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

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ABSTRACT

In order to improve the hot corrosion resistance of conventional YSZ TBC system, the overlay of Al_2O_3 coating was deposited on the TBC by EB-PVD techniques. 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). It has been found that TBC will react 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 deposited by EB-PVD was dense, continues and adherent to the TBC. 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, although there were some cracks in overlay Al_2O_3 coating and at the interface between alumina and zriconia formed during hot corrosion tests due to the presence of tensile stress in the alumina coating.

In the next reporting period, we will study the mechanisms of cracking of the overlay Al_2O_3 layer and finish the hot corrosion tests of TBC with Al_2O_3 coating deposited by high velocity oxy-fuel (HVOF) technique. The hot corrosion test of TBC with EB-PVD deposited Al_2O_3 coating will be again performed. However before hot corrosion tests, a 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.

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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 [3-4]. The majority of present-day TBCs are 8% Y_2O_3-ZrO_2 type as they exhibiting superior performance in the absence of vanadium. 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, although there is no hot-corrosion data for Al_2O_3 in vanadate salts.

In the present study, a high-purity Al_2O_3 overlay was deposited onto the surface of YSZ coating by means of EB-PVD. 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

Overlay of Al_2O_3 coating deposited by EB-PVD is consisted of γ- Al_2O_3. The Al_2O_3 overlay was dense, continues and adherent to the TBC. Hot corrosion tests were done on TBC with and without the Al_2O_3. Al_2O_3 overlay coating can prevent the YSZ from the attack by molten salts containing vanadium and arrest the penetration of the salts into the YSZ TBC, although there were some cracks in alumina coating and at the interface between alumina and zirconia formed during the hot corrosion tests.

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 100 and 250 μm, respectively. After receiving the TBC samples, overlay of Al_2O_3 coating was deposited by EB-PVD in Penn. State University in collaboration with Dr. Jogender Singh. The thickness of Al_2O_3 coating 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 into a still air furnace at 950^{o}C for 10h exposures. 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 (TBC and TBC+Al_2O_3 overlay) before the molten salt exposure. After exposure, the samples were cooled down to room temperature in the furnace. The exposured samples were cleaned in distilled water. XRD analyses were then carried out to the exposured samples. The extent of destabilization (D) of the YSZ TBC was estimated by

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

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 TBC

SEM micrographs of the cross-section and surface morphology of as-sprayed TBC, shown in Fig.1, indicated that the TBC had a typical APS microstructure [5] and contained predominantly T-phase (see A in Fig.3), with inter-splat porosity and complex pattern of microcracks. It was found that the thickness of the bond coat and YSZ was $100\,\mu m$ and $250\,\mu m$, respectively. It was visible that there were microcracks and porous on the surface of the TBC, which are considered to be the path for molten salts to attack the TBC system.

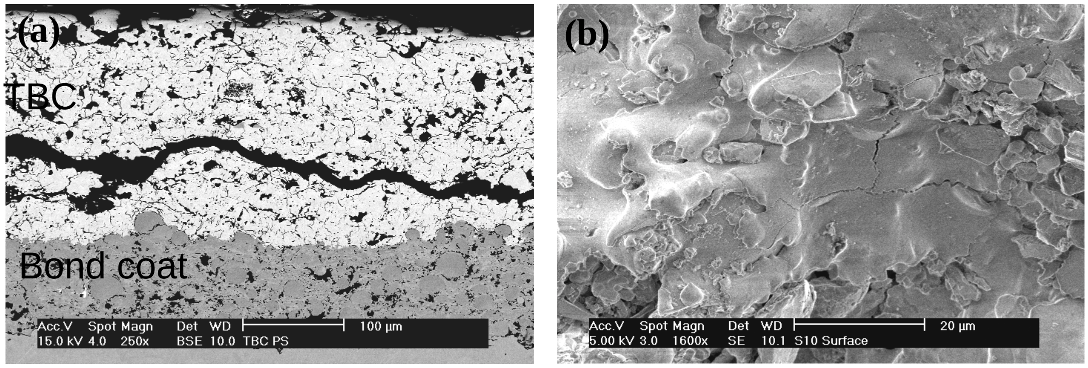

Fig.1 SEM micrographs of (a) cross-section and (b) surface of as-sprayed TBC

4.2 Microstructure of the overlay Al_2O_3 coating

Fig.2 shows the cross-section and surface SEM micrograph of the TBC with Al_2O_3 overlay coating sputtered by EB-PVD. It is seen that the Al_2O_3 coating is dense and adherent to the TBC. The thickness of the Al_2O_3 coating was estimated to be about $25\,\mu m$. The surface micrograph of as-deposited specimen revealed a 'cauliflower' type of structure or dome shaped, as shown in Fig.2. The XRD pattern of the specimen in the as-deposited condition (A in Fig.4) demonstrated that TBC contained predominantly T-phase. The broad $\gamma-$ Al_2O_3 peaks indicated either nanosize crystallites or stress with in the overlay Al_2O_3 coating.

