Degradation of EB-PVD thermal barrier coatings caused by CMAS deposits

Hui Peng, Lu Wang, Lei Guo, Wenhui Miao, Hongbo Guo, Shengkai Gong

School of Materials Science and Engineering, Beihang University, No.37, Xueyuan Road, Beijing 100191, China
AVIC Shenyang Liming Aero-engine Group Corporation Ltd., Shenyang 110043, China

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Failure mechanism

Abstract
In aero-turbine engines, thermal barrier coatings (TBCs) must be capable to withstand harsh environments, such as high-temperature oxidation and hot-corrosion. Recently, a new failure mode of TBCs caused by calcium–magnesium–alumina–silicate (CMAS) glass has attracted increasing attention. In this paper, yttria stabilized zirconia (YSZ) TBCs produced by electron beam physical vapor deposition (EB-PVD) were exposed to CMAS deposits at 1250°C. The microstructure evolution and failure mechanism of the coatings were investigated. It has been shown that CMAS glass penetrated into the YSZ ceramic layer along the inter-columnar gaps and interacted with YSZ. As a result, an interaction zone of about 20 μm thickness, which was the mixture of CMAS and YSZ with equiaxial structure, was formed in the YSZ surface layer after 4 h heat-treatment at 1250°C. Meanwhile, yttria in YSZ layer as a stabilizer was dissolved in CMAS glass and caused accelerated monoclinic phase transformation. After 8 h heat-treatment, degradation of YSZ TBC occurred by delamination cracking of YSZ layer, which is quite different from the traditional failure caused by interfacial cracking at the YSZ/metallic bond coat. Physical models have been built to describe the failure mechanism of EB-PVD TBCs attacked by CMAS deposits.

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1. Introduction

Thermal barrier coatings (TBCs) are commonly employed to protect the critical hot section components of gas turbine turbines, aiming to reduce the temperature of the underlying superalloy substrate and thereby leading to longer service life [1–3]. A TBC system is usually comprised of two parts: a ceramic top coat for thermal insulation (typical 7–8 wt% yttria stabilized zirconia, YSZ), and a bond coat (diffusion aluminde or overlay MCrAlY,
M: Ni, Co or Ni+Co) for reducing the thermal expansion mismatch between the top coat and the substrate as well as providing excellent oxidation and corrosion resistance. During the high temperature exposure, an adherent thermally grown oxide (TGO) scale is formed on the bond coat surface [4,5]. To obtain better performance, TBCs used in the ultra harsh environments are often fabricated by electron beam-physical vapor deposition (EB-PVD) technique, which yields a strain-tolerant columnar grain structure [6,7].

The most common failure mechanism for both EB-PVD and APS TBCs is the detachment of the coating from the surface due to the oxidation of the metallic substrate [8–11]. However, increasing turbine inlet temperature has engendered new failure mode, this being chemical decomposition because of the adhesion of sand/ash particles on hot TBCs surfaces, where the deposits turn into a molten calcium–magnesium–alumina–silicate (CMAS) glass [12,13]. The melting point of CMAS varies with its composition, at temperature lower than the melting point, these particles simply bounce off or cause erosive damage [14]. However, the melted CMAS can penetrate the TBCs by capillarity action due to the morphology and microstructure of the TBCs [15,16]. Especially EB-PVD TBCs which exhibit columnar structure are susceptible to attack by CMAS glassy deposits. Columnar structure is important as it tolerates stresses developed due to thermal expansion mismatch, however after the infiltration of molten CMAS, strain tolerance capability is deteriorated and the structure no longer can reduce stresses [17,18].

Recently, interactions between CMAS and YSZ TBCs and related failure mechanisms have been investigated. The studies on 7YSZ TBCs exposed to CMAS showed that coating become sufficiently depleted in yttria allowing tetragonal to monoclinic transformation and results in floating of zirconia in the CMAS melt [13,14]. The thermochemical aspects of the degradation phenomena were investigated by Krämer et al. [13]. It was explained that TBC degradation may be attributed to the fact that CMAS can easily wet the TBC and original 7YSZ dissolves in the CMAS and re-precipitates with a different morphology and composition. It was found that the speed at which CMAS attacks the TBC is very fast [13,14,19]. Mercer et al. [20] inspected a used turbine airfoil removed from service and proposed a cold shock delamination mechanism. A critical infiltration thickness above which the adhesion of sand/ash particles on hot TBCs surfaces, where the deposits turn into a molten calcium–magnesium–alumina–silicate (CMAS) glass [12,13]. The melting point of CMAS varies with its composition, at temperature lower than the melting point, these particles simply bounce off or cause erosive damage [14]. However, the melted CMAS can penetrate the TBCs by capillarity action due to the morphology and microstructure of the TBCs [15,16]. Especially EB-PVD TBCs which exhibit columnar structure are susceptible to attack by CMAS glassy deposits. Columnar structure is important as it tolerates stresses developed due to thermal expansion mismatch, however after the infiltration of molten CMAS, strain tolerance capability is deteriorated and the structure no longer can reduce stresses [17,18].

