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

Quarterly Progress Report

Reporting Period Start Date: Sep. 1, 2002
Reporting Period End Date: Nov. 30, 2002
Principal Author: Scott X. Mao
Date Report was issued (Nov. 30, 2002)
DOE Award Number: DE-FC26-01NT41189

Department of Mechanical Engineering
University of Pittsburgh
3700 O'Hara St.
Pittsburgh, PA 15261
smao@engrng.pitt.edu, Tel: 412-624-9602

ABSTRACT

In order to improve the hot corrosion resistance of conventional YSZ TBC system, the Al_2O_3 overlay coating has been successfully produced on the surface of YSZ by the Sol-gel route. The YSZ substrates were coated with boehmite sol by dip coating process, dried to form a gel film and calcined at 1200^{o}C to form *a* -Al_2O_3 overlay. The microstructures of TBC and Al_2O_3 overlay were examined by scanning electron microscopy (SEM). The results showed that micro-pores ranged from 3 *mm* to 20 *mm* and micro-cracks could be clearly seen on the surface of APS YSZ coating. The thickness of alumina overlay increased with increasing the number of dip coating circles. The small microcracks (0.5-1.0 *mm* width) on the YSZ surface could be filled and blocked by calcined alumina particles, whereas large pores remained empty and the alumina overlay was un-continuous after one time dip coating circle. Alumina overlay thicker than 5*mm* obtained by five times dip coating circles largely cracked after calcinations. As a result, multiple dip coatings up to three times were ideal for getting high quality, crack-free and continuous overlay. The optimal thickness of alumina overlay was in the range of 2.5-3.5 *mm*.

In the next reporting period, we will study the hot corrosion behaviors of YSZ TBC with Al_2O_3 overlay coating produced by sol gel route by exposure the samples to molten salts mixtures (Na_2SO_4 + 5%V_2O_5) at 950^{o}C.

TABLE OF CONTENTS

LIST OF GRAPHICAL MATERIALS

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 YSZ TBC through infiltration. Dip coating techniques were employed for the formation of alumina overlay. The surface microstructures before and after sol-gel treatment as well as the alumina overlay were examined by SEM, EDX and XRD analyses.

2. EXECUTIVE SUMMARY

High quality, crack-free and continuous alumina overlay (2.5-3.5 mm) has been successfully produced on the surface of YSZ by the Sol-gel route through three times dip coating circles 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 calcinations at 1200^{o}C.

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^{o}C. 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^{o}C 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^{o}C 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). 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 3.5g per 100cm^3.

The YSZ TBC substrates were dipped into sol and withdrawn at a speed of 2 cm/min and then dried at 80^oC to get a gel film. This procedure could be iterated several times to increase the thickness of the gel film, as show in Fig.1

