Impermeable thin Al_2O_3 overlay for TBC protection from sulfate and vanadate attack in gas turbines

Quarterly Progress Report

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ABSTRACT

In order to improve the hot corrosion resistance of conventional YSZ TBC system (YSZ/CoNiCrAlY/Inconel 601), an overlay Al_2O_3 was sprayed on the surface of TBC samples by high velocity oxy-fuel (HVOF) spray techniques. The TBC preparation in Japan was based on our technical requirement by plasma spray. Bond coat CoNiCrAlY and the YSZ was produced by low-pressure plasma spray and air plasma spray respectively. Hot corrosion tests were carried out on the TBC with and without Al_2O_3 coating in molten salts mixtures (Na_2SO_4 + 5%V_2O_5) at 950^oC for 10h. The microstructures of TBC and overlay before and after exposure were examined by means of scanning electron microscopy (SEM), energy-dispersive X-ray spectrometer (EDX) and X-ray diffraction (XRD). It has been found that TBC reacted with V_2O_5 to form YVO_4. A substantial amount of M-phase was formed due to the leaching of Y_2O_3 from YSZ. Al_2O_3 overlay coating sprayed by HVOF was dense, continues and adherent to the TBC even after exposure to the molten salts. As a result, overlay Al_2O_3 coating can prevent the YSZ from the attack by molten salts containing vanadium and arrest the penetration of salts into the YSZ along porous and cracks in the YSZ TBC. Accordingly, the amount of M-phase formed in TBC with Al_2O_3 overlay was significantly lower than that in conventional YSZ TBC system.

In the next period, the hot corrosion tests of TBC with EB-PVD Al_2O_3 coating under Na_2SO_4 + 5%V_2O_5 will be again performed at 950^oC. However before hot corrosion tests, the post-annealing will be carried at 1273K for 1h in order to transform the as-sputtered γ-Al_2O_3 overlay to crystalline α-Al_2O_3 overlay. In addition, the effect of coating thickness on corrosion resistance and the mechanisms of cracking of EB-PVD alumina layer during hot corrosion will be also investigated.

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1. INTRODUCTION

Thermal barrier coatings (TBCs) are finding increased application in overall component design of gas turbine. TBCs reduce the severity of thermal transients and lower the substrate temperature, thus improving fuel economy, engine power and component durability in engines. Yttria-stabilized zirconia (YSZ) TBCs is widely used in aero gas turbines [1-2]. Attempts to bring the advantages of TBCs to industrial and marine engines have been limited, however, in part because YSZ coatings are degraded by the reaction of Yttria with traces of sodium, sulfur, and especially vanadium present in many industrial-quality fuels, although zirconia itself shows good resistance to the molten sulfate or vanadate compounds arising from fuel impurities [3]. The majority of present-day TBCs are 8% Y_2O_3-ZrO_2 type as they exhibiting superior performance in the absence of vanadium. For example, burning clean fuel, a lifetime in excess of 10000 cycles has been reported; in contrast, when 2 ppm of vanadium was added to the fuel, lifetime was less than 100 cycles. The critical problem is that yttria reacts react with the V_2O_5 or $NaVO_3$ to form YVO_4 in the case of molten salt containing small amount of V_2O_5 as follows:

$$Y_2O_3 \text{ (in } ZrO_2) + V_2O_5 \text{ (in melt)} = 2\ YVO_4 \text{ (solid)} \qquad (1)$$

This reaction depletes the Y_2O_3 stabilizer from ZrO_2 matrix and causes destabilization (i.e., transformation of the zirconia from the tetragonal and/or cubic to monoclinic phase upon cooling, which is accompanied by a large destructive volume change.) and degradation of the YSZ coating. Destabilization of the TBCs eventually causes the delamination and spalling of the ceramics coating. In addition, molten salts can penetrate into the YSZ coatings along porous and cracks in YSZ TBC and react with the metallic bond coat.

Therefore, the proposed idea for preventing the YSZ coating system from hot corrosion is the development of a dense overlay on the outer surface of YSZ coating to isolate the YSZ coating system from the molten salts so that chemical or physical change of the YSZ coating does not occur. Thus the character of this protective coating has to be dense and impermeable.

Alumina (Al_2O_3) is a well-know oxide material that has diverse application as engineering ceramics. Alumina has high melting point and high hardness. Al_2O_3 coating on metal substrate has exhibited good resistance of wear and erosion. This allows the potential application of Al_2O_3 in gas turbines. However, Al_2O_3 has relatively high thermal conductivity (0.02-0.06W/cmK) compared with YSZ. Therefore, in the present TBC design, the YSZ coating acts as a thermal barrier and the Al_2O_3 coating plays a role in hot-corrosion and oxidation resistance, although there is no hot-corrosion data for Al_2O_3 in vanadate salts.

