDURES

2.1. Powder Preparation:

As received ceramic powders: Mullite (d_{72}: 3 \mu m, Baikowski International Corporation, USA), gadolinium silicate (Gd_2SiO_5, d_{50}: 0.9 \mu m, Praxair Surface Technologies, USA) and boron oxide (B_2O_3, purity 99.9%, Alfa Products, MA) were blended to prepare the slurries. Following three formulations have been examined in this study:

(a) 16.4 gm mullite + 4.11 gm Gd_2SiO_5 + 1.08 B_2O_3,
(b) 18.05 gm mullite + 2.46 gm Gd_2SiO_5 + 1.08 B_2O_3
(c) 18.05 gm mullite + 2.46 gm Gd_2SiO_5.

The 16.4 gm mullite + 4.11 gm Gd_2SiO_5 + 1.08 B_2O_3 powder mixture was mechanically alloyed in a planetary mill to compare the sintering characteristics of its coating with that obtained with using as blended powder mixture. This material was also used to optimize the PVB content of the slurry. Higher mullite containing mechanically alloyed mixture, 18.05 gm mullite + 2.46 gm Gd_2SiO_5 + 1.08 B_2O_3, was used for optimizing the particle loading of the ceramic suspension to yield well coated samples having a thick coat. The
boron-oxide free slurry composition containing 18.05 gm mullite + 2.46 gm Gd₂SiO₅ was mainly used to determine the environmental barrier performance during thermal cycling of the coated samples in a moisture containing environment.

2.2 Slurry preparation:

Preliminary results[1] have indicate that polyvinyl butyral (PVB), phosphate ester, and ethyl alcohol as binder, dispersant and solvent, respectively, are effective for slurry dip coating process of mullite based ceramics. Following steps were followed to prepare the slurry:

Step 1: 0.12 gm of phosphate ester (PE) is weighed in a well cleaned beaker. 20 gm of ethanol is added into the beaker, while magnetically stirring. It takes about 1 hour to allow complete dissolution of PE in ethanol.

Step 2: Ceramic powder mixture in appropriate ratio is slowly added into the solution while mixing it thoroughly by placing a magnetic stirrer bar in the beaker and covering the beaker with a plastic paper to avoid ethanol loss. The ceramic powder containing slurry is stirred for 5 hours. This step allows dispersion of the ceramic particles with the help of PE in solution.

Step 3: PVB is slowly added in the well dispersed slurry; the mixture is stirred overnight before coating.

2.3 Coating process:

α – SiC (Hexoloy™, Saint Gobain Ceramics, Niagara Falls, NY) coupons (2.5 cm × 0.5 cm × 0.2 cm) were cleaned ultra sonically with acetone and ethanol and dried. A simple
coating set-up was indigenously developed, where the $\alpha$–SiC coupons were held and rotated at a constant speed during coating process. The coupons held at one end with a clip were dipped for 30 seconds in the slurry while being rotated clock-wise and then counter clock wise. Coupons were then raised out of the slurry while being rotated rapidly to drain the excess slurry off. The coated samples are vacuum dried for three hours before being coated again if required. The dried samples were placed in an alumina boat while being supported on alumina thermocouple sheaths placed in such a way that they do not touch each other and also they do not touch the edges of the boat. The boat was placed in a bottom lifted furnace and the samples are sintered at different temperatures. The samples were heated at the rate of $5^\circ$C/min up to $500^\circ$C, held for 180 minutes, and then further heated up to the sintering temperature at the rate of $10^\circ$C /min. The samples were sintered in air for three hours at temperatures varying from 1375 - 1450 $^\circ$C before being furnace cooled to room temperature at the rate of $10^\circ$C/min.

2.4 Thermal Cycling:

The performance of slurry based EBCs was assessed for EBC durability by exposing the EBC coated $\alpha$–SiC coupons to thermal cycling in simulated lean combustion environment using an automated thermal cycling furnace. Figure 3 shows the schematic of the automated thermal cycling furnace used in this study.
Thermal cycling between 1300°C (or 1350°C) and room temperature (RT) was carried out in 96.5% H₂O vapor-balance O₂ atmosphere with flowing water vapor introduced from the bottom at a rate of 2.1 ml/min and at 1 atmosphere total pressure. Each thermal cycle consisted of heating the samples kept in a platinum-wire basket for 1 h in the hot zone followed by a rapid translation of the sample into the cold zone (room temperature) at the bottom. After a 15 minute stay at room temperature the samples were rapidly pulled back into the hot-zone of the furnace.
2.5 Characterization:

