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

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ABSTRACT

To improve the hot corrosion resistance of YSZ thermal barrier coatings, a 25 μm and a 2 μm thick Al_2O_3 overlay were deposited by HVOF thermal spray and by sol-gel coating method, respectively, onto to the surface of YSZ coating. Indenter test was employed to investigate the spalling of YSZ with and without Al_2O_3 overlay after hot corrosion. The results showed that Al_2O_3 overlay acted as a barrier against the infiltration of the molten salt into the YSZ coating during exposure, thus significantly reduced the amount of M-phase of ZrO_2 in YSZ coating. However, a thick Al_2O_3 overlay was harmful for TBC by increasing compressive stress which causes crack and spalling of YSZ coating. As a result, a dense and thin Al_2O_3 overlay is critical for simultaneously preventing YSZ from hot corrosion and spalling.

In the next reporting period, we will measure or calculate the residue stress within Al_2O_3 overlay and YSZ coating to study the mechanism of effect of Al_2O_3 overlay on spalling of YSZ coating.

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1. INTRODUCTION

Plasma sprayed thermal barrier coatings (TBCs) are widely used in gas turbine hot section components such as burners, transition ducts, shrouds, blades and vans. The most common TBC materials is Y_2O_3 (8wt%)-stabilized ZrO_2 type (YSZ) which has been developed over many years because of its high temperature stability, low thermal diffusivity and high coefficient of thermal expansion (CTE) [1,2]. However, when exposed to acidic molten salt, stabilizer yttria will be leached out from the zirconia solid solution, resulting in destabilization of the zirconia from tetragonal to the monoclinic phase and destruction of the coating.

The major failure mechanism that causes TBC spallation in gas turbine is bond coat oxidation and the growth of the thermally grown oxide (TGO), while hot corrosion of TBC will dominate coating failure in diesel engines which are usually operated with low quality fuels containing lots of impurities such as sulfur and vanadium [2].

Molten sodium salts of vanadium and sulfur oxides condense on to the TBCs at the temperature of 600-1000°C [3, 4]. Although zirconia itself shows good resistance to the molten sulfate or vanadate compounds arising from fuel impurities, yttria is leached out of the zirconia by the reaction with V_2O_5 or $NaVO_3$ to form YVO_4, causing structural destabilization of ZrO_2 (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) [5-10]. Stresses resulting from destabilization of the zirconia eventually cause the delamination and spalling of the coating.

Thus, extension of the benefits of TBCs to such impurity-containing environments requires the development of hot corrosion resistant coating. Based on Lewis acid-base concept, zirconias stabilized with india (In_2O_3) [11, 12], scandia (Sc_2O_3) [13] and ceria (CeO_2) [8,14] as well as Ta_2O_5 [6,15] and $YTaO_4$ [15] have been evaluated for their hot corrosion resistance. On the other hand, over the years there have been, and still continue to be, effects to close the surface of zirconia TBCs by laser-glazing and arc lamp [16-18] or various "seal coats" [18-25] to prevent penetration of molten deposits into the porous YSZ coating.

Alumina has a high melting point and stability without showing phase transition at high temperature like the ZrO_2 ceramics. Al_2O_3 has a small solubility particularly in molten salts and is expected to show an excellent corrosion resistance [26]. The hot corrosion tests of TiAl with Al_2O_3 coating in the sulfate melt at 900^{o}C have shown that the Al_2O_3 coating is very stable in the sulfate melt and effectively prevent intermetallic TiAl from hot corrosion attack [27]. Chen et al's experiment has demonstrated that the Al_2O_3 coating could resist hot corrosion attack of molten Na_2SO_4 salt for longer time than the YSZ coating [28]. In addition, Al_2O_3-ZrO_2 composite coatings have been explored as thermal barrier applications, showing better resistance in NaCl molten salt than YSZ [29]. This allows the potential application of Al_2O_3 in gas turbines. On the other hand, Al_2O_3 barrier layer was also deposited between the top coat and bond coat by chemical-vapor deposition (CVD) to suppress the oxidation rate of the bond coat. Recent work [30] has shown that a dense and continuous Al_2O_3 overlay on the surface of TBC deposited by EB-PVD reduced the permeability to gas and salt, and subsequently improved the hot-corrosion resistance of the TBC and suppresses the oxidation rate of the bond coat.