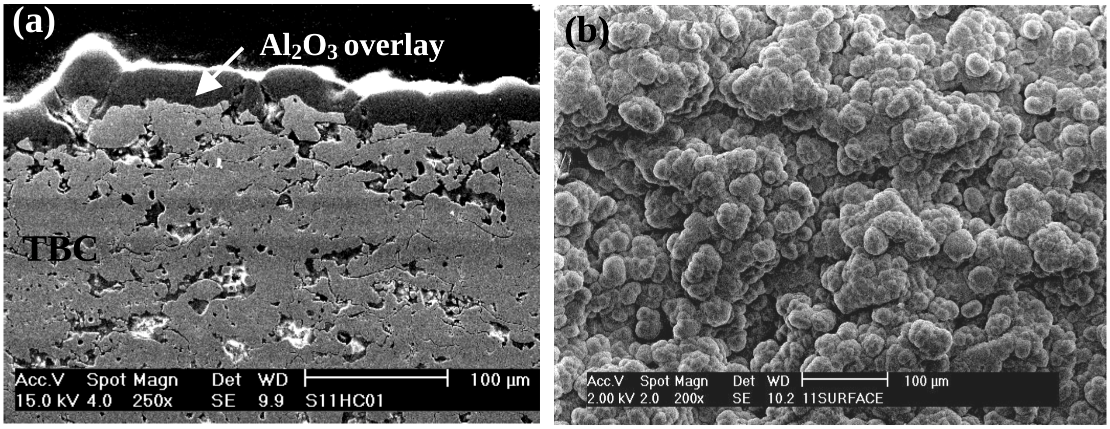

Fig.2 SEM micrographs of (a) cross-section and (b) surface of TBC with overlay Al_2O_3 coating

4.3 Hot corrosion tests

4.3.1 XRD analyses on TBC and TBC/Al_2O_3 samples

X-ray diffraction before and after exposure to molten slats has provided the information of the extent of reactions occurred during hot corrosion in TBC. The X-ray diffraction of as-sprayed TBC demonstrated that it contained predominantly T-phase of ZrO_2 (A in Fig.3). After exposure to the molten mixture of salts of Na_2SO_4 + 5%V_2O_5 at 950 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 in Introduction.

For the TBC with overlay Al_2O_3 coating, the XRD patterns after exposure to molten slats (B in Fig.4) showed a few amount of M-phase in the specimen and no YVO_4 peaks could be detected. Once the sample was heated during exposure, a part of $\gamma-$ Al_2O_3 in the coating was translated to crystalline $\alpha-Al_2O_3$. In addition, it seemed that no reaction products between Al_2O_3 and mixed molten salts could be identified from the XRD results. 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 remarkable increase in the intensity of T-phase was resulted, indicating the destabilization (D) of the TBC with overlay Al_2O_3 coating was much lower than that of TBC without overlay coating. Namely the attack of YSZ by molten salts was limited due to the present of Al_2O_3 overlay coating.

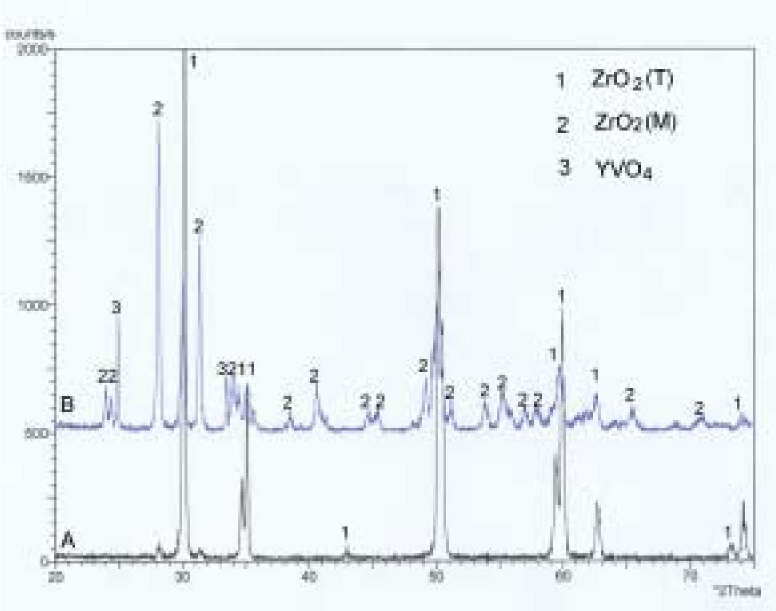

Fig.3 XRD patterns of TBC
before exposure (A) and after exposure (B) to the molten salts