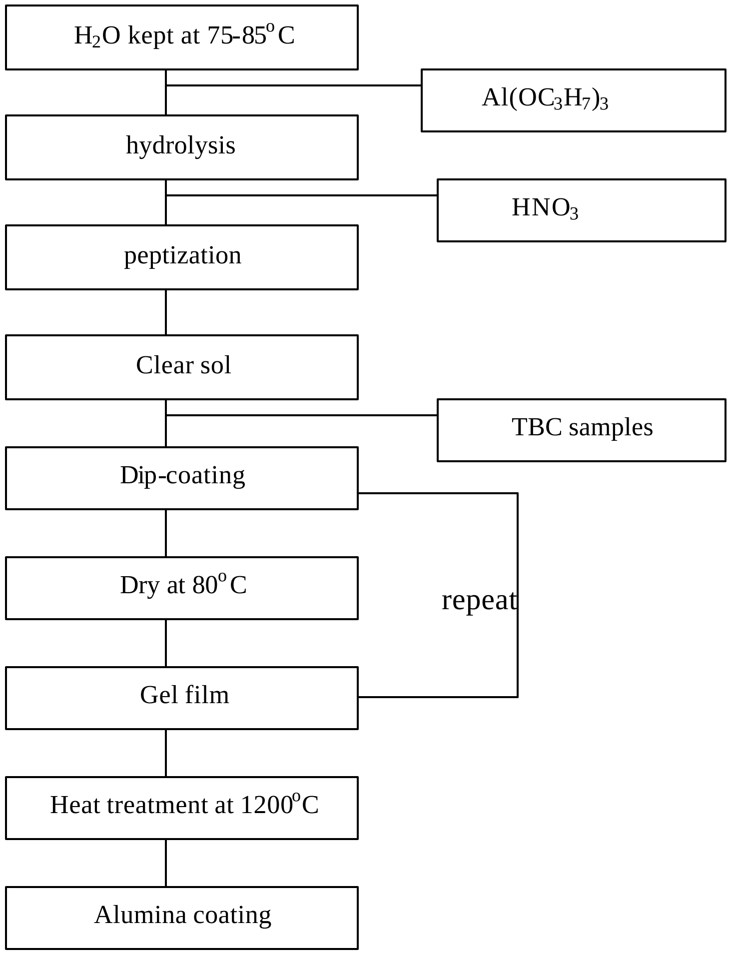

Fig. 1 Flow chart of the sol-gel processing of TBC sample

The samples with gel film were heated to 600^oC for 10h at a heating rate of 1 ^oC/min, and then heated at 1200^oC at 1^oC/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 ^oC/min.

The surface morphology of the YSZ TBC before and after sol-gel coating treatment were 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).

4. RESULTS AND DISCUSSION

4.1 Surface morphology of YSZ TBC

Fig.2 shows SEM surface morphology of as-sprayed TBC. The as-sprayed TBC 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.

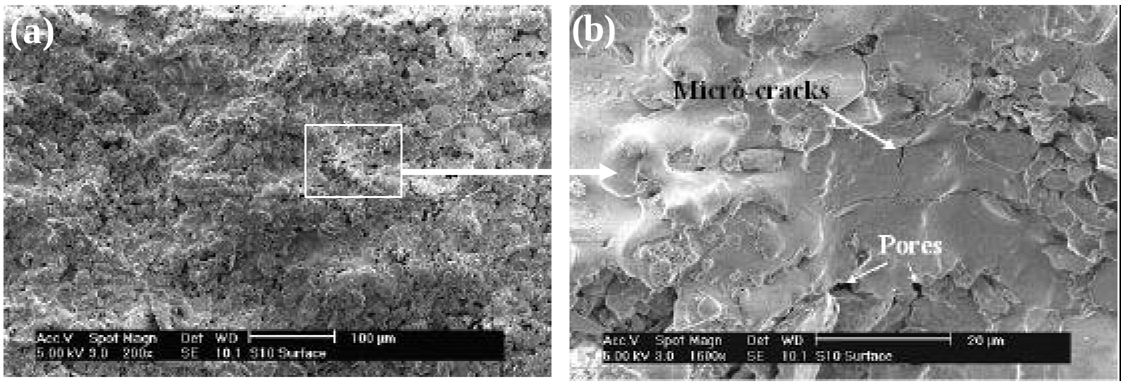

Fig.2 Surface morphology of as-sprayed TBC

4.2 Surface morphology of sol-gel modified YSZ TBC

The surface morphologies of the YSZ TBC after one time dip coating with boehmite sol and calcinations at 1200^{o}C are shown in Fig.3. It is clearly seen that the original rough YSZ surface had been modified by the sol-gel coating treatment. The surface morphology of YSZ after one time dip coating (Fig.3(a)) revealed denser structure comparing with that before dip coating (Fig.2). However, the outlines of the YSZ surface were still similar for both.