After dip coating process, the surface morphologies of the coatings before and after air sintering were examined by optical microscope. An approximately 0.5 cm long piece was cut for micro structural analysis from the as sintered or thermally cycled samples. The rest of the pre-cycled sample after cutting was exposed to additional cycles. The cut pieces of cycled samples were mounted in epoxy resin and polished using the polishing grades such as 240 microns grit diamond paper, 30 microns grit diamond paper, 9 microns grit diamond paper, 3 microns grit diamond paper and finally 0.5 microns grit alumina suspension on a micro cloth. The polished cross-sections of the coated coupons were examined by optical and scanning electron microscopes. For comparison, as coated and sintered sample cross-sections were also examined by optical and SEM.
CHAPTER III

RESULTS AND DISCUSSION

3.1. Optimization of Binder (PVB) Content in the slurry:

Figure 4 shows the effect of PVB variation on the surface morphology of as coated samples. These samples used powder mixture of 16.4 gm mullite + 4.11 gm Gd$_2$SiO$_5$ + 1.08 gm B$_2$O$_3$ and varying PVB content in the slurry. Figure (a) corresponds to 0.0 gm PVB, figure (b) to 0.4 gm PVB, figure (c) to 0.8 gm PVB and figure (d) to 1.2 gm PVB in a slurry containing the above 20 gm ceramic powder, 20 gm alcohol and 1.2 gm PE. The 0.8 g and 1.2 g PVB containing samples appear to yield the best sample coverage.
Figure 4: Optical images of the four α-SiC samples after coating and before Sintering with variation in PVB content, (a) 0g, (b) 0.4g, (c) 0.8g, (d) 1.2g
Figure 5. Optical images of the four $\alpha$-SiC samples after sintering at 1300 °C with variation in PVB content, (a) 0g, (b) 0.4g, (c) 0.8g, (d) 1.2g

The coated samples were sintered at 1300°C for 5 hours in air and the as sintered surface morphologies of these samples are shown in Figure 5. The 0 g and 0.4 g PVB slurries appear to form pitted and non-uniform coating. Only coated samples with 0.8 g PVB and 1.2 g PVB show good un-pitted sintered surface. The cross section of the coated samples observed by SEM is shown in figure 6.
Figure 6. Cross-sectional SEM views of the coating thickness with varying PVB content (a) 0g, (b) 0.4g, (c) 0.8g, (d) 1.2g.

From the figures, the coated samples with 0.8 gm PVB and 1.2 gm PVB appeared to have good coating adherence to the substrate. The coating seems to be uniform all along the surface with fewer cracks. No evidence of bubble formation at the substrate-coating interface was observed. The coating that contains 0 gm PVB and 0.4 gm PVB content did not show adequate coating coverage. The thickness of the coating increased with PVB content due to the increase in the viscosity of slurry, as shown in Figure 7.
The coated samples with 0.8 gm and 1.2 gm of PVB had a thick coating of 32 µm and 39.3 µm respectively.

Figure 7. Variation in coating thickness as a function of increasing PVB content.

3.2 Optimization of Powder Content in the Slurry:

Figure 8 shows the effect of powder loading on the surface morphology of as coated samples. In a slurry containing 0.8 gm of PVB, 20 gm alcohol and 1.2 gm PE, the powder loading was systematically varied in order to find out the optimum particle loading that provides good coverage without cracking. The coatings were all sintered for three hours in air at 1350°C+1400°C+1450°C. These powder mixtures of 18.05 gm mullite + 2.46 gm Gd₂SiO₅ + 1.08 B₂O₃ was mechanically alloyed for 30 minutes.
Figure 8(a) corresponds to 20 gm powder, figure 8(b) to 25 gm powder, Figure 8(c) to 30 gm powder, figure 8(d) to 35 gm powder and figure 8(e) corresponds to 40 gm of powder in slurry.
Figure 8. Surface morphology of as coated and sintered up to 1450°C in air with varying particle loading in the slurry: (a) 20 gm, (b) 25 gm, (c) 30 gm, (d) 35 gm, and (e) 40 gm powder in 20 gm solvent.

