Evolution of hot corrosion resistance of YSZ, $Gd_2Zr_2O_7$ and $Gd_2Zr_2O_7$+YSZ composite thermal barrier coatings in Na_2SO_4+V_2O_5 at 1050°C

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ABSTRACT

This investigation compares the hot corrosion performance of yttria stabilized zirconia (YSZ), $Gd_2Zr_2O_7$ and YSZ+$Gd_2Zr_2O_7$ composite coatings in the presence of molten mixture of Na_2SO_4+V_2O_5 at 1050°C. Characterizations using X-ray diffraction (XRD) and scanning electron microscope (SEM) indicate that in the case of YSZ, the reaction between $NaVO_3$ and Y_2O_3 produces YVO_4 and leads to the transformation of tetragonal ZrO_2 to monoclinic ZrO_2. For the $Gd_2Zr_2O_7$+YSZ composite coating, by the formation of $GdVO_4$, the amount of YVO_4 formed on the YSZ+$Gd_2Zr_2O_7$ composite coating is significantly reduced, thus the amount of monoclinic phase in the TBC coating is substantially reduced, which renders YSZ+$Gd_2Zr_2O_7$ composite coating a better hot corrosion resistance than that of YSZ. Molten salt is also found to react with $Gd_2Zr_2O_7$ to form $GdVO_4$. Comparing to YSZ, under a high temperature of 1050 °C, $Gd_2Zr_2O_7$ is more stable, both thermally and chemically, than YSZ, and exhibits a better hot corrosion resistance.

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INTRODUCTION

Thermal barrier coatings (TBCs) are frequently used on the blades and vanes of gas turbines to provide thermal insulation. Although YSZ based TBC systems have been used widely in gas turbine industry, YSZ is prone to hot corrosion caused by molten salts, such as Na, S and V, contained in low-quality fuels at high working temperatures. The search for alternative coating materials other than the well established YSZ system has consisted of two main approaches: (i) alternative materials to ZrO_2-based systems, and (ii) alternative stabilizers to $Y_2O_3$for ZrO_2-based systems. Significantly, the $A_2B_2O_7$-type rare-earth zirconate ceramics, such as $La_2Zr_2O_7$, $Nd_2Zr_2O_7$, and $Gd_2Zr_2O_7$ and $Sm_2Zr_2O_7$, have been shown recently to have lower thermal conductivity, higher melting points, relatively higher thermal expansion coefficients (TEC), higher stability, and better ability to accommodate defects than YSZ. However, for the hot corrosion behavior of $Gd_2Zr_2O_7$ and other rare earth zirconates, most of early studies reported a temperature range between 650 to 900ºC.In this Investigation, the hot corrosion behavior of $Gd_2Zr_2O_7$, YSZ and $Gd_2Zr_2O_7$+YSZ composite coatings by Na_2SO_4+V_2O_5 mixture is examined at 1050ºC.

METHODS AND MATERIALS

Inconel 738 disks of Φ25×1.5mm were employed as the substrates. TBCs composed of a ceramic top coating and a NiCrAlY bond coat (Amdry 9625, Sulzer Metco) were deposited by the atmospheric plasma spray (APS) process.

Three types of top coats, YSZ, $Gd_2Zr_2O_7$, and YSZ+ $Gd_2Zr_2O_7$ were made using agglomerated powders. The plasma spraying was carried out using a Metco 9M plasma spray system using an Ar/H_2 mixture gas.

To perform the accelerated high-temperature hot corrosion tests, a mixture of Na_2SO_4+V_2O_5 deposit was spread onto the surfaces of the TBC specimens with a salt amount of 20 mg/cm^2. The specimens were then set in an electric furnace with a maximum air atmosphere of 1050˚C for 4 hours. After each 4 hours of testing at 1050˚C, the samples were allowed to cool down for inspection. The samples were then recoated with the Na_2SO_4+V_2O_5 salt mixture and the heating profile repeated.

RESULTS AND DISCUSSION

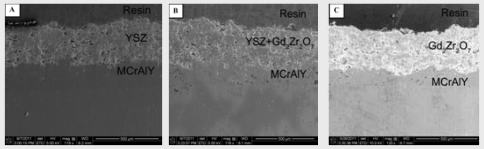

Figure 1. Cross-section of APS coatings A) conventional YSZ,B) $Gd_2Zr_2O_7$+YSZ C) $Gd_2Zr_2O_7$

Typical surface morphologies of YSZ, $Gd_2Zr_2O_7$+YSZ and $Gd_2Zr_2O_7$ specimens after hot corrosion tests are presented in Fig. 2, with porous appearances and the formation of new crystals.