However, due to the thermal expansion mismatch between YSZ coating and Al_2O_3 overlay, such surface modification using Al_2O_3 overlay might deteriorate strain tolerance of the TBC. In the present work, in order to investigate the effect of Al_2O_3 overlay on degradation and spalling of the TBC, high-purity Al_2O_3 overlays of 25 μm and 2 μm thick are deposited onto the surface of YSZ coating by means of high velocity oxy-fuel (HVOF) spray and sol-gel techniques, respectively. After exposure to air and to molten Na_2SO_4 salt containing V_2O_5 at high temperature, in addition to examinations of microstructure and visual check of TBC spallation, indentation test will also be employed to study spallation behaviors of YSZ coating with and without Al_2O_3 overlay.

2. EXECUTIVE SUMMARY

Although the attack of YSZ by the molten salt was restrained by the presence of the Al_2O_3 overlay, a thick Al_2O_3 overlay increased the compressive stress within YSZ due to the mismatch of thermal expansion between YSZ and Al_2O_3 overlay, as a result, causing the spalling of YSZ. A dense and thin Al_2O_3 overlay is critical for simultaneously preventing YSZ from hot corrosion and spalling.

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 substrate was grit-blasted with alumina particles and then deposited with a 100 μm thick CoNiCrAlY alloy (weight percent: 32%Ni, 21%Cr, 8%Al, 0.5%Y and 38.5%Co) bond coat by low-pressure plasma spray (LPPS) process. The LPPS spraying was carried out under the spraying voltage of 68 V and the current of 630 A with a primary gas Ar flow of 60 *l*/min, a secondary gas H_2 flow of 8.5 *l*/min and a carrier gas Ar of 8.5 *l*/min. The substrate with the

CoNiCrAlY bond-coat was sprayed with a 200 μm thick ZrO_2-8wt%Y_2O_3 top coat by an air plasma-spray (APS) process under the spraying current of 550 A and the spraying voltage of 68 V with a primary gas Ar of 41 *l*/min, a secondary gas H_2 flow of 10 *l*/min and a carrier gas Ar flow of 3 *l*/min. Al_2O_3 overlay of 25 thick was deposited by HVOF thermal spray on the surface of bond coat, using the Praxair HV-2000 gun with propylene as fuel. On the other hand, 2 *μm* thick Al_2O_3 overlay was prepared using sol-gel method according to a previous report .

Hot corrosion test was performed on the TBCs with and without Al_2O_3 coating. The TBC plates coated with salt mixture were placed into a still air furnace, and isothermally held at 950 ^oC up to100 hours. Approximately 50 mg/cm^2 salt mixture was sprayed on the surface of TBC using an aqueous solution (1000 g/*l* 95wt%Na_2SO_4 + 5wt%V_2O_5). After exposure, the samples were cooled down to room temperature in the furnace. 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 microstructure and composition of the coating surface and the cross-section were examined using the PHILIPS XL30 scanning electron microscope (SEM) with which an energy-dispersive spectrometer (EDS) was equipped. In the indentation test, a specimen is placed in a Rockwell hardness tester using a brale C indenter (90 angle) under 150 kg load.

4. RESULTS AND DISCUSSION

4.1 XRD analysis

The previous study demonstrated that as-sprayed TBC specimen contained predominantly T-phase of ZrO_2. After exposure to the molten mixture for 10 h, the YVO_4 phase was formed, implying the leaching of Y_2O_3 from YSZ by the reaction of Y_2O_3 with V_2O_5. As a result, the intensity of T-phase remarkably decreased, and a substantial amount of M-phase was formed due to the leaching of Y_2O_3 from YSZ. The intensity of M-phase of ZrO_2 was further increased when exposure time was prolonged to 100 h.

