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, a thin and dense $a - Al_2O_3$ overlay has been deposited on the YSZ surface by the composite-sol-gel route (CSG). The YSZ substrates were dipped with boehmite sol containing calcined $a - Al_2O_3$ particles, dried to form a gel film and calcined at 1200^oC to form a -Al_2O_3 overlay. Hot corrosion tests were carried out on the TBCs with and without Al_2O_3 coating in molten salt mixtures (Na_2SO_4 + 5%V_2O_5) at 950^oC for 10 hours.

The results showed that besides a thin and dense alumina overlay with the thickness of about 100-500 nm formed on the YSZ surface, the microcracks and porous near the surface in YSZ was also occupied by alumina because of penetration of the low viscosity precursor. As a result, the Al_2O_3 overlay remarkably refrained the infiltration of the molten salt into the YSZ coating. The amount of M-phase in the TBC coating with Al_2O_3 overlay was substantially reduced comparing to that without alumina overlay.

In the next reporting period, we will prepare the alumina overlay by CSG route with different thickness and study the hot corrosion mechanism of YSZ TBC with thin Al_2O_3 overlay coating produced by CSG.

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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 the molten salts can enter the porous TBCs and then yttria reacts with the molten salts containing V_2O_5 or $NaVO_3$ to form YVO_4 in the case of molten salt containing small amount of V_2O_5.

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, it is hoped that by forming a dense overlay on the outer surface of YSZ coating and sealing the pores and microcracks only near the YSZ coating surface, it would be possible to reduce permeability to molten salts and gases while maintaining good thermal characteristics of the coating.

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 [5]. 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 increasing the hot-corrosion resistance.

In the present work, we utilized sol-gel route to form a dense overlay with liquid precursors of alumina ceramics and seal porous within YSZ TBC through infiltration. Dip coating techniques were employed for the formation of alumina overlay. Hot corrosion tests of YSZ TBCs with and without alumina overlay were carried out by expose the samples to Na_2SO_4+5%V_2O_5 molten salt at 950^oC for 10 h. By using XRD, SEM and EDX analyses, the microstructure, hot corrosion behaviors of the surface modified TBC system with alumina overlay were described in comparison with the conventional TBC system.

2. EXECUTIVE SUMMARY

Thin and dense alumina overlay (60-1000 nm) has been successfully deposited on the surface of YSZ by the composite-sol-gel dip coating route with dipping solution consisted of 30cm^3 of 1 mol dm^{-3} boehmite sol mixed with 20cm^3 aqueous polyvinyl alcohol (PVA) solution at a concentration of 3.5g per 100cm^3 and 5 g calcined $a - Al_2O_3$ particles (300 nm) followed by calcinations at 1200^oC. CSG alumina overlay remarkably refrained the infiltration of the molten salt into the YSZ coating. The amount of M-phase in the TBC coating with Al_2O_3 overlay was substantially reduced comparing to that without alumina overlay.

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 mm, respectively. Before sol-gel coating treatment, the YSZ TBCs were cleaned with acetone in an ultrasonic bath and dried at 80^oC. The preparation of alumina coating was carried out by dip-coating method with boehmite sol.

A boehmite ($g - AlOOH$) sol was prepared under the following conditions. A mol of Aluminum isopropoxide [$Al(OC_3H_7)_3$] was added into an excess of distilled water (Al/H_2O=1:100) at 80-85^oC under vigorous stirring that was maintained for an hour allowing isopropanol to boil off. Nitric acid (0.07mol) was than added, to peptize the hydroxide precipitate. The reaction vessel was then closed and maintained for 24h at 90^oC to obtain a clear sol. In order to avoid cracking of the gel layer during drying and calcinations [6], organic additive of polyvinyl alcohol (PVA, mol wt 75000 Da) were added to the dipping solution (sol). In addition, to increase the yield of a solid material and decrease densification strain to avoid cracking, secondary ceramic particles of calcined $a - Al_2O_3$ (0.3 µm) were dispersed in the sol. This sol-gel method was called composite-sol-gel (CSG). A typical dipping solution used in this work for the synthesis of alumina overlay consisted of 30cm^3 of 1 mol dm^{-3} boehmite sol (prepared according to above procedure) mixed with 20cm^3 aqueous PVA solution at a concentration of 3.5 g per 100cm^3 and 5 g $a - Al_2O_3$ particles.