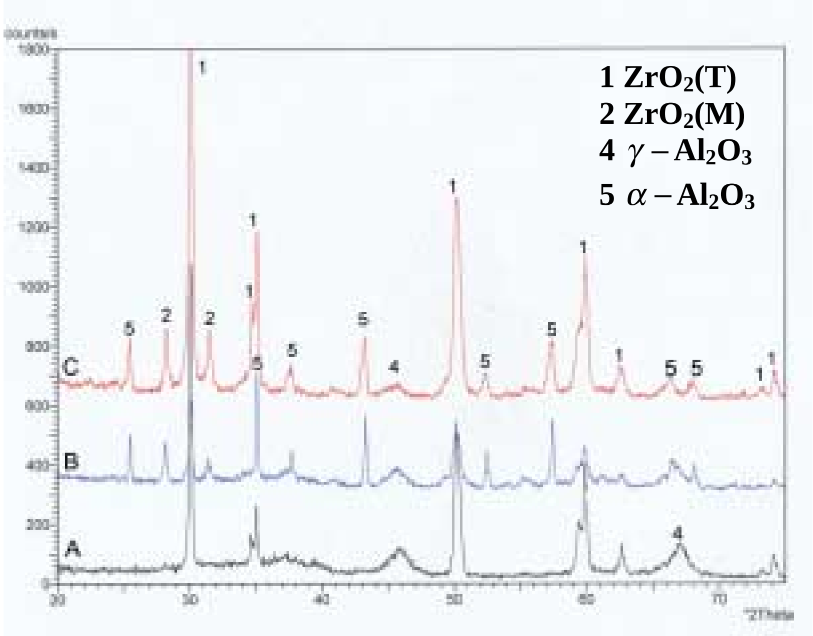

Fig.4 XRD patterns of TBC with Al_2O_3 overlay coating before and after exposure
(A: TBC with as-deposited overlay Al_2O_3 ; B: after exposure;
C: after partially removing Al_2O_3 overlay after exposure)

Based on the XRD results, destabilization (D) could be obtained, as demonstrated in Fig.5. It clearly showed that Al_2O_3 overlay coating can 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.

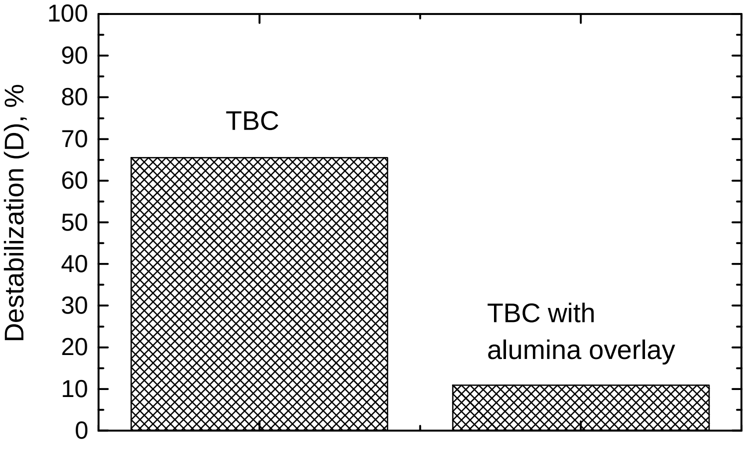

Fig.5 A comparing in destabilization (D) of the TBC with and without Al_2O_3 overlay coating

4.3.2 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.

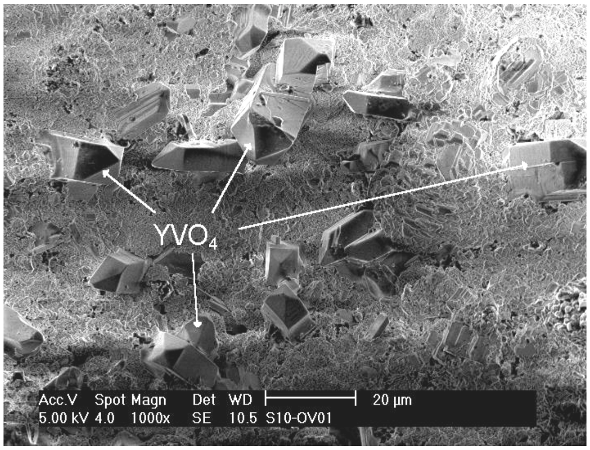

Fig.6 SEM surface micrograph of TBC after 10h hot corrosion test at 950°C showing the formation of YVO_4