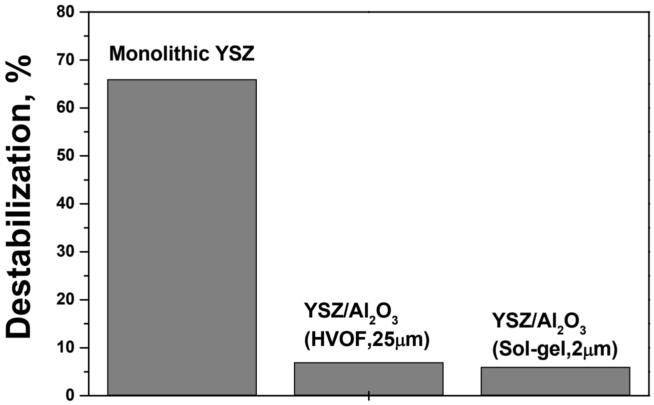

Fig.1 Destabilization fraction of zirconia in the monolithic YSZ and composite YSZ/Al_2O_3 systems;

After 10 h of exposure, the destabilization fraction of zirconia in the YSZ coating without protection of reached up to 66%, whereas the destabilization fraction of zirconia in the YSZ/Al_2O_3 system was kept at about 7%, as shown in Fig.1, even though the Al_2O_3 overlay was very thin. The destabilization fraction of zirconia in the YSZ/Al_2O_3 coating was much lower than that in YSZ coating without overlay, even though Al_2O_3 overlay is very thin. This indicated that the attack of YSZ by the molten salt was restrained by the presence of the Al_2O_3 overlay, even though the Al_2O_3 overlay is very thin.

4.2 Indentation tests

Trying to measure the YSZ/bond coat interfacial toughness lose after hot corrosion using indentation test proposed by A. Vasinonta et al [31] was failed due to much thick YSZ coating employed in the present work. For such thick YSZ, buckling never occurred during indenter test because the indenter could not throughout penetrate the YSZ coating and as a result, interface crack could not be driven by the compressive radial strains. Nevertheless, a much large compressive stress could be induced through the YSZ coating thickness during indenter test. The compressive stresses induced by indenter and due to the phase transformation of T→M were very harmful for the coating spalling.

After hot corrosion for 10 h and 100 h, visual and SEM examination showed no cracks on the YSZ surface and spalling for monolithic YSZ TBC system. On the contrary, composite YSZ/Al_2O_3 (25 μm) system showed the formation of cracks and spalling of YSZ after hot corrosion for ~100 h, as shown in Fig.2. This result demonstrated that Al_2O_3 overlay increased the compressive stress within the YSZ coating due to mismatch in thermal expansion between Al_2O_3 and YSZ. It is further evidenced by the indenter test results, as shown in Fig.3. As can be seen from Fig.3, for 10 h hot corrosion, monolithic YSZ system did not show cracking and spalling, whereas spalling was clearly observed on the YSZ/Al_2O_3 (25 μm) system. Furthermore, after 100 h hot corrosion, monolithic YSZ system only cracked during indenter test, while spalling and cracking occurred on the YSZ/Al_2O_3 (25 μm) system. Instead of thick Al_2O_3 overlay, however, when much thin Al_2O_3 overlay (2 μm) was deposited, neither crack nor spalling could be found on the sample hot corroded for ~100 h during indenter test, as demonstrated in Fig.4. These results revealed that a dense and thin Al_2O_3 overlay is critical for simultaneously preventing YSZ TBC from attack of molten salt and spalling caused by compressive stress.

4.3 Effect of overlay thickness on stress in YSZ coating and spalling of YSZ coating

It is known that phase transformation from T-phase to M-phase of ZrO_2 is accompanied by a large destructive volume change, which will induces much large compressive stress within the YSZ coating. However, the results mentioned above demonstrate that the stresses developed in monolithic YSZ coating after hot corrosion are not sufficient to cause failure, although a large amount of M-phase of ZrO_2 was formed due to hot corrosion. On the other hand, composite YSZ/Al_2O_3 (25 μm) overlay TBC system showed early failure through delamination. The mechanisms leading to delamination are what must be addressed.