In the present project, a high-purity, dense, and continuous Al_2O_3 overlay was deposited onto the surface of YSZ coating by HVOF technique. Hot corrosion tests were carried out. By using XRD, SEM and EDX analyses, the microstructure, hot corrosion behaviors of the surface modified TBC system with alumina coating were described in comparison with the conventional TBC system.

2. EXECUTIVE SUMMARY

Conventional YSZ TBC reacted with V_2O_5 to form YVO_4 during the hot corrosion tests. A substantial amount of M-phase of ZrO_2 was formed due to the leaching of Y_2O_3 from YSZ. Al_2O_3 overlay coating sprayed by HVOF was dense, continues and adherent to the TBC even after exposure to the molten salts at 950^{o}C for 10h. As a result, overlay Al_2O_3 coating can prevent the YSZ from the attack by molten salts containing vanadium and arrest the penetration of salts into the YSZ along porous and cracks in the YSZ TBC. Accordingly, the amount of M-phase formed in TBC with Al_2O_3 overlay was significantly lower than that in conventional YSZ TBC system.

3. EXPERIMENTAL

The TBC system used in this study consisted of 6061 nickel-based superalloy substrate, CoNiCrAlY alloy bond coat as well as zirconia-8%yttira (YSZ) ceramic top coating. The bond coat and the YSZ TBC were produced by LPPS and APS, with the thickness of about 100 and 250, respectively. After receiving the TBC samples, overlay of Al_2O_3 coating was deposited by HVOF spray technique. The thickness of Al_2O_3 coatings was approximately 20-30 μm .

In order to compare the hot corrosion resistance of the TBCs with and without Al_2O_3 coating, hot corrosion experiments were carried out. The samples were exposed to molten salts mixtures (Na_2SO_4 + 5%V_2O_5) by placing them in a still air furnace at 950^{o}C for 10h. A Philips PW1700 series diffractometer was employed to perform the phase analysis. X-ray diffraction (XRD) was used to determine whether reaction had taken place (as detected mainly by formation of YVO_4). XRD patterns were first obtained from the samples before salt exposure. After exposure, the samples were cooled to room temperature in the furnace. The exposured samples were cleaned in an ultrasonic cleaner in distilled water. The extent of destabilization (D) of the YSZ TBC was estimated by

$$D\,(\%) = \frac{M}{T+M}\times 100 \qquad (2)$$

Where T is the height of the zirconia tetragonal (111) peak, and M is the height of the zirconia monoclinic ($11\bar{1}$) peak in XRD test. For the sample of TBC+Al_2O_3 overlay, in order to detect the same depth as that of TBC without Al_2O_3 overlay, XRD test was done again on the sample whose overlay Al_2O_3 coating has been partially removed.

The microstructures and composition changes on the coating surface and their cross-sections after hot corrosion tests were examined using scanning electron microscopy (SEM) and an energy-dispersive X-ray spectrometer (EDX) equipped in SEM.

4. RESULTS AND DISCUSSION

4.1 Microstructure of the overlay Al_2O_3 coating

Fig.1 shows the cross-section SEM micrograph of the TBC with Al_2O_3 overlay coating sprayed by HVOF technique. It is seen that the Al_2O_3 coating is very dense and adherent to the TBC. The surface morphology of alumina overlay coating produced by HVOF was similar to that of ASP zirconia TBC layer, but the particle size was much smaller than that of TBC, probably due to the higher temperature and particle speed during HVOF deposit. Therefore, denser, non-cracks and continuous coating could be obtained, as shown in Fig.2. Al_2O_3 overlay coating deposited by HVOF was comprised of γ- Al_2O_3 and a little bit of α- Al_2O_3 (A in Fig.4).

