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Abstract

Environmental barrier coatings (EBCs) play a critical role in mitigating the degradation of SiC/SiC ceramic matrix composites (CMCs) in complex combustion environment, and improve the service life of thermal engine components. In this paper, by adjusting the parameters of atmospheric plasma spraying (APS), the spraying process of ytterbium disilicate (Yb$_2$Si$_2$O$_7$) under a lower power has been optimized. A two-layer EBC system consisting of ytterbium disilicate and silicon is prepared on the SiC/SiC composite substrate by using optimized technological parameters. The thermal resistance and water oxygen corrosion resistance of such two-layer EBC system are investigated. The results indicate that the current ytterbium disilicate/silicon EBC system exhibits good phase stability, excellent water vapor and oxygen corrosion resistance. However, the exposed silicon bonding layer tends to generate an excessive thermal growth oxide (TGO) layer known as SiO$_2$, leading to an early spallation of the coating.

Keywords  
Environmental Barrier Coating, Air Plasma Spraying, Ytterbium Disilicate, SiC/SiC Composites

1. Introduction

The improvement of thrust-to-weight ratio of advanced aero-engines is highly dependent on the development and application of advanced materials. To improve the thrust-to-weight ratio, gas turbine's inlet temperature has to be increased, which severely challenges hot-section components. Thanks to thermal
barrier coatings and sophisticated cooling technology, nickel-based superalloys can tackle current temperature challenges, but are not capable of satisfying future development of continuous increase of service temperature. Instead, silicon carbide fiber reinforced silicon carbide ceramic matrix composites (SiC/SiC-CMCs) are proposed as an ideal material for engine components such as regulating piece, seal, heat insulation screen and turbine blades etc. due to their high melting point, low density, good thermo-mechanical properties and anti-oxidation properties [1] [2] [3]. However, while considering the high temperature combustion environments with high humidity, the dense film of SiO₂ on the surface of SiC/SiC composites tends to react with water vapor to form volatile products, leading to the rapid degradation of SiC₇/SiC composites [4] [5]. Therefore, it is necessary to deposit environmental barrier coatings (EBCs) on the surface of SiC/SiC composite components to physically isolate components from the complex engine environment and ultimately extend the service life of the CMC components [6] [7].

NASA [8] [9] is leading the research on EBCs, and the research in China has made great progress in these years. It can be divided into four stages for EBC systems. Currently, researchers mainly focus on rare earth silicate systems [10] and move towards material systems of multi-layered thermal barrier coupled with environmental barrier [11]. The main preparation methods of EBCs include air plasma spraying [12] (APS), electron beam physical vapor deposition [13] (EB-PVD), plasma spraying physical vapor deposition [14] (PS-PVD), ultra-low pressure plasma spraying [15] (VLPPS), etc. APS technology has been widely used as the preparation of EBCs because of its simple operation, high efficiency and low cost. But in the process of spraying, there are inevitably unmelt powder existed in rare earth silicate coatings. Hence, it is difficult to form a coating with very high density [16]. Meanwhile, high spraying power leads to the volatilization of Si causing the deviation of coating composition. Further, the slight oxidation occurs on silicon bond coat during the spraying process [17].

In this paper, an Yb₂Si₂O₇/Si EBC prepared by APS is investigated. After optimization of APS parameters, the microstructure, phase composition, thermal stability and water vapor corrosion resistance of this EBCs system were characterized.

2. Experiment

2.1. Sample Preparation

The SiC/SiC substrates were prepared by a hybrid route combining chemical vapor infiltration (CVI) and precursor infiltration and pyrolysis (PIP) techniques. The substrates were polished, cleaned and dried before APS, without sandblasting treatment. The raw materials of Yb₂Si₂O₇ powders were commercially available (Beijing Sandspray New Material Co., Ltd.). To ensure the fluidity of the powder, the powders were subjected to a spray pelletization process. The silicon powders with particle size between 50 - 70 μm were purchased from

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Metco with a brand of 4810. A low-power APS with different current level was used to prepare $Yb_2Si_2O_7$ topcoat while Si bond coat was employed by another set of parameters. All parameters are listed in Table 1.