The 20 and 25 gm powder loading did not provide adequate coverage, and the surface appeared to show bubbles after sintering at 1450°C (Figures 8-a, b). The bubbles are due to the formation of silicon hydroxide gas which makes it difficult to escape through the glassy viscous coating layer. The bubble formation is more evident in a cross-sectional transverse SEM view of the coating-substrate interface as shown in Figure 9.
When the solid to liquid ratio was increased, the coating had a better coverage. For instance, coating with the 35 gm powder and 40 gm powder loadings yielded good adhesion and showed sintered surface with no bubbling and cracks as shown in Figures 8-d,e. Figure 10 shows the SEM cross section of sintered coating with 40gm powder in slurry. From the figure, it can be seen that the coating is adhering well to the substrate after air sintering up to 1450°C for 3 h.
Figure 10. SEM cross-sectional view of α-SiC coated with slurry containing 40 gm powder and sintered up to 1450°C in air for 3h.

The coating is about 100 μm thick and well-bonded to the α-SiC substrate. The variation in the coating thickness as a function of increasing powder loading is shown in Figure 11. From the SEM micro structures (figure 8-10) and coating thickness results 35gm or 40 gm powder loading appears to give the best combination of coating build-up and coating quality.

Figure 11. Variation in coating thickness as a function of increasing powder loading.
Figure 12 shows a high magnification view of the sintered coating. It consists of the mullite particles (bricks), indicated by 2 in the picture, imbedded in a silicate rich phase (mortar) indicated by 1 in the picture. Such a brick and mortar microstructure of the coating is expected to provide good resistance against propagation of cracks in the coating. The EDAX analysis showed the white regions containing nano particles of some other phase to be rich in Gd indicating that this region is gadolinium silicate.

![Figure 12. Coating microstructure of the 40 gm powder loaded sample after sintering in air at 1450°C for 3h.](image)

3.3. Influence of B₂O₃ addition on sintering kinetics:

3.3.1. Mullite-Gadolinium Silicate Coating:

For these experiments mechanically alloyed powder mixture of 18.05 gm mullite + 2.46 gm Gd₂SiO₅ and slurry consisting of 40 gm of powder mixture, 20 gm
ethyl alcohol, 1.2 gm PE and 0.8 gm of PVB was used to coat on α-SiC coupons. The coated samples were air sintered at temperatures varying from 1375°C to 1450°C to examine the maximum safe temperature without causing any bubble formation at the coat-substrate interface. Figure 13 shows the effect of sintering temperatures on the surface morphology of these samples. Figure 13(a) corresponds to the sample which is coated and sintered at 1430°C for 3h in air. Figure 13(b) corresponds to the same sample with additional three-hour sintering at 1450°C.

![Figure 13](image)

(a)  
(b)  

Figure 13: Mullite-Gadolinium Silicate coated α-SiC sample surface after (a) 1430°C and (b) 1450°C sintering in air.

The 1430°C sample shows good crack-free coating. As the sintering temperature was increased by 20°C the sample tended to form “fish-scale” kind of surface cracks. The cross-sectional SEM view of the coating-substrate interface showed a tendency to form small aligned pores, as shown in Figure 14 below. This observation
suggests that the maximum safe sintering temperature for the mullite-gadolinium slurry is 1430°C.

Figure 14. SEM view of the α-SiC-Coating interface for mullite-gadolinium silicate coating after 1450°C sintering in air

3.3.2. Mullite-Gadolinium Silicate-Boron Oxide Coating:

For these experiments mechanically alloyed powder mixture of 18.05 gm mullite + 2.46 gm Gd2SiO5 + 1.08 B2O3 and slurry consisting of 40 gm of powder mixture, 20 gm ethyl alcohol, 0.12 gm PE and 0.8 gm of PVB was used to coat on α-SiC coupons. The coated samples were air sintered at temperatures varying from 1375°C to 1450°C to examine the maximum safe temperature without causing any bubble formation at the coat-substrate interface. The α-SiC sample was repeatedly (three times) coated and sintered for 3h at 1400°C (Figure 15(a)). Figure 15(b) corresponds to the same sample further sintered for three hours at 1415°C, and Figure 15(c) is the surface appearance after further additional three hour treatment at 1430°C.
Figure 15. Surface appearance of a mullite-gadolinium silicate-boron oxide coated $\alpha$-SiC sample after (a) 1400$^\circ$C, (b) 1415$^\circ$C, and (c) 1430$^\circ$C sintering in air.