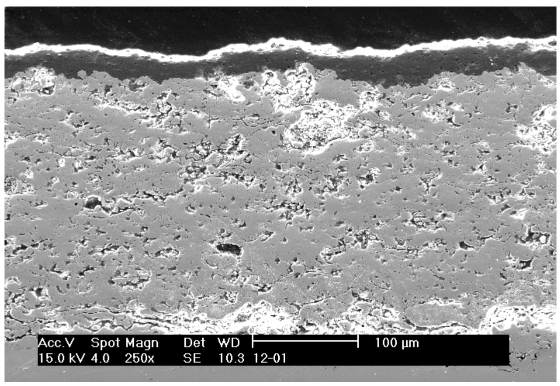

Fig.1 SEM micrographs of cross-section of TBC with HVOF overlay Al_2O_3 coating

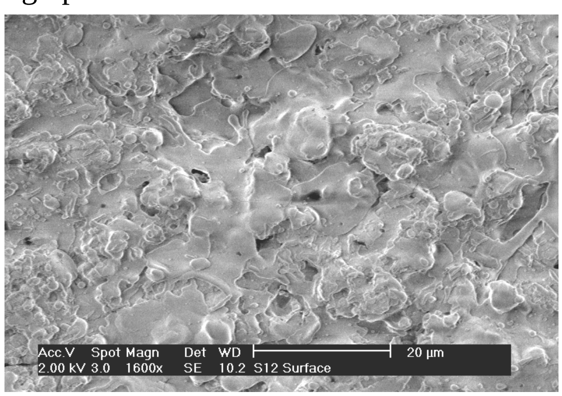

Fig.2 SEM micrographs of surface of HVOF overlay Al_2O_3 coating

4.2 Hot corrosion tests

4.2.1 XRD analyses

X-ray diffraction before and after exposure to molten slats has provided the information of the extent of reactions occurred during hot corrosion. The X-ray diffraction patterns of as-sprayed TBC specimen demonstrated that it contained predominantly T-phase (A in Fig.3). After exposure to the molten mixture of salts of Na_2SO_4 + 5%V_2O_5 at 950^oC for 10h, the XRD patterns (B in Fig.3) showed that corresponding to a remarkable decrease in intensity of T-phase of zirconia, a substantial amount of M-phase was formed due to the leaching of Y_2O_3 from YSZ resulting from the reaction of Y_2O_3 with V_2O_5 to form YVO_4 (which was found in XRD patterns) according the reaction (1) indicated above.

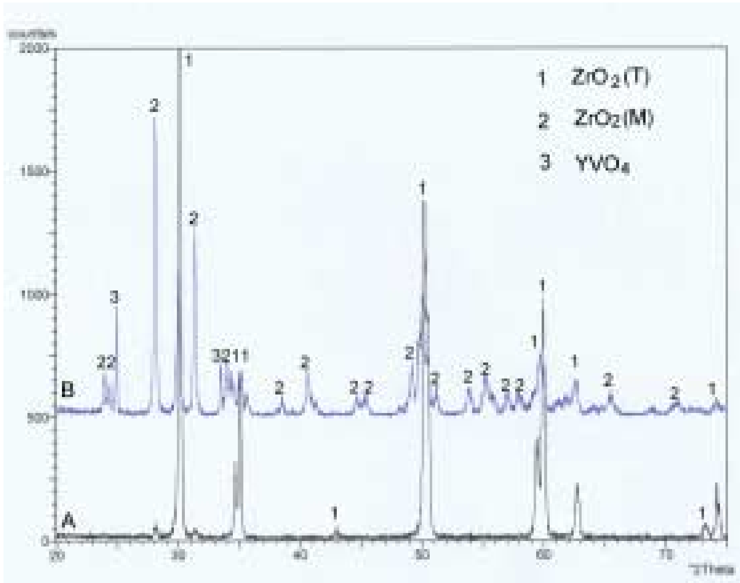

Fig.3 XRD patterns of TBC before exposure (A) and after exposure (B) to the molten salts

B in Fig.4 shows the XRD patterns of TBC with HVOF Al_2O_3 coating after exposure. It was quite notable that just a little bit amount of M-phase was formed after exposure to molten salts. A large amount of γ- Al_2O_3 was transformed to α- Al_2O_3 after subjecting to hot corrosion at high temperature. Accordingly, YVO_4 was not picked up by XRD in the specimen, probably due to its low content that was below the detection limit. From the XRD patterns of the sample whose Al_2O_3 coating was partially removed before XRD analyses, as shown in C in Fig.4, it can be found that the intensity of M-phase was still low. The attack of YSZ by molten salts was limited due to the presence of Al_2O_3 overlay coating.

