CMAS damage in thermal barrier coatings: an exploration via single crystal bulk YSZ specimen

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Abstract
More recently a new type of damage has been pronounced in thermal barrier coatings (TBCs) by calcium-magnesium-alumino-silicates (CMAS) from ingestion of siliceous minerals under certain operating conditions. In order to understand material aspect of CMAS damage, a study on material interaction between molten CMAS and yttria-stabilized zirconia (YSZ) was carried out by using a single crystal YSZ material and a synthetic CMAS product in this work. Here the effect of crystallographic orientation on the interaction was also investigated. The CMAS-covered single crystal bulk YSZ specimens were isothermally exposed at high temperature. The experimental works clearly showed that interaction between the molten CMAS and YSZ was significant resulting in the change in microstructural morphology and composition of YSZ. The extent of interaction between CMAS and YSZ depended on the crystallographic plane of the YSZ: it was the lowest in the {111} crystallographic plane.

Key words: Calcium-magnesium-alumino-silicates, Thermal barrier coatings, Single crystal yttria-stabilized zirconia, Interaction, Crystallographic plane

1. Introduction

Thermal barrier coatings (TBCs) have been widely used to protect the hot-section metallic components of gas turbine engines such as combustor liners and turbine blades from high temperatures (Goward, 1998, Miller, 1984, Okazaki, 2003, Seth, 2000). The TBCs commonly comprise of a ceramic top coat, a bond coat and a metallic substrate (Padture et al., 2002). The ceramic top coat which provides heat insulation, typically yttria-stabilized zirconia (YSZ), is deposited onto the bond coat by employing plasma splaying or electron-beam physical vapor deposition (EB-PVD) process (Goward, 1998). Since the use of TBCs has allowed higher engine operating temperatures exceeding 1200°C at the surface of the TBC top coat, it can improve thermal efficiency of the engines (Seth, 2000). Recently, at these high temperatures the TBCs can be attacked by calcium-magnesium-alumino-silicates (CMAS) resulting from the ingestion of siliceous minerals with the intake air and from unclean fuels such as syngas and biomass gas (Borom et al., 1996, Levi et al., 2012, Naraparaju et al., 2014, Vidal-Setif et al., 2012, Wright and Gibbons, 2007). The CMAS can melt and infiltrate into pores of the splayed top coat resulting in a decrease of strain tolerance and higher thermal conductivity of the top coat (Mercer et al., 2005, Kakuda et al., 2015). The molten CMAS can also interact with the top coat material leading to the morphological changes and phase transformation of the top coat and evolution of voids within the top coat (Hayashi et al., 2015, Krämer et al., 2006). However, fundamental or intrinsic mechanism of the material interaction between CMAS and YSZ has not yet been clearly understood. As one of question, nobody cannot deny such a hypothesis that materials contaminations and pores associated with thermal spraying process for TBCs can be a major source of the CMAS damage.

In this work, a clean single crystal YSZ material (dense bulk YSZ material without any pores) was used to investigate the interaction between CMAS and YSZ in the absence of contaminations and pores. The effect of
crystallographic plane on the interaction was also studied, in order to explore some possible mitigation strategies.

2. Experimental procedure

2.1 Preparation of model CMAS

A model CMAS powder was prepared in order to simulate the CMAS damage. The chemical composition of the model CMAS used is shown in Table 1. This composition is similar to that of deposits observed on the surfaces of actual blades (Borom et al., 1996). The model CMAS was prepared through the following process; the constituent oxides were mixed and the mixture was melted in an alumina crucible at 1550°C for 30 min in an electric furnace, after which the melt was quenched in Air before pulverization, as shown in Fig. 1 (Aygun et al., 2007). Onset of melting of the CMAS powder was experimentally measured by ~1210°C by a differential thermal analysis (DTA) (Hayashi et al., 2015).

<table>
<thead>
<tr>
<th>Table 1 Chemical composition of model CMAS.</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
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<tr>
<td>Mol.%</td>
</tr>
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</table>

Fig. 1 SEM image of synthetic CMAS crashed powder.

2.2 Preparation of single crystal YSZ specimen

The single crystal (SC) cubic-YSZ specimen comprised of 9.9mol% Y₂O₃-stabilized ZrO₂ was used in this study. Three kinds of the YSZ plate specimens with dimensions of about 4 x 4 x 1 mm were prepared as shown in Fig. 2, so that one of specimen surface is facing on {100}, {110} and {111} plane, respectively. After cutting, the specimen surface was mechanically polished with SiC papers.

Fig. 2 Geometry and crystallographic orientation of single crystal YSZ specimen, and extraction of three specimens with a different crystallographic plane.