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Actually, EB-PVD TBCs are more susceptible to CMAS attack because of the columnar structure, and therefore has attracted many attentions. So far, most of the attentions have been paid to investigate the degradation of TBCs on the actual turbine blades after service [13,20,21,23]. However, the failure mechanism of TBCs caused by CMAS attack is not clear yet. In this work, the microstructural evolution of the YSZ TBC under the simulated CMAS condition and thermochemical interactions between YSZ and CMAS deposits are investigated, in order to clarify failure mechanism of TBC caused by CMAS.

3. Results

Fig. 1a shows the top view of as-deposited YSZ coating in absence of CMAS at low and high (inset) magnifications. The columnar structure, a typical and characteristic feature of EB-PVD coatings, was clearly visible. The coating surface was covered by four-sided square columns whose tips exhibited a pyramidal appearance. Additionally, inter-columnar gaps were observed, which could improve the lateral strain compliance of the coating. The cross-sectional view of YSZ coating with CMAS deposits is shown in Fig. 1b. The CMAS...
layer with a thickness of about 10 μm exhibited loose and porous structure. The adherence between CMAS and YSZ layers was poor, a large gap with a wideness of about 8 μm has been observed.

Fig. 1 shows the cross-sectional SEM image of the YSZ TBCs with CMAS deposits after heat treatment at 1250 °C for 4 h. Large gap between CMAS layer and YSZ layer as presented in Fig. 1b disappeared as CMAS has penetrated into the open structure of the coating, forming a distinct interaction zone. From the closer examination of the columnar tips (inset in Fig. 2a), a series of globular particles embedded in CMAS glass can be found. The globular particles were identified as re-precipitated zirconia by EDS. The cross-sectional SEM image of control sample after heat treatment at 1250 °C for 4 h is shown in Fig. 2b. Compared with the sample with CMAS deposits, the columns and columnar tips of control sample remained intact, and only a little bit of sintering has been found. This suggests that CMAS has a detrimental effect on the durability of YSZ TBCs.

The cross-section of YSZ TBCs attacked by CMAS at 1250 °C for 4 h can be divided into four sub-regions based on the degree of the influence of CMAS on the coating, as shown in Fig. 3. The chemical compositions of the areas marked in Fig. 3 are listed in Table 1. In sub-region A, residual CMAS glass adhered tightly to the coating. Compared with original CMAS, less Mg and more Si were detected. It should be noted that Y and Zr were found in sub-region A. Fig. 3 shows that the CMAS/TBCs interaction zone with a thickness of about 23.6 μm was evident. In the upper interaction zone (sub-region B), CMAS degradation to the coating was so severe that all column tips lost their identity. In the lower interaction zone (sub-region C), coating experienced less severe attack by CMAS, and the columnar structure was faintly visible. EPMA detection was carried out at point 1 and 2 in interaction zone, and the results revealed the presence of Ca, Mg, Al and Si indicative of CMAS and Zr. It should be noted that no Y was detected, implying that the Y content was very small, which is consistent with the observation that Y migrated out into the molten CMAS glass in the region A. In region D, the number of globular particles resulting from CMAS degradation decreased dramatically. Deeper into the coating it was found that the columnar structure became more and more clear. It was found that Zr was detected as the predominant element, Ca, Mg, Al and Si contents decreased significantly, and a certain amount of Y could be detected. EPMA analysis indicates that the Y: (Y+Zr) ratio at point 5 is 3.5 mol%, essentially the same as the original 7YSZ.

Regions B and C were found to be significantly depleted in Y, Raman spectra was therefore used to figure out the phase constitution of the areas marked in Fig. 3, and the results are shown in Fig. 4. The characteristic signal of monoclinic around 180 cm⁻¹ and 340 cm⁻¹ appeared at the points of a, b and c mixed with residual tetragonal, but not at points d and e. This indicates that t-phase YSZ was transformed to m-phase due to CMAS degradation in the upper interaction zone (region B).