The YSZ substrate was dipped into sol and withdrawn at a speed of 2 cm/min and then dried at 80^oC to get a gel film. The samples with gel film were heated to 600^oC for 10h at a heating rate of 1^{o}C/min, and then heated at 1200^{o}C at 1^{o}C/min for 1h allowing the gel film to transform to $a - Al_2O_3$. The samples then were cooled down to room temperature at 1 ^{o}C/min.

Hot corrosion test was performed on the TBCs with and without Al_2O_3 coating. The TBCs plates were coated with 150 mg cm^{-2} salt mixture by spraying an aqueous solution of 95wt%Na_2SO_4 + 5wt%V_2O_5 (1000 g l^{-1}), then placed into a still air furnace, and isothermally held at 950^{o}C for 10 hours. After exposure, the samples were cooled down to room temperature in the furnace. After hot corrosion testing, the exposed samples were cleaned in de-ionized water. The Philips PW1700 diffractometer was then employed to analyze the corrosion products in the exposed samples.

The surface morphology of the YSZ before and after CSG coating treatment was examined using a scanning electron microscope (SEM). A small portion cut from the samples was polished for cross-section observation. SEM was also used to determine the alumina overlay thickness. The structure of the resulting $a - Al_2O_3$ overlay was characterized by X-ray diffraction (XRD). After hot corrosion, the microstructure, hot corrosion behaviors of the surface modified TBC system with alumina overlay were described in comparison with the conventional TBC system.

4. RESULTS AND DISCUSSION

4.1 Characteristics of coatings before corrosion

Fig.1 shows SEM surface morphology of as-sprayed YSZ. The as-sprayed YSZ had a typical APS microstructure [5]. It was visible that there were many microcracks (0.1~1 mm width) and porous (3-20 mm) on the rough surface of the TBC.

The secondary- electron and backscattered-electron morphologies of the YSZ surface after dip coating with boehmite sol followed by calcined at 1200^{o}C are shown in Fig.2. The surface morphology of YSZ after modification by CSG dip coating revealed denser structure comparing to that before dip coating (Fig.1). Fig.2(c) shows that a microcrack of 0.5-1.0 mm width on the YSZ surface was filled and blocked by alumina particles whose size was in the range of 100-350nm. The dark regions in backscattered-electron morphologies (A in Fig.2(d)) had a lower average atomic weight in comparison to the white regions (B in Fig.2(d)). Results of EDS analyses (Fig.2(e) and Fig.2(f)) showed that the dark regions had higher Al content, i.e. thicker alumina overlay, than white region. This result indicated the thickness of alumina overlay was not uniform probably due to the rough character of the YSZ surface.

The cross-section of the YSZ with alumina overlay is shown in Fig.3. The thickness of alumina overlay was ranged from 100nm to 500nm. Occupation of the microcracks and porous near the surface in YSZ by alumina because of penetration of the low viscosity precursor could also be found (as shown in Fig.3 by arrows).

4.2 XRD analysis

X-ray diffraction analysis was performed on the specimen before and after hot corrosion testing. The X-ray diffraction pattern of the as-sprayed YSZ TBC demonstrated that it contained predominantly T-phase of ZrO_2 (Pattern A in Fig.4). After exposure to the molten salts at 950^{o}C for 10 h, high YVO_4 peaks was found in XRD analyses (Pattern B in Fig.4), implying the leaching of Y_2O_3 from YSZ by the reaction of Y_2O_3 with V_2O_5 or $NaVO_3$. As a result, the intensity of T-phase remarkable decreased, and a substantial amount of M-phase was formed due to the leaching of Y_2O_3 from YSZ. This was in agreement with previous investigation on hot corrosion of YSZ coating [1-2].

Fig.5 exhibited the XRD patterns of the YSZ/Al_2O_3 system before and after hot corrosion testing. The X-ray beam of the XRD diffractometer was focused on the surface of the Al_2O_3 overlay and corresponding results were shown in Pattern A and B in Fig.5. The Al_2O_3 overlay after calcined at 1200^{o}C showed the α-phase structure (Pattern A in Fig.5). After exposure to the molten salt, the results showed that the T-phase of ZrO_2 in the YSZ coating was still predominant (Pattern B in Fig.5). And a little amount of the M-phase of ZrO_2 and YVO_4 existed in the YSZ coating. It is worth to notice that peaks correspond to α- Al_2O_3 were still evident, indicating no evidence that the chemical reaction of the Al_2O_3 overlay with the molten salt had taken place. However, a peak with the *d* value of 2.445A (as shown by arrow in Fig.5) could be found on the corroded YSZ/Al_2O_3 sample, which was considered to be $CoAl_2O_4$ phase and will be discussed when SEM results are presented.

