

# **Impermeable thin $\text{Al}_2\text{O}_3$ 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, the overlay of  $\text{Al}_2\text{O}_3$  coating was deposited on the TBC by EB-PVD techniques. Hot corrosion tests were carried out on the TBC with and without  $\text{Al}_2\text{O}_3$  coating in molten salts mixtures ( $\text{Na}_2\text{SO}_4 + 5\% \text{V}_2\text{O}_5$ ) at  $950^\circ\text{C}$  for different time up to 100h. 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  $\text{V}_2\text{O}_5$  to form  $\text{YVO}_4$ . The amount of M-phase, which was formed due to the leaching of  $\text{Y}_2\text{O}_3$  from YSZ, was increased with corrosion time.  $\text{Al}_2\text{O}_3$  overlay coating deposited by EB-PVD was dense, continues and adherent to the TBC. As a result, overlay  $\text{Al}_2\text{O}_3$  coating can prevent the YSZ from the attack by molten salts containing vanadium and decrease the penetration of salts into the YSZ along porous and cracks in the YSZ TBC. The amount of M-phase formed in YSZ covered with an overlay  $\text{Al}_2\text{O}_3$  is substantially lower than that formed in conventional YSZ TBC, even after 100h exposure to the molten salts.

In the next reporting period, the hot corrosion test of TBC with EB-PVD deposited  $\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  overlay to crystalline  $\alpha\text{-Al}_2\text{O}_3$  overlay. In addition, the effect of the thickness of overlay  $\text{Al}_2\text{O}_3$  on corrosion resistance will also be 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 [3-4]. The majority of present-day TBCs are 8%  $\text{Y}_2\text{O}_3$ - $\text{ZrO}_2$  type as they exhibiting superior performance in the absence of vanadium. The critical problem is that yttria reacts with the  $\text{V}_2\text{O}_5$  or  $\text{NaVO}_3$  to form  $\text{YVO}_4$  in the case of molten salt containing small amount of  $\text{V}_2\text{O}_5$  as follows:



This reaction depletes the  $\text{Y}_2\text{O}_3$  stabilizer from  $\text{ZrO}_2$  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 ( $\text{Al}_2\text{O}_3$ ) is a well-know oxide material that has diverse application as engineering ceramics. Alumina has high melting point and high hardness.  $\text{Al}_2\text{O}_3$  coating on metal substrate has exhibited good resistance of wear and erosion. This allows the potential application of  $\text{Al}_2\text{O}_3$  in gas turbines. However,  $\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  coating plays a role in hot-corrosion, although there is no hot-corrosion data for  $\text{Al}_2\text{O}_3$  in vanadate salts.

In the present study, a high-purity  $\text{Al}_2\text{O}_3$  overlay was deposited onto the surface of YSZ coating by means of EB-PVD. Hot corrosion tests were carried out at 950°C for 10min to 100h in the molten  $\text{Na}_2\text{SO}_4 + 5\% \text{V}_2\text{O}_5$  salts. 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  $\text{Al}_2\text{O}_3$  coating deposited by EB-PVD is consisted of  $\gamma$ -  $\text{Al}_2\text{O}_3$ . The  $\text{Al}_2\text{O}_3$  overlay was dense, continues and adherent to the TBC. Hot corrosion tests were done on TBC with and without the  $\text{Al}_2\text{O}_3$ . M-Phase in YSZ was formed after exposure to the molten salts. The amount of M-Phase in YSZ was increased with increasing corrosion time for both TBC and TBC/ $\text{Al}_2\text{O}_3$ . In the case that an overlay  $\text{Al}_2\text{O}_3$  coating covered on TBC surface, M-Phase in YSZ after corrosion was significantly lower than that in YSZ without overlay  $\text{Al}_2\text{O}_3$ . This result indicated that overlay  $\text{Al}_2\text{O}_3$  can prevent the YSZ from the attack by molten salts containing vanadium and substantially decrease the penetration of the salts into the YSZ TBC.

## 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%yttria (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  $\mu\text{m}$ , respectively. After receiving the TBC samples, overlay of  $\text{Al}_2\text{O}_3$  coating was deposited by EB-PVD in Penn. State University in collaboration with Dr. Jogender Singh. The thickness of  $\text{Al}_2\text{O}_3$  coating was approximately 20-30  $\mu\text{m}$ .