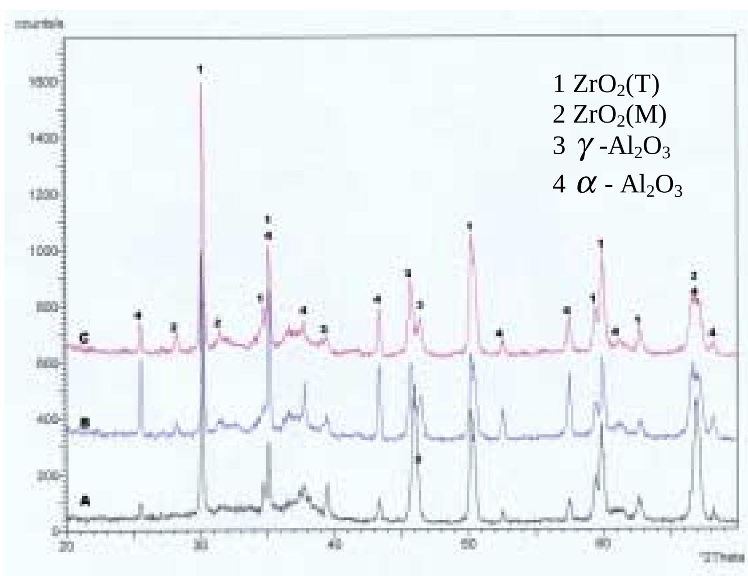

Fig.4 XRD patterns of TBC with HVOF Al_2O_3 overlay coating before and after exposure
(A: TBC with as-deposited overlay Al_2O_3 ; B: after exposure;
C: after partially removing Al_2O_3 overlay after exposure)

Based on the XRD results, destabilization (D) can be obtained for both the TBC and surface modified TBC system, as shown in Fig.5. It clearly indicated that HVOF Al_2O_3 overlay coating can significantly prevent the YSZ from hot corrosion by molten salts containing vanadium and arrest the penetration of salts into the YSZ along porous and cracks in the YSZ TBC. As a result, Al_2O_3 coating subsequently improves the hot-corrosion resistance of the conventional TBC systems.

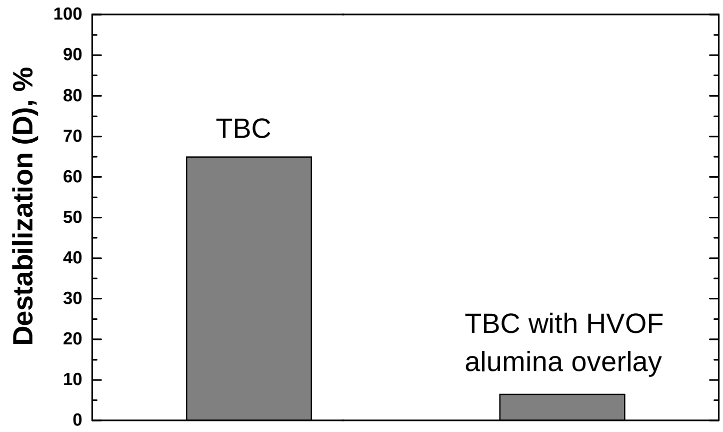

Fig.5 A comparing in destabilization (D) of the TBC without and with HVOF Al_2O_3 overlay coating

4.2.2 SEM observation

For conventional YSZ TBC system, after exposure to the salts, characteristic surface crystals among the fine zirconia grain were formed which was rich in yttrium (40.53at%) and vanadium (36.31at%) and contained no zirconium (Fig.6). The essentially equal amounts of yttrium and vanadium indicated the crystal on the surface of TBC to be YVO_4. This was consistent with the results of XRD analyses in which the peaks of YVO_4 were clearly shown. From SEM microimages of cross-section (Fig.7), it was found that YVO_4 existed not only near the surface of TBC but also in the area near the bond coat. This indicated that molten salts has deeply penetrated into the TBC along the porous and cracks.

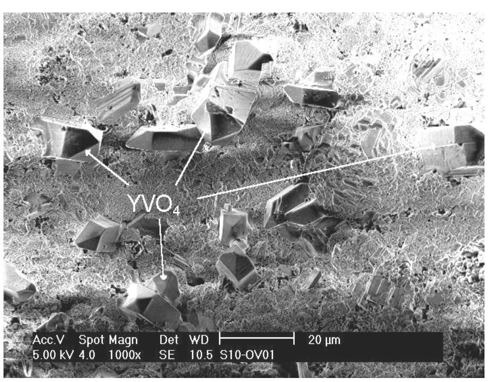

Fig.6 SEM surface micrograph of TBC after 10h hot corrosion test at 950^{o}C showing the formation of YVO_4