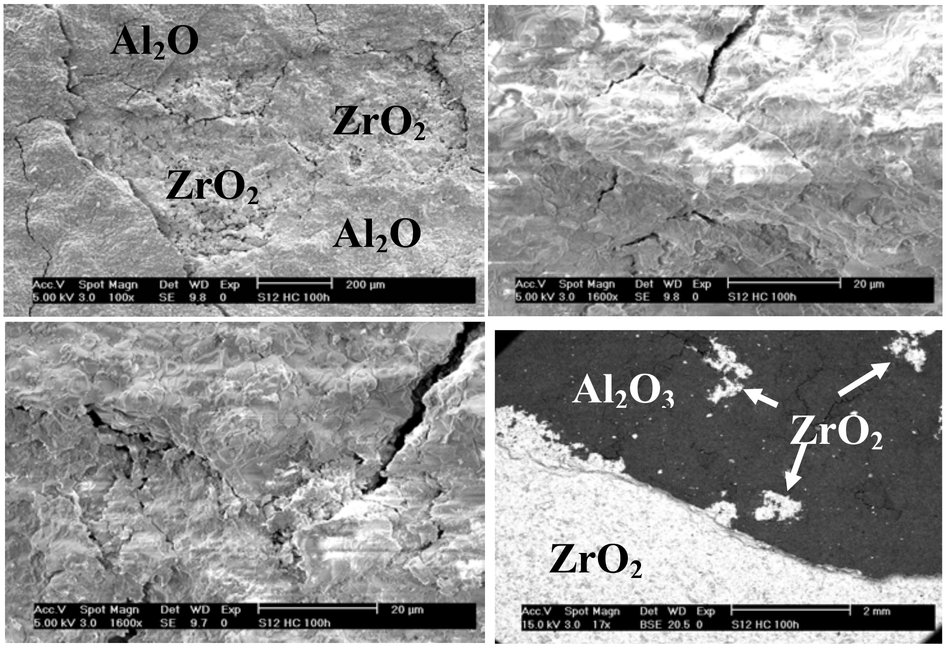

Fig.2 SEM images showing the formation of cracks and spalling of YSZ after hot corrosion for ~100 h in composite YSZ/Al_2O_3 overlay (25 μm) system.

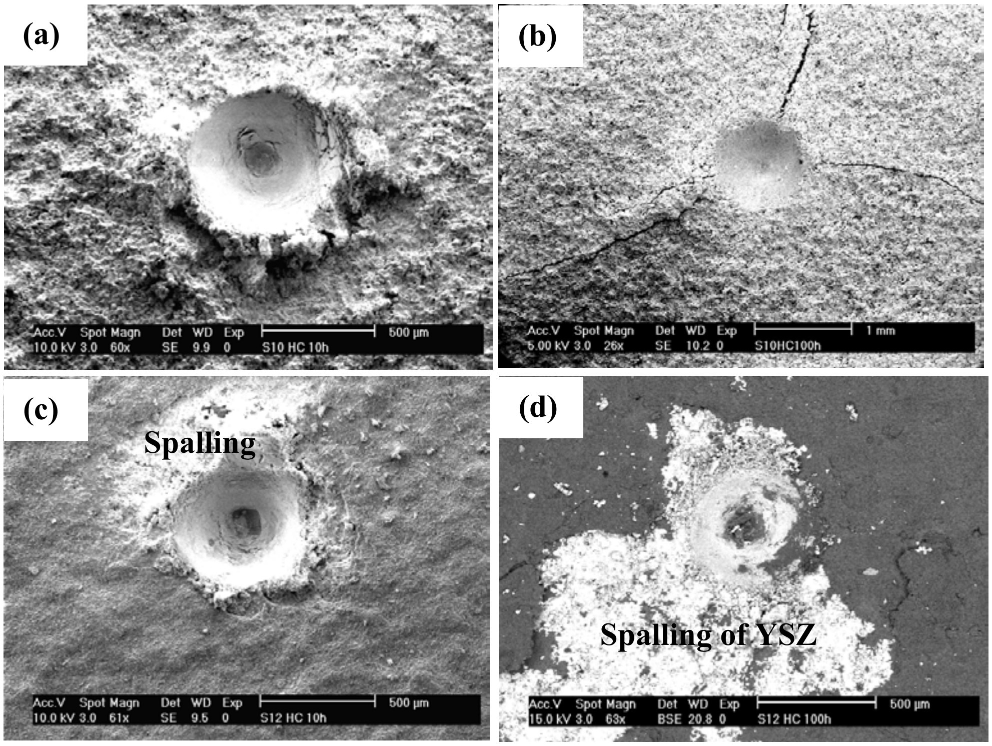

Fig.3 Cracking and spalling of YSZ coating with and without Al_2O_3 (25 μm) after hot corrosion during indenter test.(a) and (b)YSZ,10h and 100h; (c) and (d)YSZ/Al_2O_3 (25 μm), 10h and 100h