In order to compare the hot corrosion resistance of the TBCs with and without  $\text{Al}_2\text{O}_3$  coating, hot corrosion experiments were carried out. The samples were exposed to molten salts mixtures ( $\text{Na}_2\text{SO}_4 + 5\% \text{V}_2\text{O}_5$ ) by placing them into a still air furnace at 950°C for 10min to 100h 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  $\text{YVO}_4$ ). XRD patterns were first obtained from the samples (TBC and TBC+ $\text{Al}_2\text{O}_3$  overlay) before the molten salt exposure. After exposure, the samples were cooled down to room temperature in the furnace. The exposed samples were cleaned in distilled water. XRD analyses were then carried out to the exposed samples. The extent of destabilization (D) of the YSZ TBC was estimated by

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

Where T is the height of the zirconia tetragonal (111) peak, and M is the height of the zirconia monoclinic ( $1\bar{1}\bar{1}$ ) peak in XRD test. For the sample of TBC+ $\text{Al}_2\text{O}_3$  overlay, in order to

detect the same depth as that of TBC without  $\text{Al}_2\text{O}_3$  overlay, XRD test was done again on the sample whose overlay  $\text{Al}_2\text{O}_3$  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  $100\ \mu\text{m}$  and  $250\ \mu\text{m}$ , 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.

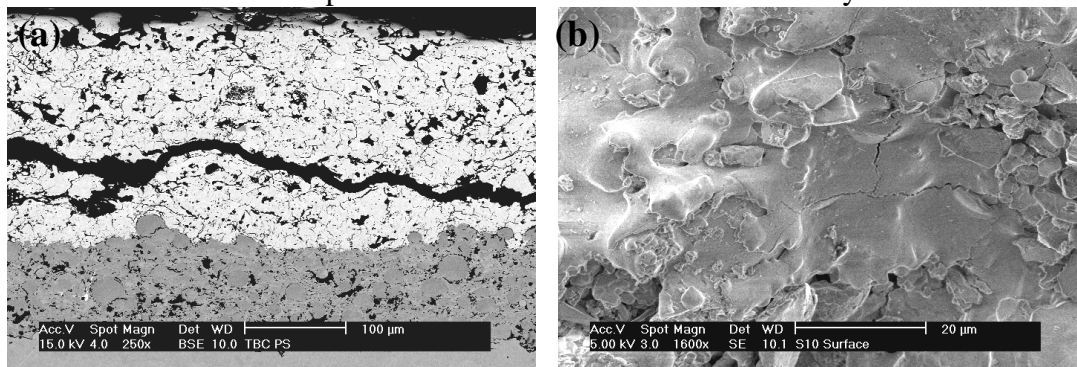


Fig.1 SEM micrographs of (a) cross-section and (b) surface of as-sprayed TBC

### 4.2 Microstructure of the overlay $\text{Al}_2\text{O}_3$ coating

Fig.2 shows the cross-section and surface SEM micrograph of the TBC with  $\text{Al}_2\text{O}_3$  overlay coating sputtered by EB-PVD. It is seen that the  $\text{Al}_2\text{O}_3$  coating is dense and adherent to the TBC. The thickness of the  $\text{Al}_2\text{O}_3$  coating was estimated to be about  $25\ \mu\text{m}$ . 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  $\gamma - \text{Al}_2\text{O}_3$  peaks indicated either nanosize crystallites or stress with in the overlay  $\text{Al}_2\text{O}_3$  coating.