In order to evaluate the hot corrosion resistance of the TBCs with and without Al_2O_3 coating, the extent of destabilization (*D*) of zirconia was estimated by

$$D\,(\%) = \frac{M}{T+M} \times 100 \qquad (1)$$

Where *T* is the intensity of the zirconia tetragonal (111) peak, and *M* is the intensity of the zirconia monoclinic ($11\bar{1}$) peak in XRD tests. The destabilization fraction of zirconia (*D%*) was obtained as demonstrated in Fig.6. The destabilization fraction of zirconia in the YSZ coating without protection of Al_2O_3 overlay reached up to 60%, whereas the destabilization fraction of zirconia in the YSZ/Al_2O_3 system kept at about 8%. The destabilization fraction of zirconia in the YSZ/Al_2O_3 coating was much lower than that in YSZ coating without overlay, which indicated that the attack of YSZ by the molten salt was refrained due to the present of the Al_2O_3 overlay and blocking of cracks and pores in the YSZ by Al_2O_3 particles.

4.3 SEM observation

Visual examination of the surface of YSZ/Al_2O_3 coating found that the surface was white before corrosion and it became blue after corrosion. Further SEM examination results are shown in Fig.6. It can be seen that Al_2O_3 overlay still covered the almost YSZ surface, but the crystals of Al_2O_3 were coarser and less dense than those before exposure (Fig.6(a) and Fig.2(b)). Trace of Na was detected on coarser Al_2O_3 crystals region. In some regions, however, coarse and faceted crystals which filled in the porous and cracks on the YSZ surface were observed (Fig.6(b)). Those crystals consisted of Al, Co and O as well as a few Cr and Zr, as shown in Fig.6(c). The YSZ coating around those crystals was visible. Quantitative EDS analyses indicated those crystals contained 53at.%O, 28at.%Al and 14at.%Co. As a result, those crystals were identified to be $CoAl_2O_4$. $CoAl_2O_4$ could also be found in XRD analyses in Fig.5, which corresponded to the peak marked with arrow.

Fig.7 demonstrates the cross-section of composite YSZ/Al_2O_3 system after 10 h of exposure. Consistence with the surface morphology, alumina overlay was still adherent to the YSZ (Fig.7(a)). It is worthy of noticing that some of the pores and cracks within the YSZ coating were filled by $CoAl_2O_4$ (marked by arrows in Fig.7(b)), which was confirmed by the EDS analysis.

5. PLANS FOR THE NEXT REPORTING PERIOD

In the next reporting period, we will prepare the alumina overlay by CSG route with different thickness and study the hot corrosion mechanism of YSZ TBC with thin Al_2O_3 overlay coating produced by CSG.

6. CONCLUSION

In order to improve the hot corrosion resistance of conventional YSZ TBC system, a thin and dense Al_2O_3 overlay coating (100-500nm) has been successfully deposited on the surface of YSZ by the composite-sol-gel (CSG) route. The YSZ substrates were dip coated with dipping solution consisted of $30cm^3$ of 1 mol dm^{-3} boehmite sol mixed with $20cm^3$ aqueous polyvinyl alcohol (PVA) solution at a concentration of 3.5g per $100cm^3$ and 5 g alumina particles, dried at 80^oC to form a gel film and calcined at 1200^oC to form α -Al_2O_3 overlay. Hot corrosion tests were carried out on the TBCs with and without Al_2O_3 coating in molten salt mixtures (Na_2SO_4 + 5%V_2O_5) at 950^oC for 10 hours.

Because of this thin and dense alumina overlay on the YSZ surface and occupation of the microcracks and porous near the surface in YSZ by alumina resulting from the penetration of the low viscosity CSG precursor, the infiltration of the molten salt into the YSZ coating was remarkably refrained. After hot corrosion, the amount of M-phase in the TBC coating with Al_2O_3 overlay was substantially reduced comparing with that without the Al_2O_3 overlay.

