Degradation of Thermal Barrier Coatings with Molten CaO–MgO–Al2O3–SiO2 (CMAS) Deposition and Hot Corrosion

Abstract

Thermal barrier coatings (TBCs) are susceptible to degradation by molten CMAS (calcium-magnesium alumino silicate) deposits and hot corrosion, when employed in gas turbine engines operating in a dust-laden environment and low quality fuels. In this study, CMAS and hot corrosion degradation of TBCs are investigated. Yttria stabilized zirconia (YSZ) and Ceria-yttria stabilized zirconia coatings in contact with a CMAS dust and hot corrosion salts deposit were subjected to heat treatment in air at temperature 1200°C for 12h. Phase transformations and microstructural evolution were examined by using x-ray diffraction and scanning electron microscopy.

1. Introduction

Thermal Barrier Coatings (TBCs) is a technique which is largely applied as a protection shield against high temperatures for the structural components in stationary and aerospace gas turbines. The Thermal Barrier Coatings (TBCs) concept involves placing a MCrAlY bond coat (M = Ni,Co) as an oxidation resistance layer and top coat thermally insulating ceramic layer between a cooled metallic component and the hot working gas to reduce heat transfer to the component [1-3].

Hot corrosion is one of the most considerable damage mechanisms for the TBCs. Low quality fuels contain some corrosive contamination such as Na and V. These contaminations cumulate on the TBCs surface as a Na2SO4 and V2O5 salts. These salts react with the yttria and cause phase transformation in the YSZ, which is tetragonal or cubic zirconia to monoclinic phase. This phase transformation lead to volume expansion approximately 3-5% and cause damages in the TBCs such as cracks or spallation on TBCs surface [4].

Since the eruption of Eyjafjallajokull volcano in Iceland on April 14th, 2010 and caused interruption of flights due to concern about the possible damage from volcanic ash during aeroplane flying, the interaction between volcanic ash and thermal barrier coatings has been paid attention by materials scientists. Unlike traditional failure mechanisms, with the increase of the operating temperature of engine turbine, there is a degradation mechanism of hot section turbine materials, known as the calcium-magnesium-alumino-silicates (CMAS) degradation. Molten CMAS attacks on the YSZ top coat layer is becoming more apparent and requires the attention of materials scientists. When the engine is in operation, airborne ashes, dusts and debris are ingested into the engine, they melt, and form CMAS before being deposited on the surface of hot area of turbine. Molten CMAS also penetrates into the YSZ top coat, and shortens the lifetime of TBCs [5,6].

In studies up to the present day, the simutlaions of hot corrosion and CMAS effots on TBCs were examined separately. In this study, corrosive salts and CMAS dust applied on TBCs together and damage mechanisms on the TBC have been investigated.

2. Experimental Details

2.1. Materials and coatings

316L stainless steel disk-shaped samples with the diameter of 25.4 mm and with the thicknesses of 2 mm have been used as substrate. Prior to bond coat production, the substrate was grit-blasted by using 50-80 grain mesh alumina particles in order to remove surface oxides and improve adhesion of bond coat. A commercial Sulzer Metco Amdry 997 (Ni-23Co-20Cr-8.5Al-4Ta-0.6Y) powder was selected to manufacture the bond coats. The spray torches (APS and HVOF gun) was fastened on a three-axis CNC table and gun speed was selected as 600 mm/min. Grit-blasted samples were clamped on the turntable and turntable speed has been selected as 100 rpm and a number of passes was selected to be 12. Amdry 997 bond coat powder was coated by using DJ2700 HVOF gun.
Commercial Sulzer Metco 204NS (ZrO$_2$–8 wt.% Y$_2$O$_3$) and Sulzer Metco 205NS (25 % CeO$_2$ - 2.5 % Y$_2$O$_3$ - ZrO$_2$) powders were selected for top coat materials. XRD patterns of YSZ and CYSZ powders are given in Figure 1 a).

![Figure 1. XRD patterns of YSZ and CYSZ powders (a) and coatings (b).](image)

YSZ powder has mostly tetragonal Zr$_{0.9}$Y$_{0.1}$O$_{1.96}$ (JCPDS card no:010-082-1241) phase and a few monoclinic ZrO$_2$ (JCPDS card no:010-086-1450) phase. CYSZ powder has mostly tetragonal Zr$_{0.86}$Y$_{0.14}$O$_{1.93}$ (JCPDS card no:010-082-1243) phase, monoclinic ZrO$_2$ (JCPDS card no:010-072-1669), and cubic CeO$_2$ phase.

<table>
<thead>
<tr>
<th>Process parameters of plasma spray</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paramaters</td>
</tr>
<tr>
<td>Current (A)</td>
</tr>
<tr>
<td>Primary gas,Ar (scfh)</td>
</tr>
<tr>
<td>Secondary gas, H$_2$ (scfh)</td>
</tr>
<tr>
<td>Carrier gas flow rate, Ar (scfh)</td>
</tr>
<tr>
<td>Number of passes</td>
</tr>
<tr>
<td>Spray distance (mm)</td>
</tr>
<tr>
<td>Gun speed (mm/min)</td>
</tr>
<tr>
<td>Turntable speed (rpm)</td>
</tr>
</tbody>
</table>

Three types of coatings have been produced by air plasma spray (APS) method by using Sulzer Metco 9MB plasma spray gun. Gun nozzle was a commercial Sulzer Metco 730C and powder injection angle was perpendicular to plasma flame. Process parameters of plasma spraying are listed in Table 1.