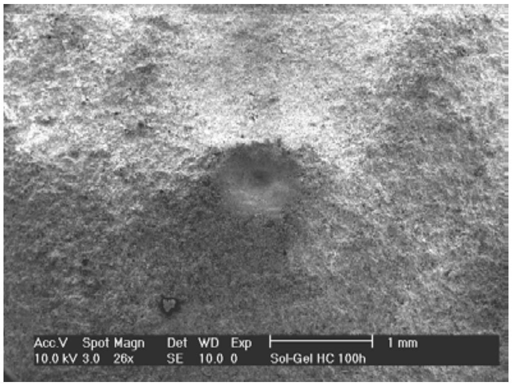

Fig.4 SEM image showing no cracks and spalling of YSZ in YSZ/Al_2O_3 overlay(2 μm) system after hot corrosion of 100 h.

Due to thermal expansion mismatch between Al_2O_3 overlay and YSZ coating, stresses developed on cooling can lead to spalling or delamination of YSZ coating. The stress caused by the thermal expansion is formulated by

$$\sigma_{YSZ} = \frac{E_a^{'} \times E^{'} \times H_a}{E_a^{'} \times H_a + E^{'} \times H}(\alpha_a - \alpha) \times \Delta T \qquad (1)$$

$$\sigma_a = \frac{E_a^{'} \times E^{'} \times H}{E_a^{'} \times H_a + E^{'} \times H}(\alpha - \alpha_a) \times \Delta T \qquad (2)$$

where, $E_a^{'} = E_a/(1-\nu_a)$, and $E^{'} = E/(1-\nu)$. E, ν and α are Young's modulus, Poisson's ratio, and thermal expansion coefficient of the YSZ coating respectively; E_a, ν_a and α_a are Young's modulus, Poisson's ratio, and thermal expansion coefficient of Al_2O_3 overlay respectively; H and H_a are the thickness of YSZ coating and Al_2O_3 overlay, respectively. The Young's modulus of YSZ is 50 GPa and that of Al_2O_3 overlay is 375 GPa. ν and ν_a are supposed to be 0.1 and 0.25 respectively. α and α_a are 11×10^{-6} and 8×10^{-6}, respectively. ΔT, difference between exposure temperature and room temperature after cooling, can be taken as -930^{o}C (950^{o}C-20^{o}C). Thus the stresses encountered in YSZ coating on cooling to room temperature are approximately 73.35MPa and 10.4MPa for Al_2O_3 overlay thickness of 25 μm and 2 μm, respectively. It clearly shows that the effect of Al_2O_3 overlay on the residual stress in YSZ coating can be significantly reduced when a much thin overlay is deposited. Similarly, the stress in Al_2O_3 overlay after cooling can be estimated to be -734MPa and -1300MPa, for Al_2O_3 overlay thickness of 25 μm and 2 μm, respectively.

Upon cooling, planar stress states will be developed in the YSZ coating due to CTE mismatch between the YSZ coating and the bond coat, and Al_2O_3 overlay, causing spalling of the YSZ coating. Based upon the above stresses estimation, a tensile stress was developed in YSZ coating near the YSZ/Al_2O_3 overlay interface after cooling due to the presence of Al_2O_3 overlay. It might be found that the compressive stress with in the YSZ coating could be increased due to this tensile stress, as illustrated in Fig.5. As the Al_2O_3 overlay thickness was decreased to 2 μm, the effect of Al_2O_3 overlay on the compressive stress could be negligible. Consequently, the spalling of YSZ coating due to the presence of Al_2O_3 overlay can be minimized.