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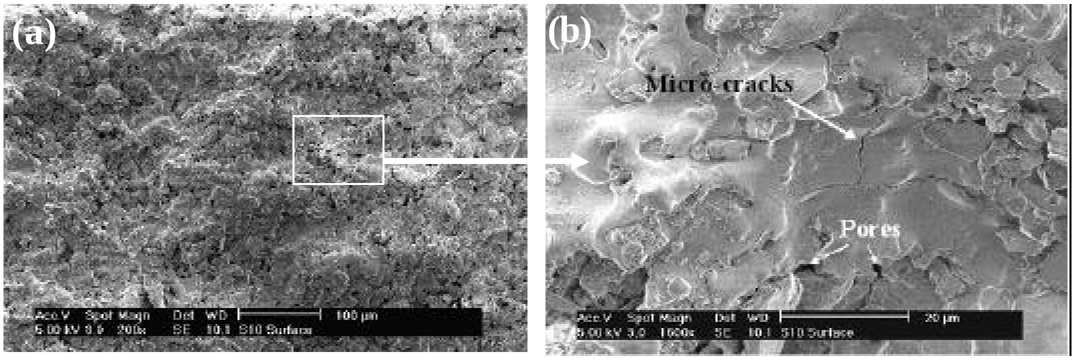

Fig.1 Surface morphology of as-sprayed TBC

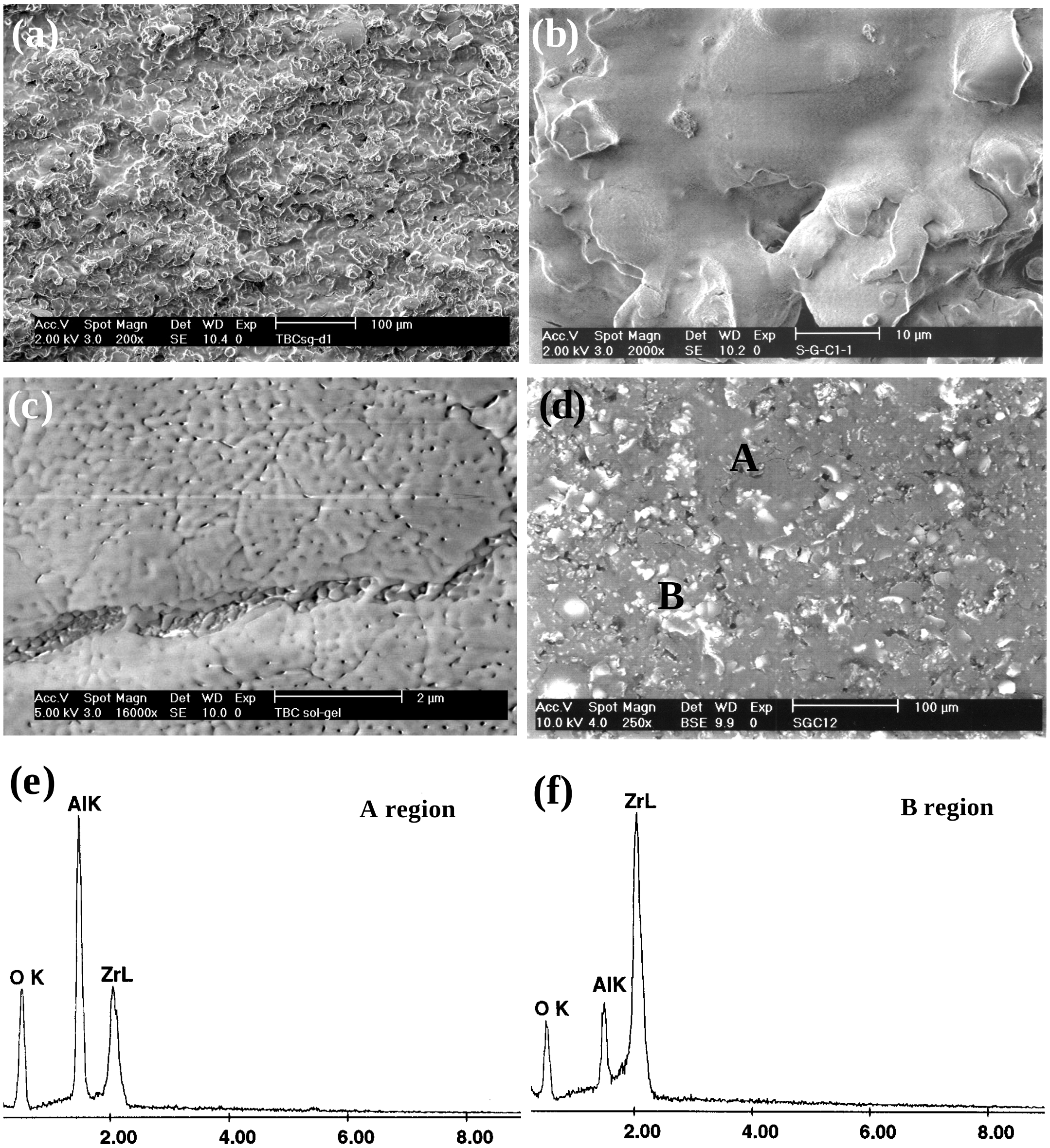

Fig.2 Surface morphology of YSZ deposited with CSG alumina coating