2.3 Experimental work on CMAS damage

The interaction between CMAS and YSZ was investigated through high temperature exposure of the SC YSZ
specimens by directly contacting with the model CMAS, where the model CMAS mixture was uniformly spread on the surface of the YSZ specimens (~0.8mg/mm²): Fig. 3. The CMAS-covered specimens were isothermally exposed at 1250°C for 5h, 20h and 100h using an electric furnace in air, followed by cooling to room temperature. In this work, the cooling rate was an experimental variable: it was 6°C/min (furnace cooling) and ~2500°C/min (forced air cooling). The specimens after exposure were embedded in epoxy and then polished using SiC and diamond papers in order to observe the cross section. The changes in microstructure were characterized using a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS).

3. Results and discussion

3.1 Interaction between SC YSZ and CMAS

Figures 4(a)-(c) show the cross-sectional micrographs of the CMAS-affected SC YSZ specimens where the CMAS was mounted on {111} crystallographic plane for 5h, 20h and 100h at 1250°C with furnace cooling, respectively. It is found that the change in microstructure of the YSZ was significant near the CMAS/YSZ interface and the thickness of the CMAS-affected area increased with increasing exposure time. This region is referred as “interaction zone” in this work. Figure 4(e) presents the high magnification image of the interaction zone squared in Fig. 4(c). The corresponding transverse cross-sectional micrographs along the dotted lines in Fig. 3(c) are given in Figs. 4(f) and (g), respectively. The interaction zone can be classified into two layers: those are an upper region where fine particles about a few...
microns aggregate (Fig. 4(f)) and a bottom region that has a cellular structure perpendicular to the YSZ interface (Fig. 4(g)), respectively. Furthermore, the comparison of the cross-sectional micrographs of the specimens with different cooling rates (Figs. 4(c) and (d)) shows no difference in the microstructural morphology and thickness of the interaction zone, indicating that the interaction zone was formed during the high temperature duration period rather than the cooling.

Figure 5 and Table 2 present the elemental analysis around the interaction zone on the CMAS-affected specimen (exposed at 1250°C for 100h with furnace cooling). It is found that Y content was significantly reduced in the upper and lower parts of the interaction zone (Table 2). Some amount of Ca and trace of Al and Mg was penetrated into their parts. The CMAS elements (Ca, Mg, Al and Si) were detected at dark gray areas, or points d and e in the interaction zone in Fig. 5, indicating that the interaction zone was completely filled with CMAS. Zr and Y are identified in the CMAS phase around the interaction zone (Table 2). These reveal that the morphological and compositional changes are an essence of CMAS damage resulting from the interaction between CMAS and YSZ from a material aspect. Note again the material tested here is a bulk YSZ. In other words, the CMAS damage can appear not only in a porous ceramic top coat by spraying method (Borom et al., 1996, Vidal-Setif et al., 2012, Krämer et al., 2006) but in a clean dense bulk YSZ even without any pores.

The morphology of the cellular structure in the interaction zone seems to be similar to that of the solidification of a molten metal at liquid/solid interface observed by Totten et al. (Totten et al., 2004). In this work, the cellular structure appears to be growing within CMAS phase toward the bulk-YSZ (Fig. 4(a)-(c)). Additionally, the CMAS phase includes large amounts of Zr and Y (Table 2). These facts suggest that the YSZ dissolved into the CMAS and then the dissolved ZrO\(_2\) reprecipitated again in the molten CMAS phase. This process leads to the growth of the reprecipitated ZrO\(_2\) toward the bulk-YSZ, resulting in the formation of the cellular structure (Fig. 4(c) and (e)). Krämer et al. also proposed that the dissolution and reprecipitation of ZrO\(_2\) occurred during interaction between YSZ and CMAS (Krämer et al., 2006). It can be considered that the reduction of Y and the incorporation of Ca occurred along with the dissolution and reprecipitation (Table 2). Belykh et al. indicated that the reaction between a silicate glass including CaO and an YSZ causes the substitution of Ca\(^{2+}\) ion for Y\(^{3+}\) in the YSZ (Belykh et al., 2003).

Fig. 5 Example of regions analyzed by using EDS. (a) bulk-YSZ, (b) cellular structure, (c) fine particles, (d) interface between cellular structure and bulk-YSZ, (e) interface between fine particles and cellular structure, and (f) CMAS phase on the fine particles, in the CMAS-affected YSZ \{111\} plane specimen at 1250°C for 100h with furnace cooling (6°C/min).

Table 2 Chemical composition at each region shown in Fig. 5 (wt.%).