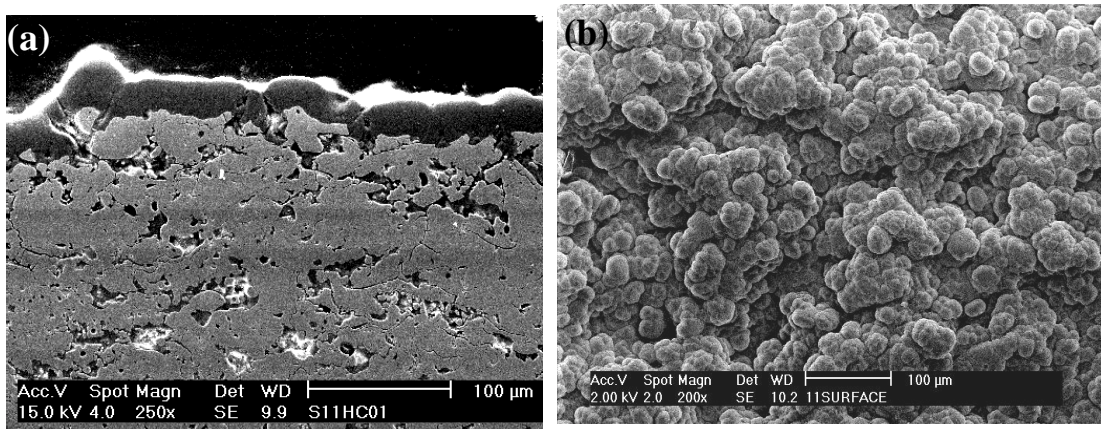


Fig.2 SEM micrographs of (a) cross-section and (b) surface of TBC with overlay  $\text{Al}_2\text{O}_3$  coating

### 4.3 Hot corrosion tests

#### 4.3.1 XRD analyses on TBC and TBC/ $\text{Al}_2\text{O}_3$ 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  $\text{ZrO}_2$  (A in Fig.3). After exposure to the molten mixture of salts of  $\text{Na}_2\text{SO}_4 + 5\% \text{V}_2\text{O}_5$  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  $\text{Y}_2\text{O}_3$  from YSZ resulting from the reaction of  $\text{Y}_2\text{O}_3$  with  $\text{V}_2\text{O}_5$  to form  $\text{YVO}_4$  (which was found in XRD patterns) according the reaction (1) indicated in Introduction.

For the TBC with overlay  $\text{Al}_2\text{O}_3$  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  $\text{YVO}_4$  peaks could be detected. Once the sample was heated during exposure, a part of  $\gamma - \text{Al}_2\text{O}_3$  in the coating was translated to crystalline  $\alpha - \text{Al}_2\text{O}_3$ . In addition, it seemed that no reaction products between  $\text{Al}_2\text{O}_3$  and mixed molten salts could be identified from the XRD results. From the XRD patterns of the sample whose  $\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  overlay coating.

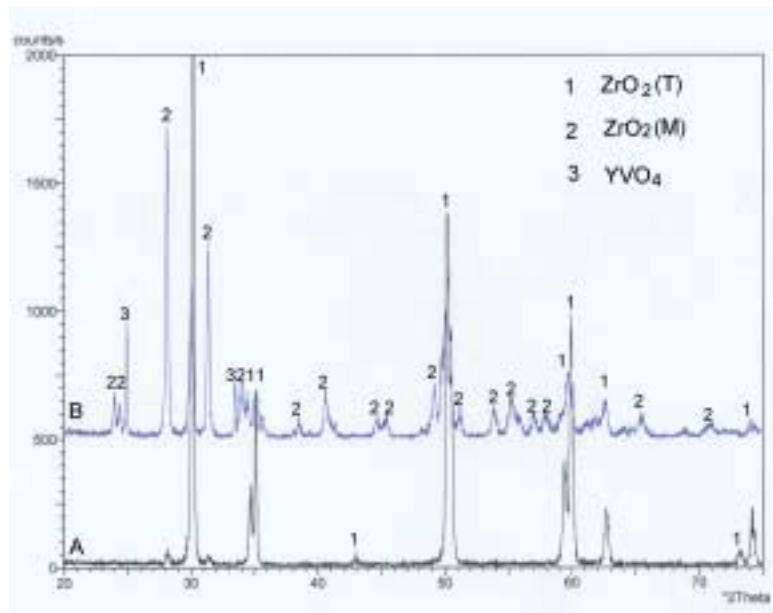


Fig.3 XRD patterns of TBC before exposure (A) and after exposure (B) to the molten salts