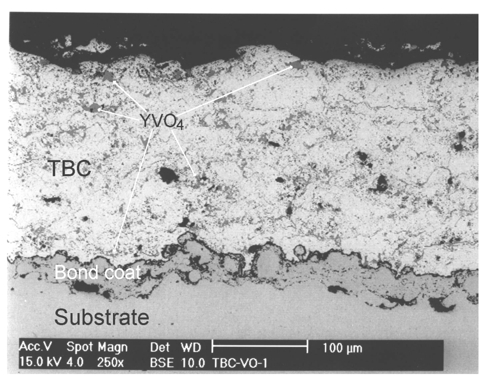

Fig.7 SEM microimages of cross-section of TBC after exposure at 950^{o}C for 10h

In the case of TBC system that has overlay Al_2O_3 coating sprayed by HVOF, the surface was still dense even after exposure to the molten salts for 10h at 950^oC, as shown in Fig.8.

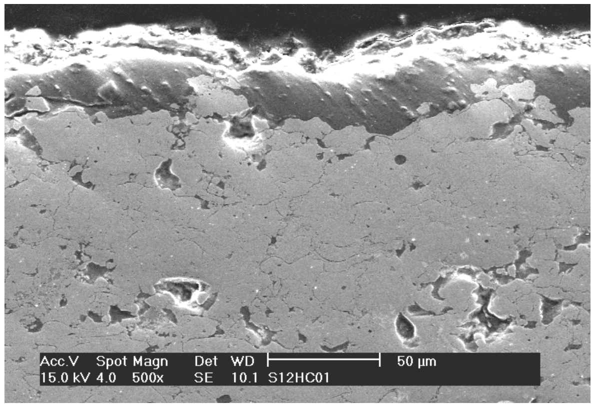

Fig.8 SEM micrograph of TBC with HVOF Al_2O_3 overlay after exposure to the salts

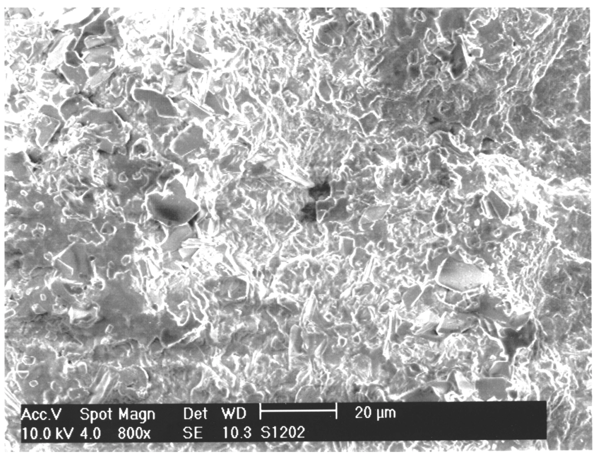

Fig.9 Surface SEM micrograph of HVOF overlay coating after exposure to the salts

Fig.9 shows the micrograph of the sample with HVOF Al_2O_3 coating subjected to hot corrosion test. It was noticeable that the alumina coating was very sense, continuous and coherent to the TBC, and the microstructure of the surface did not have notable variation comparing to that of as-coated specimen, although it has been translated to α- Al_2O_3 from γ-Al_2O_3. The much less formation of M-phase revealed the excellent barrier action of alumina layer sprayed by HVOF to prevent the TBC from the attack of molten salts.

4. PLANS FOR THE NEXT REPORTING PERIOD

The hot corrosion tests of TBC with EB-PVD Al_2O_3 coating under Na_2SO_4 + 5%V_2O_5 will be again performed at 950^oC. However before hot corrosion tests, the post-annealing will be carried out in vacuum (residual pressure 10^{-3} Pa) at 1273K for 1h in order to transform the as-sputtered Al_2O_3 overlay to crystalline α-Al_2O_3 overlay. In addition, the effect of coating thickness on corrosion resistance and the mechanisms of cracking of EB-PVD alumina layer during hot corrosion will be also investigated.

5. CONCLUSION

An overlay Al_2O_3 was sprayed on the surface of conventional YSZ TBC samples by high velocity oxy-fuel (HVOF) spray techniques, in order to improve the hot corrosion resistance of TBC. Hot corrosion tests were carried out on the TBC with and without Al_2O_3 coating in molten salts mixtures (Na_2SO_4 + 5%V_2O_5) at 950^{o}C for 10h. The microstructures of TBC and overlay before and after exposure were examined by means of scanning electron microscopy (SEM), energy-dispersive X-ray spectrometer (EDX) and X-ray diffraction (XRD).

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