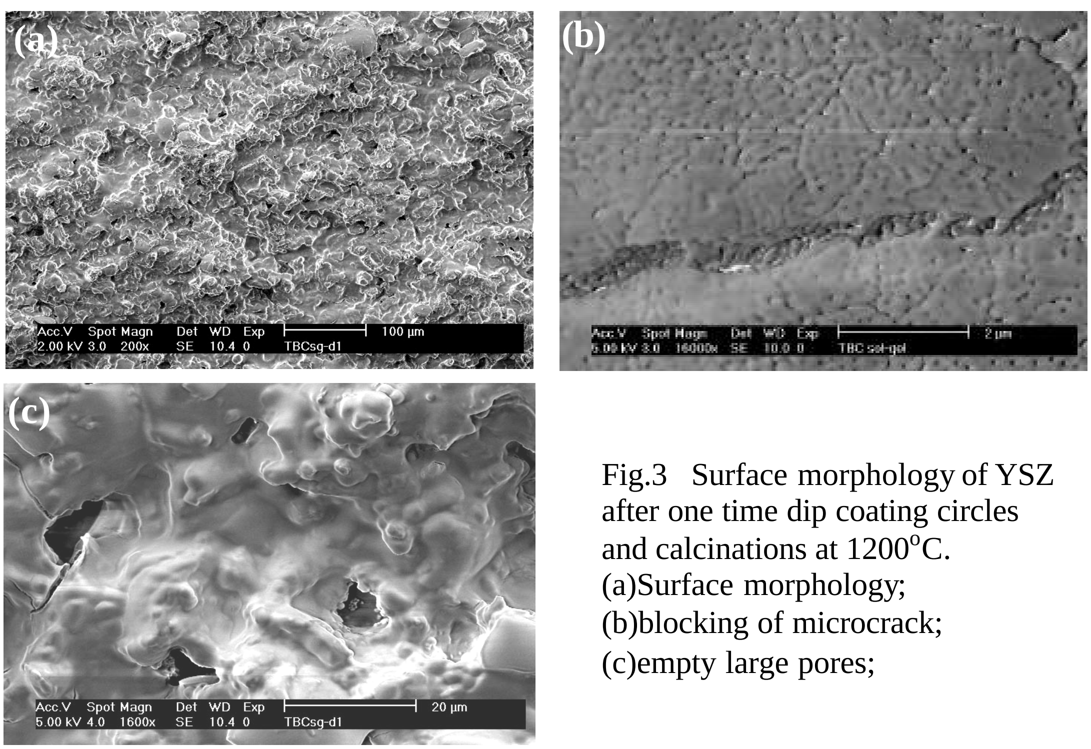

Fig.3 Surface morphology of YSZ after one time dip coating circles and calcinations at 1200^{o}C.
(a)Surface morphology;
(b)blocking of microcrack;
(c)empty large pores;

Fig.3(b) shows that a microcrack of 0.5-1.0 *mm* width on the YSZ surface was filled and blocked by calcinated alumina particles whose size was in the range of 100-250nm, whereas large pores remained empty (Fig.3(c)) because large shrinkage took place during drying and calcinations due to the high water content in the gel.

When the number of dip coating circles was increased to three times, the roughness of the YSZ surface was significantly decreased and the YSZ surface was completely covered by alumina overlay, the pores and microcracks could rarely be found in this case (Fig.4(a)). Fig.4(b) shows a typical image of a large pore (≈ 20*mm* in diameter) that had been filled by gelled sol and blocked, but cracked again after calcinations due to large stress concentration around the pore. As the dip coating circles was further increased to five times, however, a lot of cracks were formed within the calcined alumina overlay (Fig.5).

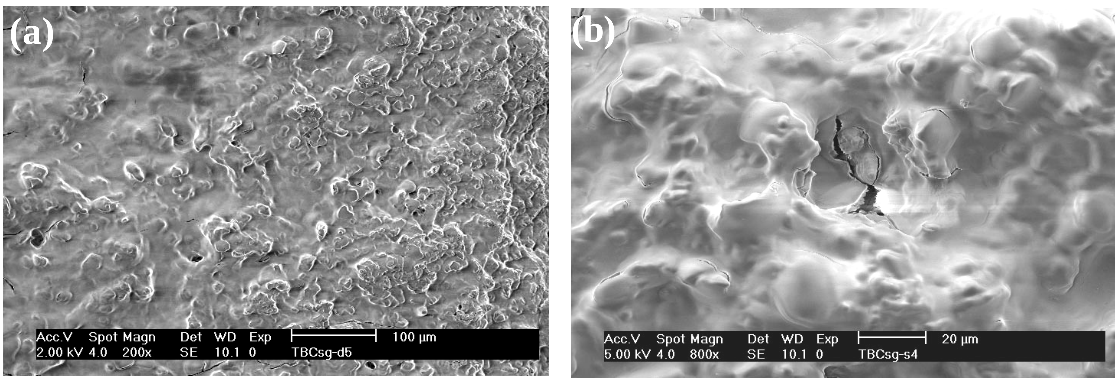

Fig.4 Surface morphology of YSZ after three times dip coating circles and calcinations at 1200°C. (a) Surface morphology; (b)blocking of large pores;