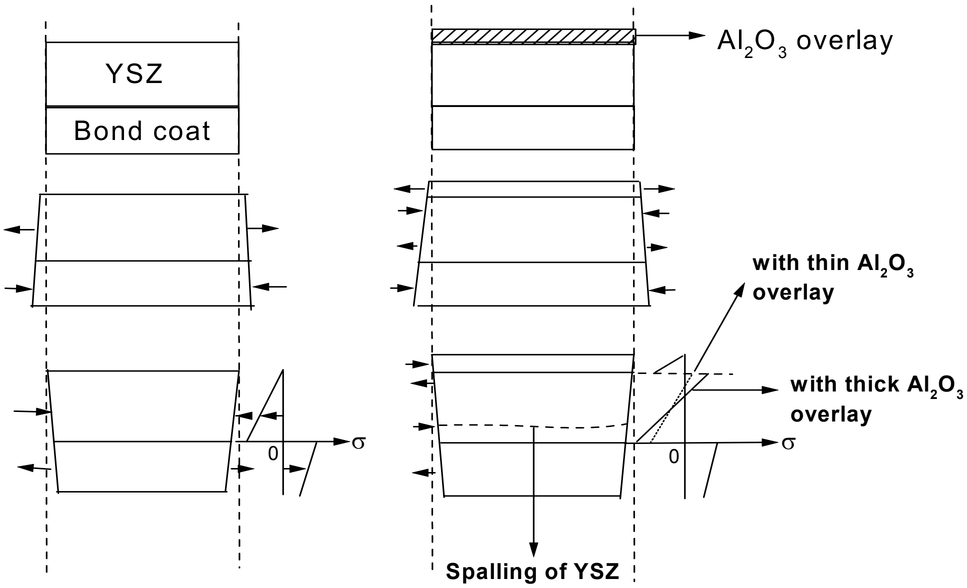

Fig.5 Illustration of effect of overlay
on the compressive stress within the YSZ coating.

5. PLANS FOR THE NEXT REPORTING PERIOD

In the next reporting period, we will measure or calculate the residue stress within Al_2O_3 overlay and YSZ coating to study the mechanism of effect of Al_2O_3 overlay on spalling of YSZ coating.

6. CONCLUSION

(1) A thick Al_2O_3 overlay was harmful for TBC by increasing compressive stress which causes crack and spalling of YSZ coating.
(2) A dense and thin Al_2O_3 overlay is critical for simultaneously preventing YSZ from hot corrosion and spalling.

7. REFERENCES

[1] M. J. Stiger, N. M. Yanar, M. G. Topping, F. S. Pettit, and G. H. Meier, “Thermal barrier coatings for the 21st century,” *Z. Metallkd*, **90**[12] 1069-1078 (1999).
[2] L. Singheiser, R. Steinbrech, W.J. Quadakkers, R. Herzog, “Failure aspects of thermal barrier coatings”, *Mat. High Temp,* **18** [4] 249-259 (2001)
[3] I. Gurrappa, “Hot corrosion of protective coatings,” *Mat. Manuf. Process*, **15** [5]: 761-773 (2000).

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

[5] R L. Jones, “Thermogravimetric study of the 800 degree reaction of zirconia stabilizing oxides with SO_3-$NaVO_3$,” *J. Electrochem. Soc*., **139**, 2794-2799 (1992).

[6] K. L. Luthra, H. S. Spacil, “Impurity deposits in gas-turbines from fuels containing sodium and vanadium ,” *J. Electrochem. Soc*., **129**[3] 649-656 (1982).

[7] N. S. Bornstein and W. P. Allen, “The chemistry of sulfidation corrosion - Revisited,” *Mater. Sci. Forum,* **127,** 251-254 (1997).

[8] A. S. Nagelberg, “Destabilization of yttria-stabilized zirconia induced by molten sodium vanadate-sodium sulfate melts,” *J. Electrochem. Soc.,* **132**[10] 2502-2507 (1985).

[9] R. L. Jones, C. E. Williams and S. R. Jones, “Reaction of vanadium compounds with ceramic oxides,” *J. Electrochem. Soc.,* **133**[1] 227-230 (1986).

[10] R L. Jones, “High temperature vanadate corrosion of yttria-stabilized zirconia coatings on mild steel,” *Surf. Coat. Tech.,* **37**, 271-284 (1989).

[11] R. L. Jones and C. E. Williams, “Hot corrosion studies of zirconia ceramics,” *Surf. Coat. Tech.,* **32**, 349-358 (1987).

[12] D. W. Susnitzky, W. Hertl and C. B Carter, “Destabilization of zirconia thermal barriers in the presence of V_2O_5,” *J. Am. Ceram. Soc*., **71**[11] 992-1004 (1988).