The 1400$^\circ$C and 1415$^\circ$C treatments yield good coating coverage without any surface cracks. The 1430$^\circ$C treatment shows some hairline cracks forming on the coating surface.

Results of the cross-sectional SEM views of the coating-substrate interface for these three samples are shown in Figure 16; 16(a) corresponds to 1400$^\circ$C, 16(b) to 1415$^\circ$C, and 16(c) to 1430$^\circ$C. As expected, the coating becomes more and denser as the
sintering temperature is increased. However, this densification is also combined with increasing tendency for the coating to develop hairline cracks. These cracks became more frequent for the 1430°C sintering. Therefore, it has been decided that the maximum safe sintering temperature for the boron-oxide containing mullite-gadolinium silicate slurry will be 1415°C.

Figure 16. SEM images of the SiC-Coating interface for mullite-gadolinium silicate-boron oxide coating after (a) 1400°C (b) 1415°C (c) 1430°C sintering in air.
3.4 Thermal Cycling Effect:

For these experiments mechanically alloyed powder mixture of 18.05 gm mullite + 2.46 gm Gd$_2$SiO$_5$ and slurry consisting of 40 gm of powder mixture, 20 gm ethyl alcohol, 1.2 gm PE and 0.8 gm of PVB was used to coat on four $\alpha$-SiC coupons. The $\alpha$-SiC samples were repeatedly (three times) coated and air sintered for 3h at 1430°C. The as sintered samples are then thermal cycled in combustion environment at varying thermal cycling temperatures (1300°C and 1350°C). Two samples were thermal cycled at 1300°C one for 100 cycles and the other for 300 cycles. The other two samples were thermal cycled at 1350°C one for 100 cycles and the other for 300 cycles.

The optical images of the as thermal cycled samples in are shown in Figure 17; 17(a) and (b) corresponds to the optical images of the thermal cycled samples between 1300°C and room temperature (RT) for 100h and 300h exposure, respectively. Similarly, Figures 17(c) and (d) corresponds to the optical images of thermal cycled samples between 1350°C and RT for 100h and 300h exposure.
Figure 17: Optical images of the α-SiC coated samples sintered up to 1430°C and thermal cycled at (a) 1300°C for 100 cycles. (b) 1300°C for 300 cycles. (c) 1350°C for 100 cycles. (d) 1350°C for 300 cycles, respectively.

As shown in the Figure 17, the samples thermal cycled at 1300°C (figure 17(a) and (b)), yielded a good coating adherence to substrate with limited bubbles on the chamfered regions compared to that of the sample with high thermal cycling temperature (1350°C). After 100h exposure of 1350°C cycling, the coating appeared to be adhering to substrate. Formation of the bubbles is due to the Si(OH)$_4$ gas formation at the coating-substrate interface. In contrast, the coated samples after 300 thermal cycles showed coating delamination from the substrate with strong surface cracks.
Figure 18: low magnification SEM cross-sections of the coated $\alpha$-SiC samples sintered up to 1430°C and thermal cycled at (a) 1300°C for 100 cycles. (b) 1300°C for 300 cycles. (c) 1350°C for 100 cycles. (d) 1350°C for 300 cycles.

Figure 18 shows the SEM cross-sectional views of the thermal cycled $\alpha$-SiC coated samples. 18(a) corresponds to thermal cycling temperature of 1300°C for 100 cycles, 18(b) to 1300°C for 300 cycles, 18(c) to 1350°C for 100 cycles and 18(d) 1350°C for 300 cycles. When the samples were thermal cycled between 1300°C and room temperature for 100 h and 300 h in combustion environment, there was no increase in oxidation
damage thickness (5 μm). However, a 300 h exposure at 1300°C yielded a partial coating delamination as shown in figure 18(b).

From the figures 18(a) and (c), it is seen that the coating showed excellent adherence to the substrate after 100 h exposure at 1300°C and 1350°C. Also, the oxidation damages formed at coating-substrate interface had almost similar thickness of about 5 μm when exposed to 100 h of 1300°C and 1350°C, respectively. In contrast, the coated samples after 300 h exposure at 1300°C and 1350°C (Figs. 18(b) and (d)) had severe damages with strong surface cracks and coating delamination from the substrate. The oxidation damage thickness was increased to 10 μm when cycled at 1350°C for 300 h (Fig. 18(d)). This increase in oxidation damage thickness might be due to higher oxygen diffusion rate across the coating at elevated temperatures.
CHAPTER IV
CONCLUSION

From the results and discussion, the following conclusions can be drawn:

1. EBC Optimization:

Mullite/Gd$_2$SiO$_5$ EBCs had an excellent adherence to $\alpha$-SiC substrate when sintered in air up to 1430°C.