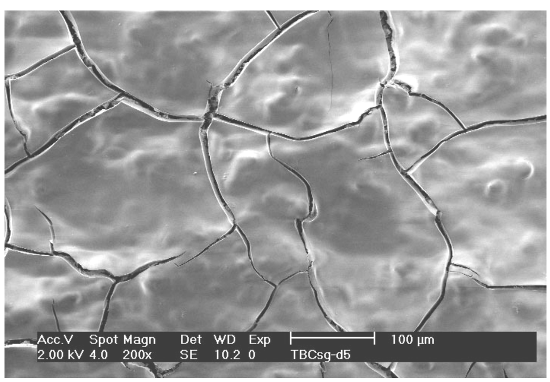

Fig.5 Surface morphology of YSZ after five times dip coating circles and calcinations at 1200°C, showing the formation of lot of cracks.

4.3 Cross-section observation of sol-gel modified YSZ TBC

The cross-section of the YSZ TBC with alumina overlay obtained with different dip coating circles are demonstrated in Fig.6. With one time dip coating circles, the alumina overlay was thin (1.0-1.8 *mm*) and un-continuous (Fig.6(a)). On contrary, a smooth and continuous alumina overlay with a thickness in the range of 2.8-3.5 *mm* was observed on the YSZ surface in the case of three times dip coating (Fig.6(b)). The thickness of alumina overlay with five times dip coating circles was more than 5 *mm*, and longitudinal cracks could be seen within the overlay (Fig.6(c)).