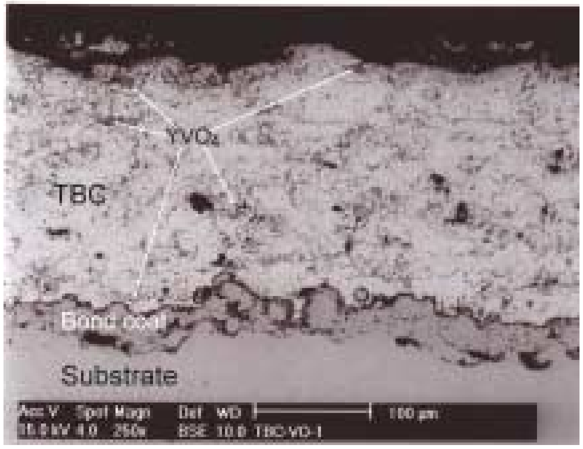

Fig.7 SEM microimages of cross-section of TBC after exposure at 950°C for 10h

In the new TBC system that has overlay of Al_2O_3 coating deposited by EB-PVD, the surface morphology was transformed to uniformly faceted shape after exposure due to the formation and growth of alumina crystal (Fig.8(a)). In addition, there were crystallites marked with A in Fig.8(b) that grew along a preferred direction. They contained O, Na, Al and S, as show in Fig.8(c). These crystallites were considered to be $NaAlO_2$ that seemed to be dense, as suggested by Chen et al [6]. However, the morphology of $NaAlO_2$ crystallites were different from that described in literature [6] where $NaAlO_2$ covered the APS sprayed Al_2O_3 coating. Due to partially spallation of Al_2O_3 grains, fine zirconia grains beneath the alumina cover layer could also be found on the surface in some large interspaces between alumina grains, as shown in Fig.8(d). It seemed that there was no evidence of the reaction between Al_2O_3 and V_2O_5. The thickness of Al_2O_3 coating after exposure was about the same as that of as-deposited coating (Fig.9). However, the crystal Al_2O_3 layer was less dense comparing to the amorphous layer before exposure because of the presence of interspaces between Al_2O_3 grains, and cracks in the Al_2O_3 overlay and at the interface between Al_2O_3 overlay and the TBC.

The main problem associated with the Al_2O_3 overlay is the cracking of the EB-PVD alumina coating during hot corrosion tests. The reason for the formation of cracks was considered to be (1) the conversion to crystal $\alpha-Al_2O_3$ from γ- Al_2O_3 is associated with a volume shrinkage that easily causes internal cracking; (2) the heating cycle causes tensile stresses in the alumina due to the mismatch in thermal expansion coefficient (TEC) between alumina (TEC $\approx 8-9\times10^{-6}/^{o}C$) and zirconia (TEC $\approx 11-13\times10^{-6}/^{o}C$), which will very easily crack under this tensile straining.