(a) The optimized slurry used in this work that produced a successful dense EBC with best coating coverage contained 20 g ethanol (solvent), 0.8 g PVB (binder) and 0.12 g PE (dispersant) along with a solid:liquid ratio as 2:1. The mullite and Gd$_2$SiO$_5$ powders were planetary milled to 30 mins in order to have molecular level uniform mixing.

(b) Addition of 5 wt% B$_2$O$_3$, a sintering aid added to mullite and Gd$_2$SiO$_5$ powders further reduced the sintering temperature from 1430°C to 1415°C without bubble formation on the surface.
2. Thermal Cycling:

The durability of mullite/Gd$_2$SiO$_5$ EBCs were performed by thermal cycling in simulated combustion environment (96.5% H$_2$O vapor- 3.5% O$_2$ atmosphere) at 1300°C and 1350°C for 100 and 300 h exposures.

(a) Mullite/Gd$_2$SiO$_5$ EBCs had a better protection from environmental (water-vapor) attack up to 1350°C for 100 h with excellent coating adherence to substrate.

(b) When exposed to 300 h, partial coating delamination from the substrate was observed even at a thermal cycling temperature of 1300°C. At higher cycling temperature of 1350°C after 300 h exposure, most of the coating was delaminated from substrate with strong surface cracks.

(c) The interfacial oxidation damage thickness was about 5 µm when thermal cycled at 1300°C for 100 and 300 h exposure. A similar thickness of 5 µm was observed when cycled at a higher temperature of 1350°C for 100 h. When increased to 300 h exposure at 1350°C cycling, the damage thickness increased twice (10 µm). This thickness increase can be explained due to higher oxygen diffusion across the coating.
CHAPTER V

SUMMARY

SiC/SiC composites are the ideal candidate materials for the next generation gas turbine engines and hot structural components in combustion environments. Due to their poor oxidation resistance in salt and water vapor containing environments, development of effective EBC is very critical. The current state-of-the-art mullite/BSAS EBCs protected the substrate in combustion environment up to a temperature of 1300°C. Earlier studies report that mullite-rare earth based EBCs deposited by plasma spraying process had higher temperature capability than the current state-of-the-art mullite/BSAS based EBCs (4). Due to the various limitations in plasma spraying process, in our study, slurry based mullite/Gd₂SiO₅ EBCs were developed for α-SiC ceramics which is considered as the model material of SiC/SiC composites.

The slurry compositions were optimized to obtain a dense EBC with uniform coverage to the substrate. Mullite/Gd₂SiO₅ EBCs chemically adhered well to α-SiC substrate without bubble formation when sintered in air up to 1430°C for 3 h. Under the combustion environment (96.5% H₂O vapor- 3.5% O₂ atmosphere), our mullite/Gd₂SiO₅ EBCs were still adherent to the α-SiC substrate well up to 1350°C for 100 h with minimal interfacial
oxidation damage (5 µm). A further increase in exposure time to 300 h led to coating delamination with an oxidation damage thickness of about 10 µm at the coating-substrate interface.

Therefore, from the results, it can be summarized that mullite/Gd₂SiO₅ EBCs are capable to protect SiC/SiC composite substrates in combustion environment up to 1350°C.
CHAPTER VI

PROPOSED FUTURE RESEARCH

1. In the present study, slurry based mullite/gadolinium silicate (Gd$_2$SiO$_5$) EBCs were developed and the durability of these EBCs were performed up to 1350°C exposed to 300 h. As a proposed research work, slurry based mullite/rare-earth silicate EBCs with various rare-earths such as lutetium silicate, hafnium silicate and ytterbium silicate on α-SiC substrates can be developed and their long term performance can be evaluated in terms of adherence.

2. In the presently developed mullite/ Gd$_2$SiO$_5$ EBCs, thermal cycling experiments can be performed at lower cycling temperatures of 1250°C or 1200°C with an increased exposure time.
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