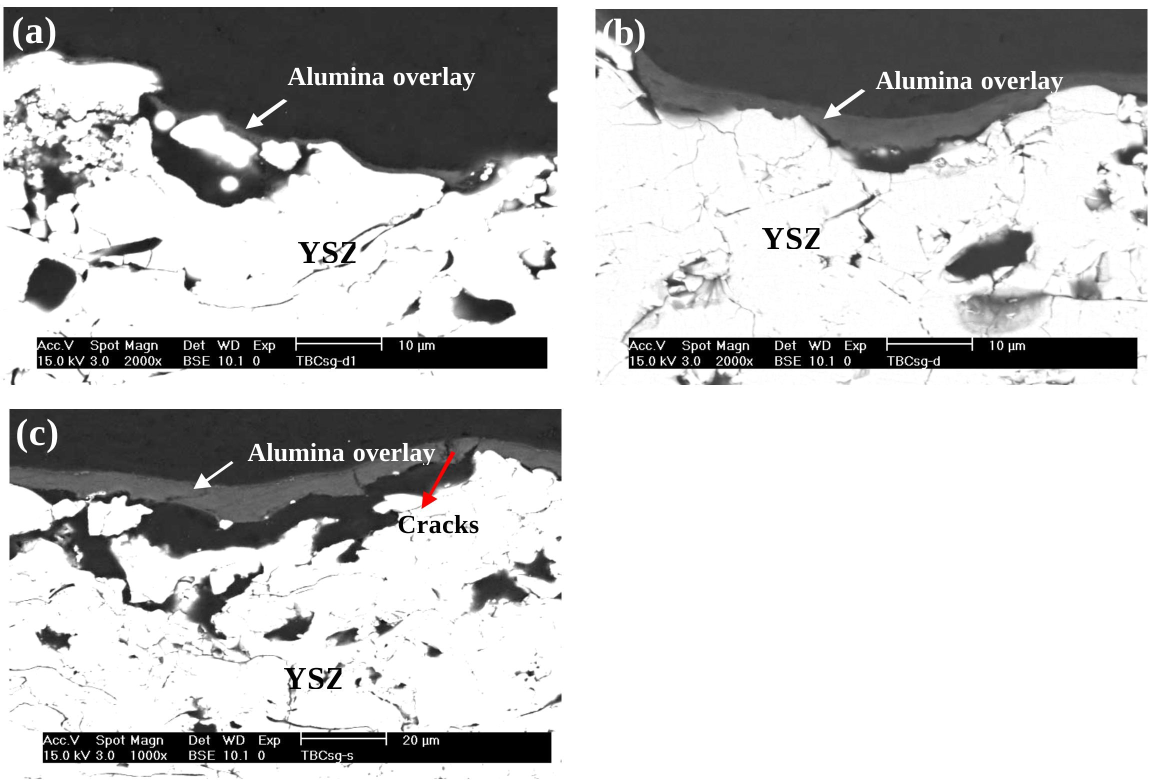

Fig.6 Microstructure of cross-section of YSZ after different times dip coating circles and calcinations at 1200^{o}C. (a) one time; (b)three times; (c) five times;

Fig.7 shows the variation of thickness of alumina overlay with number of coating circles, indicating that the thickness of the coating grew with the number of coating circles.

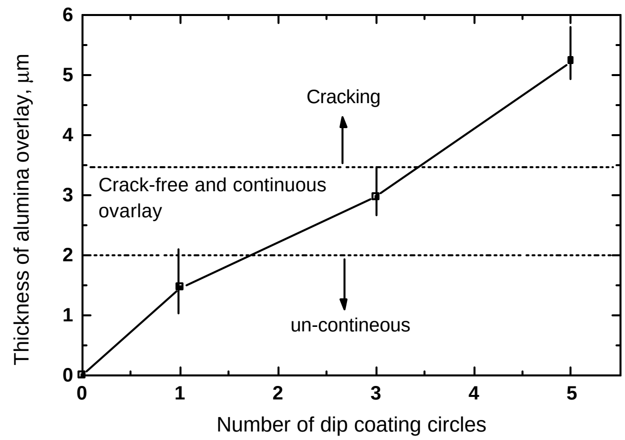

Fig.7 Effect of the number of dip coating circles on the thickness of alumina overlay.

Based on these results, it was suggested that a crack-free overlay could be obtained, as the thickness of alumina overlay is less than 3~3.5 mm. A very thin overlay less than 2 mm, however, was also less continuous because the YSZ substrate is very rough. On the other hand, when the thickness of alumina overlay was more than 5 mm, the overlay is easy to crack after calcinations. As a result, the thickness of the overlay should be optimized to be about 2.5-3.5 mm, as in the case that YSZ was coated with three times dip coating circles.

In addition, from the SEM cross-section micrographs shown in Fig.6, it was found that alumina overlay was separated from YSZ substrate in some locations at their interface. Fig.8 shows a typical microstructure where the outlines of alumina overlay and YSZ were a perfect match. This indicated that the sol could wet the YSZ and form a sol film that was adherent to the substrate. However, upon calcinations at high temperature, the YSZ will expands more than alumina overlay and a tensile stress will develops within alumina overlay 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). The thicker the alumina overlay, the larger the tensile stress. On the other hand, because of the high water content in the gel, large shrinkage took place during drying and calcinations. As a result, separation from the YSZ substrate and cracking of alumina overlay occurred during calcinations at high temperature.

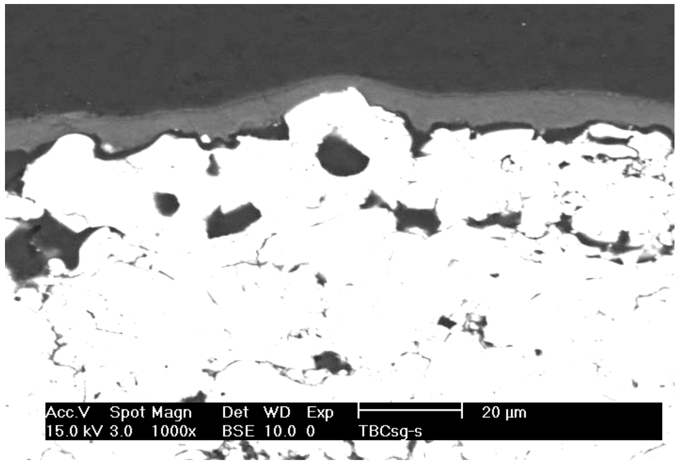

Fig.8 A typical microstructure showing perfect match of the outlines of alumina overlay and YSZ