Fig. 5 shows the surface morphologies of YSZ TBCs with CMAS deposits heat-treated at 1250 °C for 8 h. Reticular vertical cracks with a wideness of about 200 μm were observed.
on the surface of the sample. Wrinkles can be found in Fig. 5a, the size of which is 3–5 crack grids. Spallation and delamination of the coating were evident in Fig. 5b. Micro-chemical characterization was carried out by EDS on the surface of coating, as well as in the spallation and delamination regions, as summarized in Table 2. EDS analysis revealed that the Y: Zr ratio in the surface region of coating was about 1:50 (position A and B), much lower than the original 7YSZ. It was found from EDS analysis that CMAS has penetrated into the delamination region (position C). In region D, large amount of Al was detected, the Zr content decreased sharply, suggesting that the ceramic coating has spalled off in this region. Also, Si, Ca and Mg were detected, indicating that CMAS has penetrated into the bottom of the ceramic coating, which was mainly responsible for the premature failure of the coating.

Fig. 6 shows the cross-sectional SEM image of YSZ TBCs with CMAS deposits heat-treated at 1250 °C for 8 h. Partial spallation of coating was observed, but the TGO was still adhered to the ceramic coating. A large number of vertical cracks existed in the ceramic coating, and transverse cracks were also found. When the cracks propagated to the edge of the vertical cracks, delamination and spallation of the coating would occur, and additionally, the bulking failure was observed. It has been found that the edge of the buckled region was still intact, but a large amount of CMAS glass has been found in the buckled region. Residual CMAS deposit was also found on the surface of buckled area.

![Fig. 3](image-url)

**Fig. 3** Cross-sectional view of YSZ TBCs attacked by CMAS at 1250 °C for 4 h, revealing the CMAS penetrated zone. The image has four sub-regions.

![Fig. 4](image-url)

**Fig. 4** Raman spectra obtained from the positions marked in Fig. 3.

![Fig. 5](image-url)

**Fig. 5** Surface morphologies of YSZ TBCs with CMAS deposits heat-treated at 1250 °C for 8 h.

<table>
<thead>
<tr>
<th>Constituent/at%</th>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Y</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original CMAS</td>
<td>22</td>
<td>19</td>
<td>14</td>
<td>45</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Glassy deposition</td>
<td>21.14</td>
<td>5.12</td>
<td>14.46</td>
<td>56.07</td>
<td>1.46</td>
<td>1.75</td>
</tr>
<tr>
<td>1 (10 μm)</td>
<td>2.80</td>
<td>5.53</td>
<td>8.25</td>
<td>40.35</td>
<td>–</td>
<td>25.07</td>
</tr>
<tr>
<td>2 (20 μm)</td>
<td>10.94</td>
<td>2.84</td>
<td>5.80</td>
<td>20.59</td>
<td>–</td>
<td>59.83</td>
</tr>
<tr>
<td>3 (30 μm)</td>
<td>8.57</td>
<td>2.10</td>
<td>5.12</td>
<td>17.42</td>
<td>1.52</td>
<td>65.27</td>
</tr>
<tr>
<td>4 (40 μm)</td>
<td>5.52</td>
<td>2.02</td>
<td>3.30</td>
<td>11.69</td>
<td>2.71</td>
<td>74.76</td>
</tr>
<tr>
<td>5 (50 μm)</td>
<td>3.38</td>
<td>–</td>
<td>2.13</td>
<td>6.08</td>
<td>3.10</td>
<td>85.31</td>
</tr>
</tbody>
</table>

**Table 1** Chemical compositions (excluding the element of O) of the CMAS glassy deposition and positions 1–5 in Fig. 3.
4. Mechanics governing CMAS degradation to EB-PVD TBCs

4.1. CMAS/YSZ TBCs interaction and YSZ phase transformation

From a mechanical point of view, infiltration of CMAS reduces the strain tolerance of the YSZ layer, due to the blocking of inter-columnar gaps. It was reported that CMAS deposits have significant effects on the microstructure and thermal properties of plasma sprayed YSZ coatings [22,24]. Because the EB-PVD coatings are too thin to remove them from the substrates, it is difficult to measure thermal properties of free standing EB-PVD YSZ coatings after CMAS attack. However, different microstructures were observed in four sub-regions as presented in Fig. 3, implying different thermal properties. This would cause thermal expansion mismatch during thermal cycling, and the considerable internal stress would accumulate in the coatings, resulting in the local delamination and spallation.