<table>
<thead>
<tr>
<th>Region Description</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Y</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Bulk-YSZ</td>
<td>25.2</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>15.7</td>
<td>58.6</td>
</tr>
<tr>
<td>b. Cellular structure</td>
<td>25.8</td>
<td>0.1</td>
<td>-</td>
<td>0.4</td>
<td>1.2</td>
<td>8.3</td>
<td>64.2</td>
</tr>
<tr>
<td>c. Fine particles</td>
<td>26.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.6</td>
<td>0.8</td>
<td>2.3</td>
<td>69.8</td>
</tr>
<tr>
<td>d. Interface between cellular structure and bulk-YSZ</td>
<td>35.2</td>
<td>1.5</td>
<td>3.7</td>
<td>13.2</td>
<td>15.2</td>
<td>14.2</td>
<td>17.0</td>
</tr>
<tr>
<td>e. Interface between fine particles and cellular structure</td>
<td>37.6</td>
<td>2.0</td>
<td>4.8</td>
<td>16.3</td>
<td>18.6</td>
<td>15.9</td>
<td>5.0</td>
</tr>
<tr>
<td>f. CMAS phase above the fine particles</td>
<td>37.9</td>
<td>2.0</td>
<td>5.0</td>
<td>16.7</td>
<td>18.4</td>
<td>15.4</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Kato and Araki, on the other hand, presented that the reaction between a zircon refractory and a molten glass resulted in the decomposition of the zircon crystal, followed by the precipitation of fine ZrO$_2$ particles and the dissolution into the glass phase (Kato and Araki, 1986). The fine ZrO$_2$ particles observed in upper region of the interaction zone (Fig. 4(f)) seem to be formed by the re-dissolution of the reprecipitated ZrO$_2$ into the CMAS. The difference in composition between cellular structure and fine ZrO$_2$ particles supports the above postulation. The fine ZrO$_2$ particles at the most upper part of the interaction zone also seems to dissolve into the CMAS because the composition of CMAS on fine ZrO$_2$ particles has Zr and Y (Table 2).

One of the reasons for the occurrence of the dissolution and reprecipitation in stages is expected to be due to little solubility of ZrO$_2$ into CMAS as expected from the phase diagrams with some CMAS oxides and ZrO$_2$ such as CaO-SiO$_2$-ZrO$_2$, CaO-Al$_2$O$_3$-SiO$_2$-ZrO$_2$ and CaO-MgO-SiO$_2$-ZrO$_2$ (Krämer et al., 2006, Roth and Vanderah, 2005, Roth et al., 1981): even though the ZrO$_2$ dissolves into the CMAS, the local saturation of ZrO$_2$ immediately occurs in the CMAS, leading to the reprecipitation of the ZrO$_2$.

Summarizing the above findings, the CMAS damage is intrinsic from material aspect: it is extremely difficult to prevent the CMAS damage progression inside the top coat comprised of YSZ, even if a dense layer is formed on the surface of the top coat to arrest the physical infiltration of CMAS into open pores in the top coat.

### 3.2 Effect of crystallographic plane on the interaction between CMAS and YSZ

The effect of crystallographic plane on the CMAS damage was explored by means of the SC YSZ specimens prepared by Fig. 2. Figure 6 shows the change in thickness of the infiltration zone associated with crystallographic plane. Here, the thickness of the interaction zone was measured at 15 positions at regular intervals from the cross-sectional micrographs on each specimen, and the error bar reveals the scatter. It can be seen that the thickness of the infiltration zone was the lowest in the {111} plane specimen, followed by {110} plane and {100} plane specimens in order.

In the cubic-YSZ, the {111} plane has the lowest surface energy, followed by {110} plane and {100} plane specimens (Ballabio et al., 2004, Christensen and Carter, 1998). This order is qualitatively consistent with the results of Fig. 6. In other words, the CMAS damage would be evolved under an influence of crystallographic surface. When it is the case, the finding of Fig. 6 can be applied to minimize CMAS damage. As an example, the columnar grains developed by EB-PVD process have strong texture depending on the process condition (Suzuki et al, 2008); hence, the condition in which the texture associating with {111} plane is supposed to be beneficial for the CMAS damage reduction.

![Fig. 6 Change in thickness of interaction zone associated with crystallographic plane](exposed at 1250°C for 100h, followed by furnace cooling).
4. Conclusion

The material aspects of CMAS damage on TBCs and the effect of crystallographic plane on the interaction between CMAS and YSZ were investigated by means of single crystal bulk YSZ specimen. The following conclusions can be drawn from this study.

1) The CMAS damage was metallurgically essential, which associated with the morphological and compositional changes by the reaction between CMAS and YSZ. The reaction could take the infiltration of CMAS into the YSZ without any pores. It was suggested that the mechanism would involve the process consisting of the dissolution of YSZ and the reprecipitation of ZrO$_2$.

2) The CMAS damage developed depending on the crystallographic plane of YSZ; it was the lowest on the {111} plane.

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References


Roth R. S. and Vanderah T. A., Phase equilibria diagrams, The American Ceramic Society, Vol.XIV, (2005), pp.573 Fig.11563.