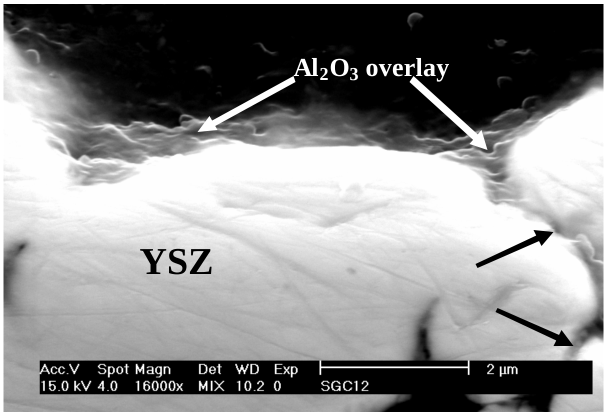

Fig.3 Cross-section of YSZ with CSG alumina overlay

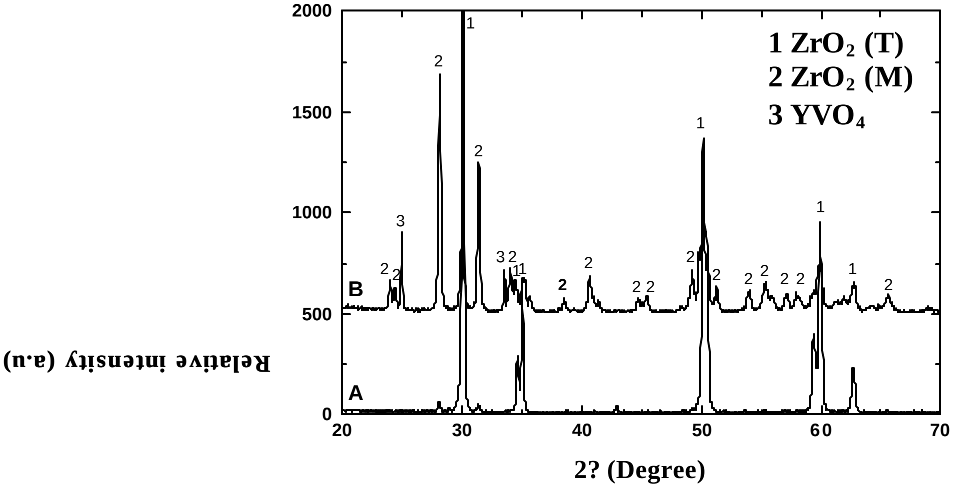

Fig.4 XRD patterns of TBC before exposure (A) and after exposure (B) to the molten salts