### 2.2. Characterization

Thermal treatment in air as well as in water vapor and oxygen corrosion of the bi-layer EBCs are investigated. The thermal treatments were under 1300˚C, 1400˚C, and 1500˚C respectively for 10 hours; the water vapor and oxygen corrosion test was carried out at 1300˚C in an alumina tube furnace, where the volume ratio of oxygen to water vapor was kept as 1:1. The test was carried out in a cycle of 20 h, and samples were taken out every 2 cycles for characterization.

Scanning electron microscope (SEM, MIRA3, Tescan, China) was used to observe the surface and cross-section morphology of the coatings. Energy dispersive spectrometer (EDS, x-max20, Oxford Instrument, UK) was used to measure element distribution. The image analysis software (ImagJ) was used to perform the threshold segmentation of the images. The specific method was to partition the samples and select 5 images evenly, where the resolution of the images and the width of the field of view were consistent. XRD (D8-advance, Bruker, 0.02˚/step, Cu-Kα, 10˚ - 90˚) analysis was carried out to investigate the phase composition of the coating under various treatments.

### 3. Result and Discussion

#### 3.1. Optimization of Spraying Parameters

Figure 1 shows the SEM images of cross-section morphology of $Yb_2Si_2O_7$ coatings prepared by three different parameters of low power. The topcoat is dense

![Figure 1](image)

Figure 1. Cross-sectional morphologies of $Yb_2Si_2O_7$ topcoats. (a) parameter 2; (b) parameter 3; (c) parameter 4.

<table>
<thead>
<tr>
<th>Material</th>
<th>Current (A)</th>
<th>Ar (slm)</th>
<th>H$_2$ (slm)</th>
<th>Power (KW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter 1</td>
<td>Si</td>
<td>500</td>
<td>70</td>
<td>1</td>
</tr>
<tr>
<td>Parameter 2</td>
<td>$Yb_2Si_2O_7$</td>
<td>300</td>
<td>45</td>
<td>2</td>
</tr>
<tr>
<td>Parameter 3</td>
<td>$Yb_2Si_2O_7$</td>
<td>350</td>
<td>45</td>
<td>2</td>
</tr>
<tr>
<td>Parameter 4</td>
<td>$Yb_2Si_2O_7$</td>
<td>400</td>
<td>45</td>
<td>2</td>
</tr>
</tbody>
</table>
on the whole with a morphology of multi-layer stacking, and the defects in the
topcoat are mainly spherical pores and interlayer cracks. The average porosity
measured by image method are 11.5%, 8.1% and 10.0%, respectively. The change
of grayscale of the photo is mainly caused by the loss of Si. The more Si loss is,
the higher the brightness of the area will be. It is difficult to characterize the ex-
act Si loss and the corresponding phase composition of the image. But it can be
observed in Figure 1 that the brightness region of the coating increases with the
increase of power.

In the Parameter 4, interlayer cracks and mud cracks obviously increased, and
the reason can be summed up in the increasing of Yb₃SiO₅ or even Yb₂O₃. As the
high melt point of the two phases (Yb₃SiO₅ for 1950°C, Yb₂O₃ for 2415°C), the
molten particles in the spraying process are not able to make the previous layer
melt, leading to an obvious interlayer interface. When the particles are rapidly
cooling in the substrate, lamella contraction occurs with the release of the ther-
mal stress, which results in the growth of micro cracks. Comparing to the
cross-section morphologies of parameter 2 and parameter 3, the areas of pores,
cracks and unmelt particle areas are greatly reduced, although there are still
some remained.

Figure 2(a) shows the XRD patterns of the topcoats prepared by different
three parameters at 1300°C. And the XRD patterns of the raw powder, the
as-sprayed topcoats and the topcoats after annealing are shown in Figure 2(b).
After thermal treatment at 1300°C, the coatings in three parameters transform
into a highly crystalline state, and the main phase composition is Yb₃Si₂O₇ and
Yb₂SiO₅. The phase content does not change significantly with the change of pa-
rameters. The other XRD pattern indicates that the as- sprayed coatings are
amorphous, and the phase composition of raw powder and the annealed topcoat
are nearly the same. These two patterns all suggest that the phase change in the
spraying process is slight due to the selection of low power parameters.

Based on the calculation results of porosity, cross-section morphologies and
phase evolutions, it can be concluded that parameter 3 is an optimal spraying
parameter for APS and the low power is necessary to keep the original phase
composition. Then thermal treatment and water oxygen corrosions will be performed using optimized parameter 3.