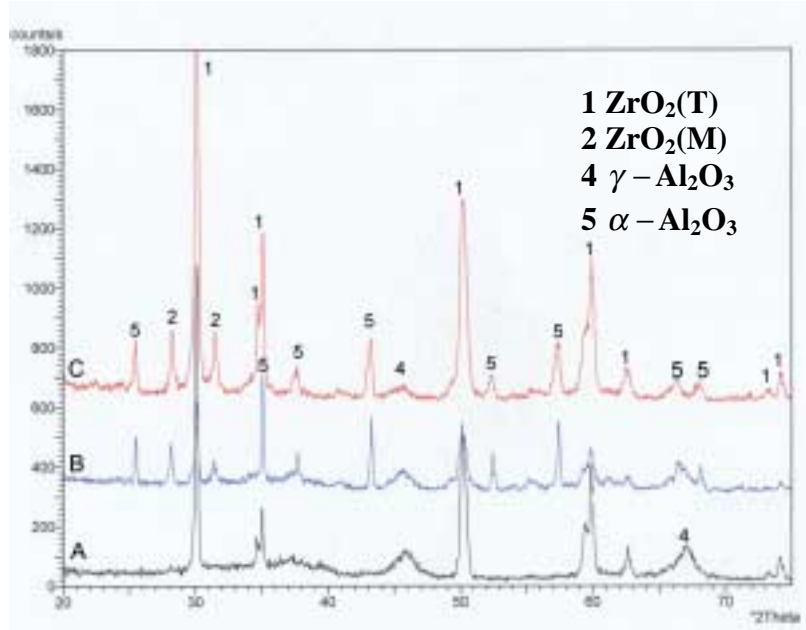


Fig.4 XRD patterns of TBC with  $\text{Al}_2\text{O}_3$  overlay coating before and after exposure  
 (A: TBC with as-deposited overlay  $\text{Al}_2\text{O}_3$  ; B: after exposure;  
 C: after partially removing  $\text{Al}_2\text{O}_3$  overlay after exposure)

#### 4.3.2 Effect of exposure time on hot corrosion behaviors of TBC and TBC/ $\text{Al}_2\text{O}_3$ samples

Based on the XRD results, destabilization (D) of the samples could be obtained. As demonstrated in Fig.5, the amount of M-phase formed in YSZ for both the TBC and TBC/ $\text{Al}_2\text{O}_3$  system was increased with increasing exposure time. But it clearly showed that destabilization (D) in TBC/ $\text{Al}_2\text{O}_3$  system is much lower than that in TBC, indicating that  $\text{Al}_2\text{O}_3$  overlay coating can prevent the YSZ from hot corrosion by molten salts containing vanadium and substantially decrease the penetration of salts into the YSZ TBC.

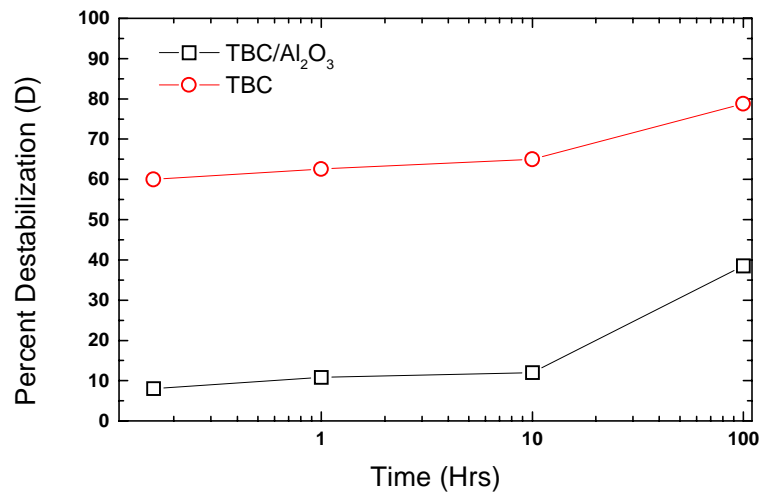


Fig.5 Effect of corrosion time on destabilization (D) of the TBC with and without  $\text{Al}_2\text{O}_3$  overlay coating



### 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  $\text{YVO}_4$ . This was consistent with the results of XRD analyses in which the peaks of  $\text{YVO}_4$  were clearly shown. From SEM microimages of cross-section (Fig.7), it was found that  $\text{YVO}_4$  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.