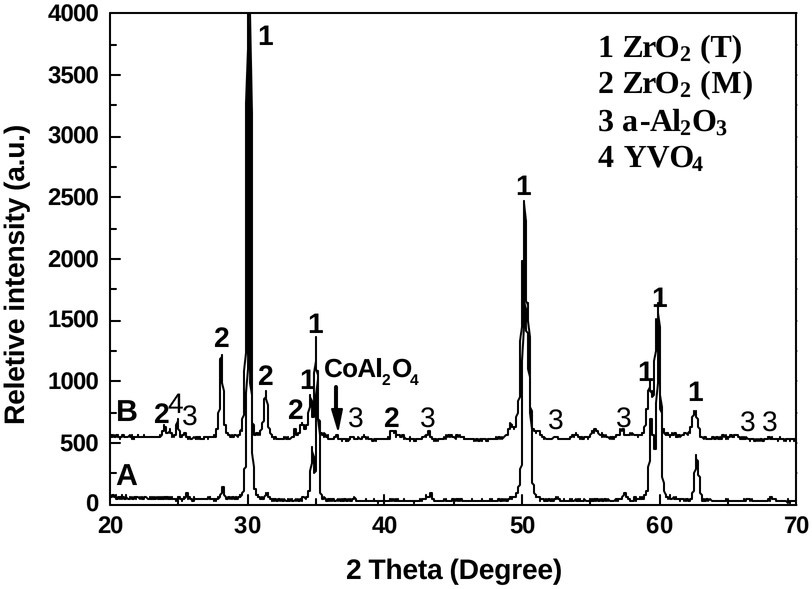

Fig.5 XRD patterns of YSZ coated with CSG alumina overlay before exposure (A) and after exposure (B) to the molten salts

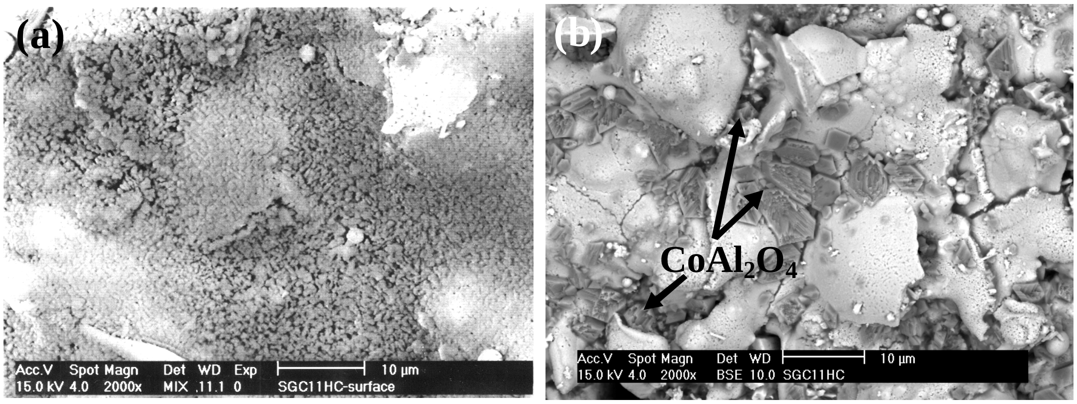

Fig.6 Surface photographs of YSZ with alumina overlay after exposure

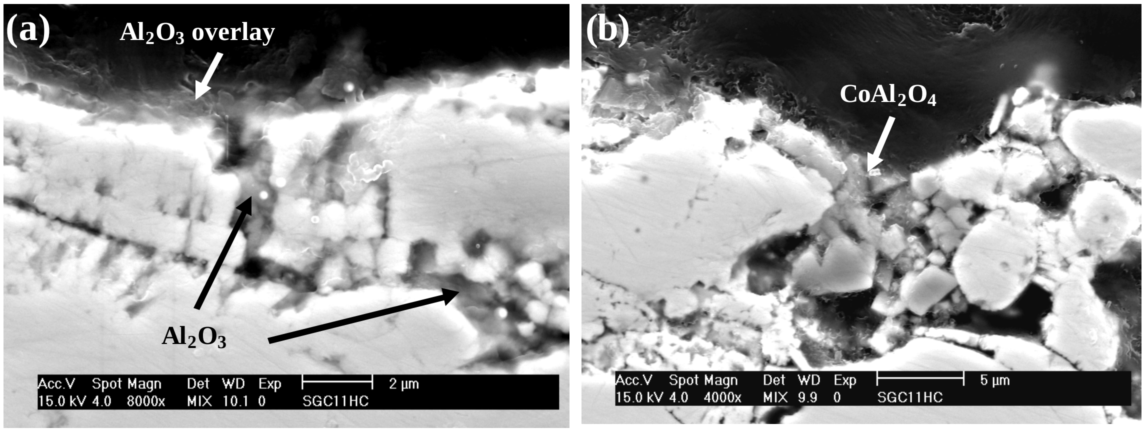

Fig.7 Cross-section of YSZ with alumina overlay after exposure