EMPA evaluation of cross-section of YSZ TBCs with CMAS deposits after 4 h heat treatment at 1250 °C showed that yttria was dissolved in to CMAS glass, as shown in Fig. 3 and Table 1. It was reported that the stabilizers in the zirconia would go to the glassy melt when the CMAS dissolves and accumulates in the coatings [21,25,26]. When the stabilizer concentration is high enough, crystalline phase would be formed, resulting in CMAS arrest. However, the stabilizer concentration in YSZ is not high enough to cause glass crystallization. Instead, the original metastable tetragonal zirconia would dissolve and tetragonal zirconia would form due to the Y depletion at high temperatures. Upon cooling, phase transformation would occur, which has detrimental effect on the TBCs life. The detection of m-ZrO2 in the upper interaction zone by Raman spectra supports the statement of phase transformation, as shown in Fig. 4. After 8 h heat treatment at 1250 °C, only a small proportion of CMAS glass can be found on the surface of TBCs, as shown in Fig. 6. The result of EDS detection showed that the Y content on the surface was much lower than that of original 7YSZ. Moreover, wrinkles, delamination and spallation of 7YSZ TBCs have been observed, as shown in Fig. 7. In general, CMAS glass absorbed the stabilizer (yttria) present in original YSZ resulting in Y depletion, followed by phase transformation upon cooling, which would lead to the failure of 7YSZ TBCs. This mechanism is believed to be active in the present case.

4.2. Vertical cracks in TBCs

Although the columnar microstructure of EB-PVD TBCs provides high strain tolerance, the columnar grain boundaries are also the path for CMAS infiltration. Additionally, sintering of TBCs occurs during heat treatment and tensile stress generates in the TBCs, which result in vertical cracks, as shown in Fig. 7a and b. It is believed that the vertical cracks may be beneficial to thermal cycling performance of the coatings by reducing the strain energy in the coatings [27,28]. However, vertical cracks also provide convenience for CMAS infiltration, which would accelerate the exfoliation of coatings. Line scanning EDS, as shown in Fig. 7a shows a

<table>
<thead>
<tr>
<th>Constituent/at%</th>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Y</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy deposition</td>
<td>17.62</td>
<td>6.31</td>
<td>14.28</td>
<td>57.12</td>
<td>2.21</td>
<td>2.46</td>
</tr>
<tr>
<td>A</td>
<td>6.28</td>
<td>6.34</td>
<td>5.47</td>
<td>23.16</td>
<td>1.12</td>
<td>57.63</td>
</tr>
<tr>
<td>B</td>
<td>7.85</td>
<td>3.43</td>
<td>7.68</td>
<td>12.63</td>
<td>1.38</td>
<td>67.03</td>
</tr>
<tr>
<td>C</td>
<td>4.81</td>
<td>1.96</td>
<td>5.42</td>
<td>7.43</td>
<td>5.41</td>
<td>74.98</td>
</tr>
<tr>
<td>D</td>
<td>10.14</td>
<td>16.88</td>
<td>43.13</td>
<td>23.29</td>
<td>–</td>
<td>6.56</td>
</tr>
</tbody>
</table>

Fig. 6 Cross-sectional SEM image of YSZ TBCs with CMAS deposits heat-treated at 1250 °C for 8 h.

Fig. 7 Cross-sectional SEM micrographs of YSZ TBCs that has interacted with CMAS deposits, showing apparent vertical cracks. Samples were heat-treated at 1250 °C for 4 h (a) and 8 h (b).
sharp increase on the Ca, Mg, Al and Si contents across the vertical crack, implying the vertical crack was filled with CMAS glassy deposits. Small spherical particles found at the bottom of YSZ layer or even at the TGO/YSZ interface indicated that the regions near the vertical crack were subject to much severe CMAS attack, as shown in Fig. 7a and b. Additionally, it can be observed from Fig. 7b that when transverse cracks in the coating propagated to the edge of vertical cracks, wrinkle or spallation within the scope of several crack grids would occur.

In general, the mechanics governing CMAS degradation to EB-PVD TBCs can be concluded as follows. On one hand, the infiltration of CMAS altered the microstructure of YSZ layer and interaction zone formed, the thermal properties of interaction zone were different from those of undamaged YSZ layer. This would cause thermal expansion mismatch between interaction zone and undamaged YSZ layer during thermal cycling, resulting in delamination in YSZ layer. On the other hand, phase transformation occurred since yttria existed in original YSZ was absorbed by CMAS glass, which would cause cracks in YSZ layer, leading to delamination. Additionally, the existence of vertical cracks in YSZ layer due to the sintering accelerates the CMAS corrosion of TBCs.