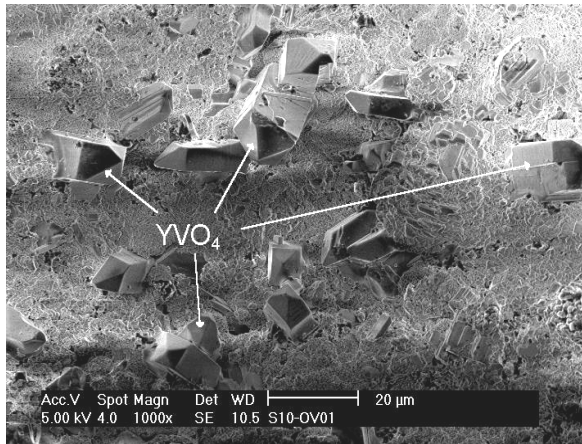


Fig.6 SEM surface micrograph of TBC after 10h hot corrosion test at 950°C showing the formation of  $\text{YVO}_4$

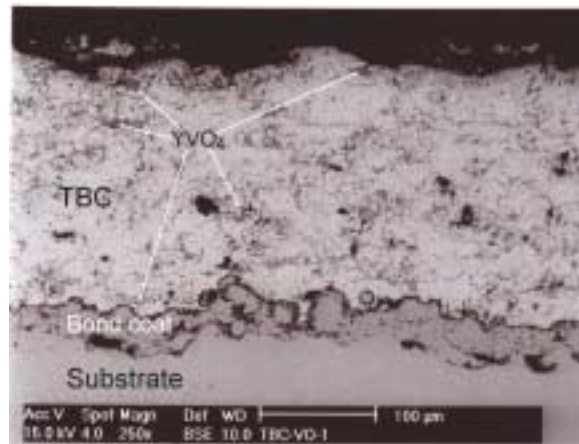


Fig.7 SEM microimages of cross-section of TBC after exposure at 950°C for 10h

In the new TBC system that has overlay of  $\text{Al}_2\text{O}_3$  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. These crystallites were considered to be  $\text{NaAlO}_2$  that seemed to be dense, as suggested by Chen et al [6]. It seemed that there was no evidence of the reaction between  $\text{Al}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ . The overlay  $\text{Al}_2\text{O}_3$  was still continues and adherence to the TBC. The thickness of  $\text{Al}_2\text{O}_3$  coating after exposure was about the same as that of as-deposited coating (Fig.9).



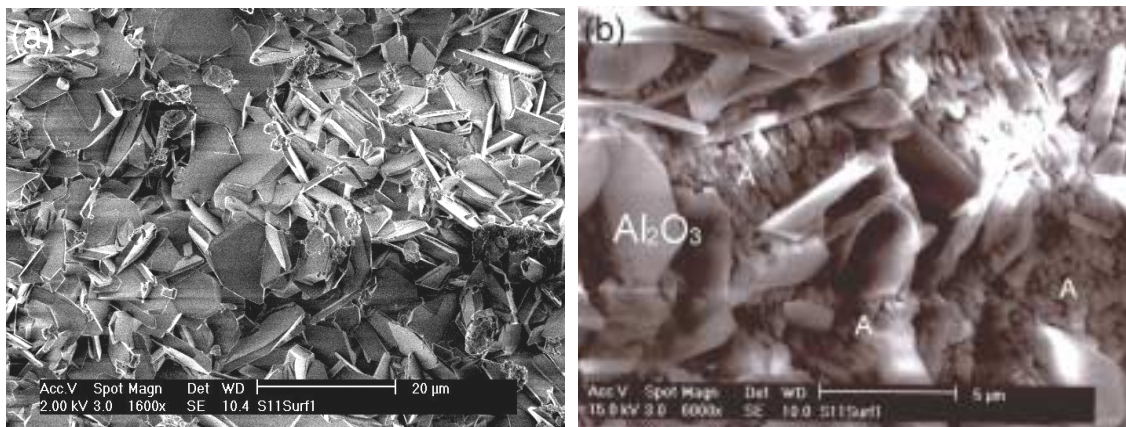


Fig.8 SEM surface micrograph of TBC with overlay  $\text{Al}_2\text{O}_3$  coating after exposure for 10h at  $950^\circ\text{C}$ . (a) faceted  $\text{Al}_2\text{O}_3$  grains on the surface; (b) crystalline marked with A;