3.2. Thermal Stability

XRD patterns of Yb$_2$Si$_2$O$_7$ topcoats with parameter 3 after thermal treatment at 1300˚C - 1500˚C are shown in Figure 3(a), which is corresponding to the surface morphologies in Figures 3(b)-(d) separately. The XRD patterns show that with the increasing of annealing temperature, the phase composition is stable, consisting of Yb$_2$Si$_2$O$_7$ and little Yb$_2$SiO$_5$, and the intensity of Yb$_2$SiO$_5$ phase is reduced. There is no evidence that any reaction was taken in the isolate thermal treatment in air [18]. According to the microstructure, it can be inferred that the rapid grain growing may bring some influence on the XRD detecting. The surface morphologies show that the surface layers are not in dense stacks, and there are pores remained and microcracks occurred due to the thermal stress.

3.3. Water Vapor and Oxidation Resistance

The overall structure is shown in Figure 4(a) and Figure 4(b). The system is clearly divided into three layers which are well bonded. There are no obvious cracks or declination. For as-sprayed Yb$_2$Si$_2$O$_7$ topcoat, the morphology of cross-section is quite different from the corroded sample for 120 h, which changes from layered rough state to dense smooth state after corrosion. Meanwhile, the phase distribution changed from unobvious to obvious dark and bright two-phase distribution. The topcoat along with the bond coat provides oxidation resistance for SiC$_x$/SiC composites, and there is slight oxidation due to the diffusion of oxygen. As the Figure 4(c) and Figure 4(d) shown, the interface between Yb$_2$Si$_2$O$_7$ topcoats and Si bond coat combines well as sprayed, and forms a SiO$_2$
Figure 4. Cross-sectional SEM photos of EBC (a) as-sprayed; (b) corrosion for 160 h; Interfaces between Yb$_2$Si$_2$O$_7$ topcoat and Si bond coat (c) as-sprayed; (d) corrosion for 160 h at 1300˚C.

Figure 5. Surface of Yb$_2$Si$_2$O$_7$ topcoats (a) annealed in 1300˚C; (b), (c) different areas corroded for 160 h.

layer called thermal growth oxide (TGO) after corrosion for 160 h. The TGO is a critical cause for the decline of EBC system, due to its special phase transition and volume change at 220˚C. When the Si or SiC is exposed to the corrosion environment, the excessive formation of TGO will face great stress and rapid volatilization resulting in the failure of the EBC system [19].

Figure 5 shows the microstructure on the surface of Yb$_2$Si$_2$O$_7$ topcoats. After corrosion for 160 h, the grain boundary is corroded, but in other areas, the topcoat was protected by a new, dense material. According to the EDS analysis, the new material is rich of Al, which is mentioned to have the reactions as following:

\[
3\text{Yb}_2\text{Si}_2\text{O}_7(\text{s}) + 10\text{Al(OH)}_3(\text{g}) \rightarrow 2\text{Yb}_3\text{Al}_2\text{O}_12(\text{s}) + 6\text{Si(OH)}_4(\text{g}) + 3\text{H}_2\text{O}(\text{g})
\]

The product has even better resistance compared to other rare earth silicates [20].

Though, it is difficult to avoid the spraying defects in the EBC, which weakens the mechanical properties of the coatings. The effects of EBC systems for protecting SiC/SiC composites from oxidation and corrosion are proved to be indeed excellent.

4. Conclusions

The APS parameters are optimized in the low power level. The bi-layer EBC prepared by the optimized process underwent a thermal treatment as well as a water vapor and oxygen corrosion at 1300˚C. The results can be summarized as following:
1) Low power in APS is needed for less phase change taking place in the process. And parameter 3 is convinced to be the better one due to its fewer pores and better morphology.

2) Oxidation is mainly taken place between the Yb$_2$Si$_2$O$_7$ topcoats and Si bond coat. Corrosion occurs on the surface of Yb$_2$Si$_2$O$_7$ topcoats, and Yb$_3$Al$_5$O$_{12}$ makes a contribution to the oxidation resistance. The bi-layer Yb$_2$Si$_2$O$_7$/Si EBC system is eventually convinced to be an excellent choice for future gas engine components.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References