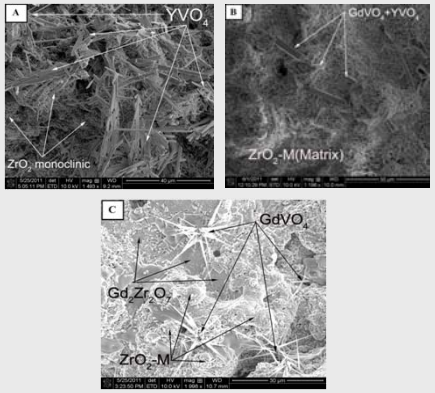

Figure 2. A) conventional YSZ, B) $Gd_2Zr_2O_7$+YSZ C) $Gd_2Zr_2O_7$ after hot corrosion in Na_2SO_4+V_2O_5 at 1050ºC

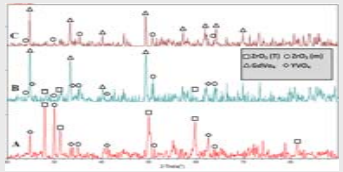

Figure 3. XRD of A) conventional YSZ, B) $Gd_2Zr_2O_7$+YSZ C) $Gd_2Zr_2O_7$ after hot corrosion in Na_2SO_4+V_2O_5 at 1050ºC

Chemical degradation during the hot corrosion:

$$V_2O_5 + Na_2SO_4 \rightarrow 2\,(NaVO_3) + SO_3 \quad (1)$$

$$ZrO_2\,(Y_2O_3) + 2(NaVO_3) \rightarrow ZrO_2 + 2(YVO_4) + Na_2O \quad (2)$$

After the depletion of Y_2O_3, cracking and spallation of ZrO_2 happens.

RESULTS AND DISCUSSION

For $Gd_2Zr_2O_7$+YSZ and $Gd_2Zr_2O_7$ coatings

$$Gd_2Zr_2O_7(s) + 2\,NaVO_3\,(l) \rightarrow 2GdVO_4(s) + 2ZrO_2\,(\text{monoclinic}) + Na_2O \quad (3)$$

$$Gd_2O_3(s) + 2NaVO_3\,(l) \rightarrow GdVO_4(s) + Na_2O \quad (4)$$

As shown in Fig. 4(a), large harmful horizontal cracks have formed throughout the thickness of coating.

For YSZ+$Gd_2Zr_2O_7$ composite coatings, only a few visible cracks, but no spallation.

Figure 4c shows a $Gd_2Zr_2O_7$ coating cross-section, which has no significant degradation and spallation after hot corrosion

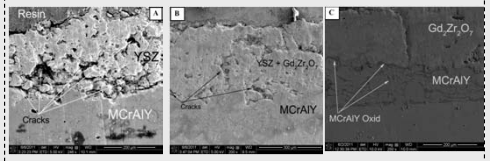

Figure 4. Cross-section of A) YSZ, B) $Gd_2Zr_2O_7$+YSZ C) $Gd_2Zr_2O_7$ after hot corrosion in Na_2SO_4+V_2O_5 at 1050ºC

CONCLUSIONS

The reactions between yttria (Y_2O_3) and V_2O_5 or $NaVO_3$ produce YVO_4, leaching Y_2O_3 from the YSZ and causing progressive tetragonal to monoclinic destabilization transformation.

Molten Na_2SO_4+V_2O_5 mixture reacts with the bulk $Gd_2Zr_2O_7$ layer to form $GdVO_4$ and monoclinic ZrO_2. The production of $GdVO_4$ partially consumes V_2O_5 and thus postpones the formation of YVO_4 crystals and consequently less monoclinic ZrO_2 and less YVO_4 crystals are formed.

Under the test, bulk $Gd_2Zr_2O_7$ layer started to degrade after 36 hours of hot corrosion testing (9 cycles), which is much better than the YSZ case (5 cycles).

$Gd_2Zr_2O_7$ has a better hot corrosion resistance at a temperature of 1050°C than that of YSZ coatings.

ACKNOWLEDGMENTS

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