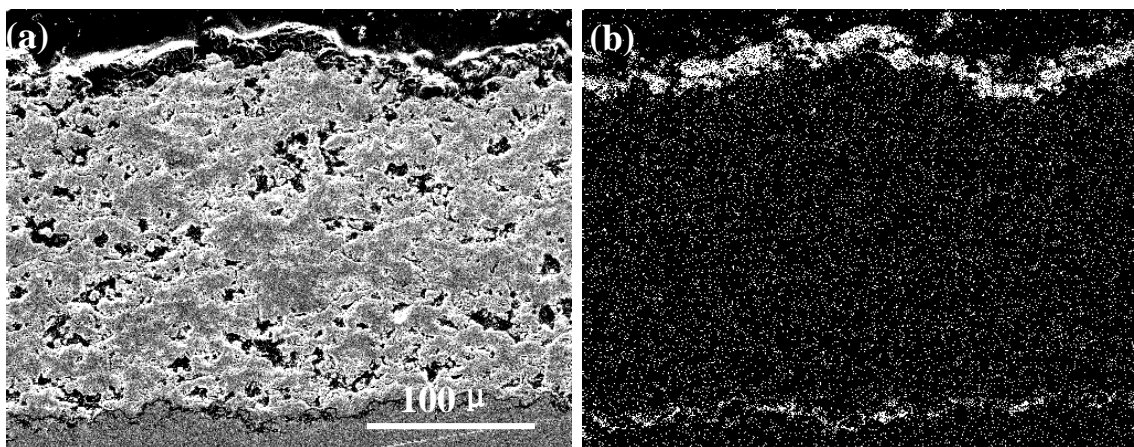


Fig.9 SEM microimages of cross-section of TBC with  $\text{Al}_2\text{O}_3$  coating after exposure at  $950^\circ\text{C}$  for 10h. (a) SEM and (b)  $\text{Al } K_\alpha$

The main problem associated with the  $\text{Al}_2\text{O}_3$  overlay is the cracking of the EB-PVD alumina coating during hot corrosion tests, as shown in Fig.9. The reason for the formation of cracks was considered to be (1) the conversion to crystal  $\alpha - \text{Al}_2\text{O}_3$  from  $\gamma - \text{Al}_2\text{O}_3$  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 ( $\text{TEC} \approx 8 - 9 \times 10^{-6} / ^\circ\text{C}$ ) and zirconia ( $\text{TEC} \approx 11 - 13 \times 10^{-6} / ^\circ\text{C}$ ), which will very easily crack under this tensile straining.

## 5. PLANS FOR THE NEXT REPORTING PERIOD

In the next reporting period, the hot corrosion test of TBC with EB-PVD deposited  $\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  overlay to crystalline  $\alpha - \text{Al}_2\text{O}_3$  overlay. In addition, the effect of the thickness of overlay  $\text{Al}_2\text{O}_3$  on corrosion resistance will also be investigated.

## 6. CONCLUSION

An overlay  $\text{Al}_2\text{O}_3$  coating with thickness of 25  $\mu\text{m}$  has been successfully deposited on TBC. It has been found that overlay  $\text{Al}_2\text{O}_3$  coating deposited by EB-PVD was dense, continues and adherent to the TBC. In hot corrosion tests,  $\text{Al}_2\text{O}_3$  coating rarely reacted with the molten salts. After exposure to the molten  $\text{Na}_2\text{SO}_4 + 5\% \text{V}_2\text{O}_5$  salts at  $950^\circ\text{C}$  up to 100h, just a few M-phase of zirconia was formed and no  $\text{YVO}_4$  could be detected comparing to the conventional TBC system. As a result,  $\text{Al}_2\text{O}_3$  coating play a key role in preventing the TBC from the attack by molten salts.

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