Figure 1 b) shows XRD pattern of as sprayed YSZ and CYSZ TBCs. As it is seen in Figure 1 b), as-sprayed YSZ coating has tetragonal Zr$_{0.9}$Y$_{0.1}$O$_{1.96}$ (JCPDS card no:010-082-1241) and monoclinic ZrO$_2$ (JCPDS card no:010-086-1450) phases. As understood from the Figure 1 a) and b), some of the monoclinic phase of zirconia in the YSZ powder, transform into the tetragonal phase after sprayed with APS method because of rapid solidification of YSZ powders during the APS process [7-9].

As-sprayed CYSZ coating has only tetragonal Zr$_{0.86}$Ce$_{0.14}$O$_2$ (JCPDS card no:01-038-1437). Monoclinic and cubic phases in the CYSZ powder disappear because of some of CeO$_2$ evaporate and some of CeO$_2$ disperse in the coating during the APS process [9-12].

2.2 Hot Corrosion+CMAS Tests

V$_2$O$_5$ and Na$_2$SO$_4$ powders were selected as corrosive salts. 50 wt.% V$_2$O$_5$ and 50 wt.% Na$_2$SO$_4$ salts were mixed in turbula for 2 hours. The corrosive salt with a concentration of 30 mg/cm$^2$ was spread over the surface coatings leaving 3mm distance from the edge to avoid edge effect. After that, corrosive salts and CMAS dust applied on as-sprayed substrates respectively. The samples were heated up to 1200 °C and held for 60 h in an electric furnace with air atmosphere, then allowed to cool down inside the furnace. Sample surface images of before and after Hot Corrosion + CMAS tests are given in Figure 2.

Figure 2. Macro photo of YSZ and CYSZ TBCs before and after CMAS+Hot corrosion tests.

2.3 Microstructure and chemical analysis

Microstructure, morphology and chemical composition of the surface and the cross-section of the coatings have been examined by field emission electron microscopy (JEOL JSM 7000F) equipped with EDS. X-ray diffraction (Rigaku Miniflex) has
been used to determine the crystalline structure of the coatings and hot corrosion products.

3. Results and Discussion

The cross-sections of the YSZ and CYSZ TBCs including bond coats and top coats were given in Figure 3. As the characteristic feature of the TBCs, porosity and cracks in the top coat were observed clearly [19]. Thickness of bond coats was measured approximately to be 100 $\mu$m and top coats of the three sample groups measured approximately to be 275 $\mu$m, 240 $\mu$m, 200 $\mu$m, respectively. After HVOF and APS process, uniform adhesive structure was obtained all around the coatings.

Figure 3. Cross section SEM image of YSZ(a) and CYSZ(b) coating.

Figure 4 shows cross sectional SEM images of YSZ and CYSZ TBCs after hot corrosion+CMAS tests. After hot corrosion salts and CMAS dust penetrate into the TBCs microstructure and fill porosity and intersplats crack. In addition, a CMAS reaction region is observed between bond coat and top coat for both YSZ and CSZ coated specimens[17,18].

Figure 4. Cross sectional SEM image of TBCs after hot corrosion+CMAS tests, a,b)YSZ, c,d) CYSZ

Surface SEM images of YSZ TBCs shown in Figure 5. Microstructure of coating surface and microstructure of CMAS penetrated zone are seen in Figure 5a. Dispersed CMAS throughout the coating cause loss of porosity.

Previous studies reported that, after hot corrosion test, YVO$_4$ corrosion product is formed on YSZ coating surface[13-15].

Figure 5. Surface SEM images of YSZ TBCs after hot corrosion+CMAS tests.

In this study, YVO$_4$ corrosion product has not been demonstrated. It is assumed that, some compounds within CMAS react with hot corrosion salts and different compounds are formed. SEM images of different CMAS deposits are given in Figure 6.

Figure 6 shows surface SEM images of CYSZ after CMAS+hot corrosion test.

Figure 6. Surface SEM images of CYSZ TBCs after hot corrosion+CMAS tests.

As it seen in Figure 6, an unusual CMAS deposits are observed on coating surface. Unlike previous studies about CYSZ TBCs, YVO$_4$ or CeVO$_4$ corrosion product has not been demonstrated in this study[13-16].

XRD patterns of YSZ and CYSZ TBCs after CMAS+hot corrosion tests shown in Figure 7. As it seen in Figure 7, the amount of monoclinic phase is increased after CMAS+hot corrosion tests.
In CSZ coatings, a phase transformation has not occurred after CMAS+hot corrosion tests but because of adhesion and deposition of CMAS+hot corrosion products on the surface, some undefined peaks are observed on XRD analysis.

**Figure 7.** XRD patterns of YSZ and CYSZ TBCs after CMAS+hot corrosion tests.

It is assumed that, these peaks belong to compounds which are reaction product of CMAS + hot corrosion\[16,17\].

4. Conclusion

In this study, corrosive salts and CMAS dust applied on TBCs together and structure changes of TBCs have been investigated. Melted CMAS dust and hot corrosion salts penetrate throughout porosities and intersplats crack. YVO$_4$ corrosion product has not been demonstrated because of a reaction between CMAS and hot corrosion salts. Absence of YVO$_4$ corrosion product provides a phase stability on coatings.

References