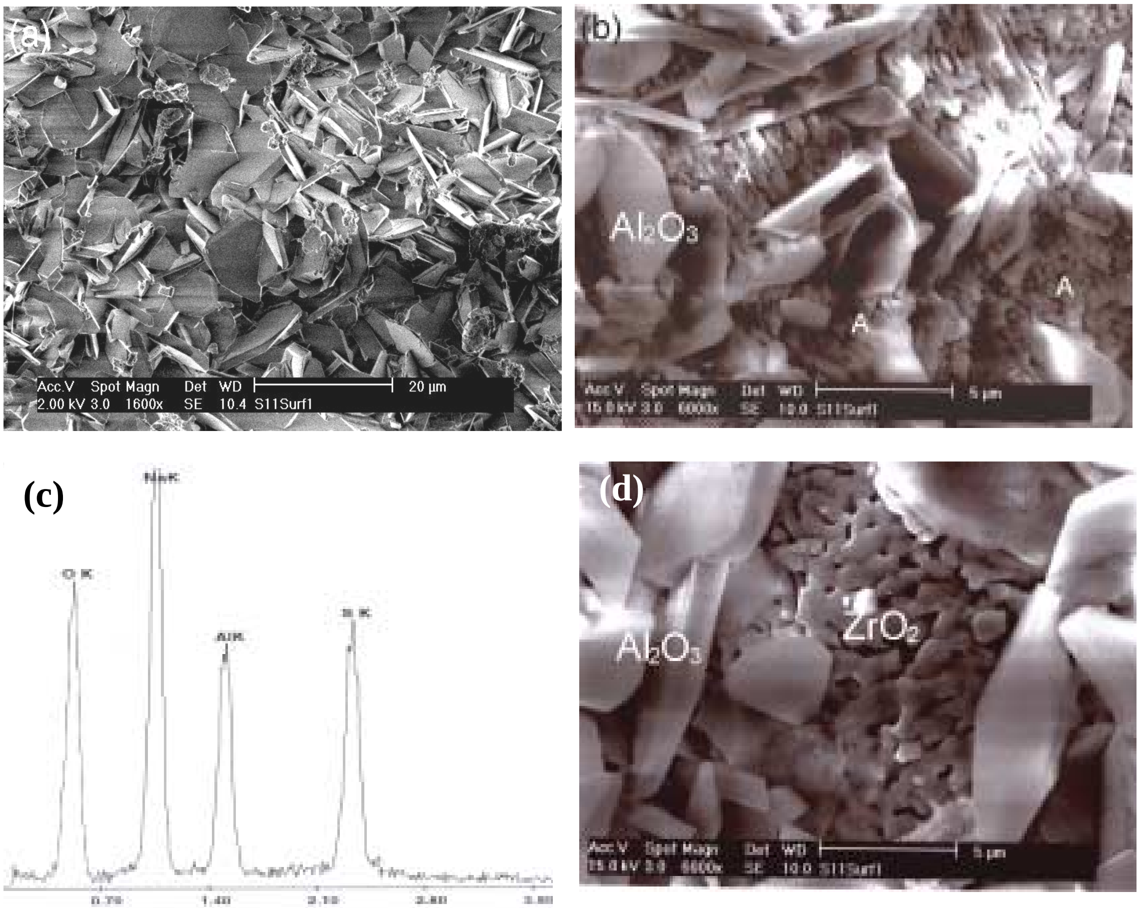

Fig.8 SEM surface micrograph of TBC with overlay Al_2O_3 coating after exposure for 10h at 950^{o}C. (a) faceted Al_2O_3 grains on the surface; (b)crystalline marked with A; (c) composition in A indicated in (b); (d) ZrO_2 on the surface

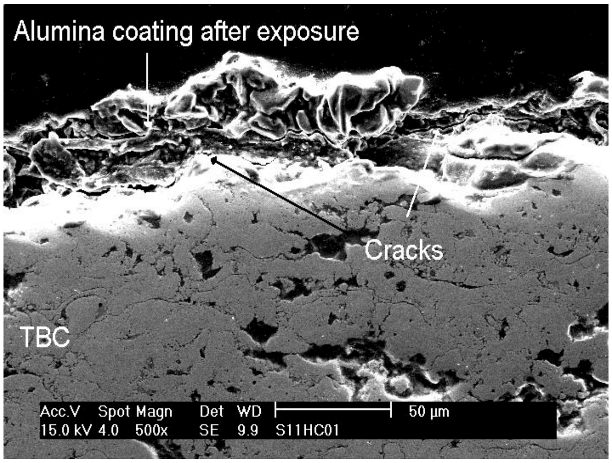

Fig.9 SEM microimages of cross-section of TBC with Al_2O_3 coating after exposure at 950C for 10h (no evidence of reaction products YVO_4 has been found)

5. PLANS FOR THE NEXT REPORTING PERIOD

Currently we have finished processing the overlay Al_2O_3 on the TBC samples by HVOF in collaboration with State University of New York at Stony Brook. Hot corrosion testing of TBC with HVOF Al_2O_3 coating under Na_2SO_4 + 5%V_2O_5 in a furnace with an air atmosphere will be carried out. The mechanisms of cracking of EB-PVD alumina layer during hot corrosion will also be investigated. The hot corrosion test of TBC with EB-PVD Al_2O_3 coating will be again performed. 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.

6. CONCLUSION

An overlay Al_2O_3 coating with 25 μm thickness has been successfully deposited on TBC. It has been found that overlay Al_2O_3 coating deposited by EB-PVD was dense, continues and adherent to the TBC. In hot corrosion tests, Al_2O_3 coating rarely reacted with the molten salts. After exposure to the molten Na_2SO_4 + 5%V_2O_5 salts, just a few M-phase of zirconia was formed and no YVO_4 could be detected comparing to the conventional TBC system. As a result, Al_2O_3 coating play a key role in preventing the TBC from the attack by molten salts, although there were some cracks in overlay Al_2O_3 coating and at the Al_2O_3/TBC interface formed during hot corrosion tests.

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