Another phenomena that should be pointed out was that the pores near the YSZ surface were still empty although a continuous overlay thicker than 10 *mm* had been formed (Fig.8). Usually, the sol with low viscosity favors the penetration into the pores of the porous substrate, rather than the formation of a surface coating layer [7]. The morphology of YSZ coated with the present sol, shown in above, revealed the presence of a continuous surface layer, but absence of the penetration. This indicated that the sol used in the present work had relative higher viscosity. But we think the formation of a continuous alumina overlay using a sol with relative higher viscosity is more advantageous than the penetration with a low viscosity sol to protection of YSZ, as long as the overlay is crack-free.

If we use a sol with low viscosity (usually low viscosity corresponds a low concentration of alumina), although the sol can penetrate into the small pores, it is still difficulty to fill and block the pores because of the extreme small particles ranged from 2-20nm in the sol that does not match the pores size in YSZ. In addition, large shrinkage of the gel takes place during drying and calcinations due to the high water content in the gel.

5. PLANS FOR THE NEXT REPORTING PERIOD

In the next reporting period, we will study the hot corrosion behaviors of YSZ TBC with Al_2O_3 overlay coating produced by sol gel route described above by exposure the samples to molten salts mixtures (Na_2SO_4 + 5%V_2O_5) at 950°C.

6. CONCLUSION

In order to improve the hot corrosion resistance of conventional YSZ TBC system, the Al_2O_3 overlay coating has been successfully produced on the surface of YSZ by the Sol-gel 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, dried at 80^{o}C to form a gel film and calcined at 1200^{o}C to form a -Al_2O_3 overlay. The microstructures of TBC and Al_2O_3 overlay were examined by scanning electron microscopy (SEM). The main results of this study are as following:

(1) The thickness of alumina overlay increased with increasing the number of dip coating circles.

(2) The small microcracks (0.5-1.0 *mm* width) on the YSZ surface could be filled and blocked by calcined alumina particles, whereas large pores remained empty and the alumina overlay was un-continuous after one time dip coating circle.

(3) Alumina overlay thicker than 5 *mm* obtained by five times dip coating circles largely cracked after calcinations.

(4) Multiple dip coatings up to three times were ideal for getting high quality, crack-free and continuous alumina overlay.

(5) The optimal thickness of alumina overlay was in the range of 2.5-3.5 *mm*.

7. REFERENCES

[1] I.Gurrappa. Thermal barrier coating for hot corrosion resistance of CM 247 LC superalloy. J. Mater.Sci.Lett., 17(1998)1267-1269

[2] R.L.Jones. Thermogravimetric study of the 800 **degree** reaction of zirconia stabilizing oxides with SO_3-$NaVO_3$. J. Electrochem.Soc., 1992, 10(39)2794-2799

[3] R.L.Jones. India as a hot corrosion-resistant stabilizer for zirconia. J.Am.Ceram.Soc., 1992, 75(7)1818-1821

[4] S.A.Muqtader and R.K.Sidhu. Destabilization behavior of ceria-stabilized tetragonal zirconia polycrystals by sodium sulphate and vanadium oxide melts. J.Mater.Sci.Lett., 12(1993)831-833

[5] H.C.Chen et al. Degradation of plasma-sprayed alumina and zirconia coatings on stainless stell during thermal cycling and hot corrosion. Thin solid films. 223(1992)56-64

[6] V. T. Zaspalis, W. Van Praag, K. Keizer et al. Synthesis and characterization of primany alumina, titania and binary membranes. J. Mater. Sci. 27(1992)1023-1035

[7] C. Agrafiotis and A. Tsetsekou. J. Euro. Ceram. Soc., 22(2002)423-434