5. Physical models of failure mechanism for EB-PVD YSZ TBCs attacked by CMAS deposits

As we know, traditional failure of YSZ TBCs are usually caused by interfacial cracking at the YSZ-metallic bond coat, while delamination was found in YSZ layer in the present study, as shown in Figs. 5b, 6 and 7b. On the basis of the discussion earlier physical models may be built to describe the failure mechanism of EB-PVD TBCs attacked by CMAS deposits, as shown in Fig. 8. Fig. 8a shows the schematic of failure mechanism from a mechanical point of view, i.e., the TBCs system can be divided into three layers of CMAS-YSZ interaction zone, undamaged YSZ layer and bond coat. After exposure at high temperature, stress due to thermal expansion mismatch generated in TBCs upon cooling. The biaxial stress is given as [29]:

\[ \sigma = \frac{E_0 \Delta \alpha \Delta T}{(1 - \nu)} \]  

(1)

where \( \Delta \alpha = \alpha_{\text{interaction zone}} - \alpha_{\text{undamaged YSZ}} \) is the mismatch of thermal expansion coefficient between interaction zone and undamaged YSZ, \( E_0 \) is elastic modulus, \( \nu \) is Poisson ratio, \( \Delta T \) is the difference between stress free state and measurement state temperature. And the corresponding plane strain is:

\[ \varepsilon = \frac{\Delta \alpha \Delta T}{a} \]  

(2)

The elastic stored energy \( (J = \pi \varepsilon V/2) \) for a unit area of variety layers can be approximated as [30]:

\[ J \approx \frac{E_0 \varepsilon (\Delta \alpha)^2 (\Delta T)^2}{(1 - \nu)} \]  

(3)

where, “V” represents the thickness of variety layers.

As discussed earlier, the microstructure and thermal properties of CMAS-YSZ interaction zone were different from those of undamaged YSZ layer. According to Eq. (3), elastic stored energy \( J \) would be produced in CMAS-YSZ interaction zone upon cooling. When \( J \) is higher than the energy required to create a new surface formed by delamination process, delamination will occur in YSZ layer, as shown in Fig. 8a. Delamination can be noticed in Figs. 5b, 6 and 7b. Therefore, minimizing \( J \) is necessary to improve the lifetime of TBCs. According to Eq. (3), minimizing \( J \) can be achieved by reducing the thickness of CMAS-YSZ interaction zone. Actually, many efforts have been made to alleviate CMAS infiltration and hence reduce the thickness of interaction zone, however, no satisfactory results have been achieved up till now.

Another possible mechanism of CMAS attack in the present study was phase transformation, which is illustrated schematically in Fig. 8b. \( \text{ZrO}_2 \) phase transformation from tetragonal to monoclinic phase is martensitic transformation, very quick and uncontrolled [31,32]. This phase transformation is accompanied with 3–5% volume expansion, and thus generates stress in ceramic coating. When the stress was large enough, micro-cracks generated, as depicted in Fig. 8b. As discussed above, the regions near the surface and vertical cracks were subject to much severe CMAS corrosion, and therefore more phase transformation occurred in these regions, which would lead to micro-cracks. Micro-cracks due to phase transformation have been found in Figs. 6 and 7b. The propagation of these micro-cracks would disrupt the YSZ structure and deteriorate the integrity of TBCs.

6. Conclusions

CMAS glass was found to penetrate into the YSZ layer along the inter-columnar gaps and interacted with YSZ, leading to accelerated degradation of EB-PVD YSZ TBCs. After 4 h heat-treatment at 1250 °C, an interaction zone of about 20 μm
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thick was found in the YSZ surface layer. The interaction zone was the mixture of CMAS and YSZ with equiaxed structure, and it was sufficiently depleted in yttria. After 8 h heat-treatment, degradation of YSZ TBC occurred by delamination cracking of YSZ layer, due to the thermal expansion mismatch between interaction zone and undamaged YSZ layer and phase transformation, which is quite different from the traditional failure caused by interfacial cracking at the YSZ/metallic bond coat. Physical models have been built to elaborate the failure mechanism of EB-PVD TBCs attacked by CMAS deposits.

Acknowledgments

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