[13] R. A. Miller and C E. Lowell, “Failure mechanism of thermal barrier coatings exposed to elevated temperature,” *Thin solid films*, **95**, 265-273 (1982).

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

[15] R. L. Jones and R. F. Reidy, “Vanadate hot corrosion behavior of India, yttria-stabilized zirconia,” *J. Am. Ceram. Soc*., **76**[10] 2660-2662 (1993).

[16] R. L. Jones, “Scandia-stabilized zirconia for resistance to molten vanadate-sulfate corrosion,” *Surf. Coat. Tech.,* **39/40**, 89-96 (1989).

[17] S. A. Muqtader, R. K. Sidhu, E. Nagabhushan, K. Muzaffaruddin and S. G. Samdani, “Destabilization behavior of ceria-stabilized tetragonal zirconia polycrystals by sodium sulphate and vanadium oxide melts,” *J. Mater .Sci. Lett*., **12**, 831-833 (1993).

[18] S. Raghavan and M J. Mayo, “The hot corrosion resistance of 20 mol% $YTaO_4$ stabilized tetragonal zirconia and 14 mol% Ta_2O_5 stabilized orthorhombic zirconia for thermal barrier coating applications,” *Surf. Coat. Tech.,* **160**, 187-196 (2002).

[19] A. Petitbon, L. Boquet and D. Delsart, “Laser surface sealing and strengthening of zirconia coatings,” *Surf. Coat. Tech.,* **49**, 57-61 (1991).

[20] Z. Liu, “Crack-free surface sealing of plasma sprayed ceramic coating using an excimer laser,” *Appl. Surf. Sci.,* **186**, 135-139 (2002).

[21] S. Ahmaniemi, P. Vuoristo and T. Mantyla, “Improved sealing treatment for thick thermal barrier coatings,” *Surf. Coat. Tech.,* **151-152**, 412-417 (2002).

[22] T. Mantyla, P. Vuoristo and P. Kettunen, “Chemical vapor deposition densification of plasma-sprayed oxide coatings,” *Thin solid films*, **118**, 437-444 (1984).

[23] I. Berezin and T. Troczynski, “Surface modification of zirconia thermal barrier coatings,” *J. Mater. Sci. Lett*., **15**, 214-218 (1996).

[24] T. Troczynski, Q. Yang and G. John, "Post-deposition treatment of zirconia thermal barrier coatings using sol-gel alumina," *J. Therm. Spray Tech.,* **8**(2), 229-234 (1999).
[25] M. Vippola, J. Vuorinen, P. Vuoristo, T. Lepisto and T. Mantyla, "Thermal analysis of plasma sprayed oxide coatings sealed with aluminum phosphate," *J. Euro. Ceram. Soc*., **22**, 1937-1946 (2002).
[26] M. G. Lawson, F. S. Pettit, J. R. Blachere, "Hot corrosion of Al_2O_3 ," *J. Mater. Res*., **8**, 1964-1971 (1993).
[27] Z. Tang, F. Wang, W. Wu, "Effect of Al_2O_3 and enamel coatings on 900^oC oxidation and hot corrosion behaviors of gamma-TiAl," *Mater. Sci. Eng. A*, **276**, 70-75 (2000).
[28] H. C. Chen, Z. Y. Liu, Y. C. Chuang, "Degradation of plasma-sprayed alumina and zirconia coatings on stainless steel during thermal cycling and hot corrosion," *Thin solid films*, **223**, 56-64 (1992).
[29] P. Ramaswamy, S. Seetharamu, K. B. R. Varma and K. J. Rao, "Al_2O_3-ZrO_2 composite coatings for thermal barrier applications," *Comp. Sci. Tech*., **57**, 81-89 (1997).
[30] Zheng Chen, N. Q. Wu and Scott X. Mao, "Effect of Al_2O_3 overlay on hot-corrosion behavior of yttria-stabilized zirconia coating in molten sulfate-vanadate salt," Thin solid films, 443(1-2), 46-52 (2003).
[31] Aditad Vasinonta and Jack L. Beuth, "Measurement of interfacial toughness in thermal barrier coating systems by indentation", 68, 843-860(2001)