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Oxidation resistance of YSZ-alumina composites compared to normal YSZ TBC coatings at 1100 °C

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ABSTRACT

In the present work oxidation behavior of plasma sprayed YSZ-alumina composite TBC coatings on Ni-base (IN-738LC) super alloy substrate was studied and compared to normal YSZ. Cyclic oxidation process in 4 h intervals was performed in an air electrical furnace at 1100 °C and the specimens were cooled in the furnace during each cycle. Preliminary checking was done with naked eye and further investigation was achieved using scanning electron microscopy. If there were any cracks or spallation in the coating's edge, the tests were stopped, the time was recorded and coating microstructure was studied. YSZ-alumina composites were made by applying alumina layer at the top of YSZ or mixed with YSZ as a TBC layer on the bond coat. Composite coatings of YSZ-alumina having alumina as a top coat and the mixed YSZ-alumina layer, showed better resistance than normal YSZ in oxidation test. It was observed that alumina overlay on YSZ has promoted the oxidation resistance of the coatings for longer times by preventing infiltration of oxygen through YSZ layer.

1. Introduction

The need to improve efficiency and higher energy output of energy generating systems caused the application of advanced materials and the coatings have a significant role towards this advance for the work pieces under high temperatures [1].

High temperature coatings are used to prevent surface degradations or as thermal barriers against hot atmosphere. The work pieces life span is deteriorated by their surface alterations which are usually done through corrosion, oxidation or erosion of solid particles. Simultaneous existence of these factors results in work piece strengthening drop in its ductility and eventually occurrence of its premature failure (the simultaneous presence of these factors will result in strength drop and finally accelerates work-piece failure with out coating) [2]. Applying coatings significantly improves the work pieces performance and increases their durability. The extent of components requiring coatings is widely increasing especially in industrial gas turbines and aero turbines [1,3,4].

Common thermal barrier coatings (TBCs), typically comprise a MCrAlY (M: nickel, cobalt or a mixture of these two) bond coat and a high temperature resistant yttria-stabilized zirconia (YSZ) top coat which is applied by thermal spray on super alloys surface [5]. The main disadvantage of TBCs is the decohesion from the bond coat which is caused by oxidation and formation of thermally grown oxide (TGO) or infiltration of detrimental factors such as vanadium salts, which results in phase transformation and spalling upon thermal cycling, and high temperature oxidation [6–9]. In recent years composite layer of (Al_2O_3/YSZ) coatings have been proposed to improve TBC performance [10,11]. In such coatings, due to the existence of the Al_2O_3 layer, the infiltration of oxygen or other detrimental species is prevented and the formations of TGO and zirconia phase transformation are retarded. Therefore thermal and mechanical properties of TBCs are improved which eventually increase the life of these coatings [11].

In spite of present efforts the subject needs more investigation to reduce the short comings of such composite coatings. Previous work of this group indicated the improvement of the coating [11].

The aim of the present research is to investigate and make a comparison between common YSZ coating and a composite coating comprising of Al_2O_3/YSZ as top layer or Al_2O_3 as dispersed particles. This will enable us to understand the mechanism of TBC failure and improve its durability. In the present work, the coatings were applied by plasma spray, their oxidation behavior were studied and compared.

2. Experimental procedures

The substrate was IN-738LC Ni base super alloy (its composition is listed in Table 1) cut in the shape of Ø25 mm × 10 mm disks.

Amdry 962 (Sulzer Metco, USA) NiCrAlY was used as bond coat material, Metco 204NS-G (Sulzer Metco, USA) YSZ zirconia powders and Metco 105NS (Sulzer Metco, USA) Al_2O_3 powders were used for the top coat using Metco 3MB air plasma spray (APS) process. SEM micrograph from the morphology of applied powders to form

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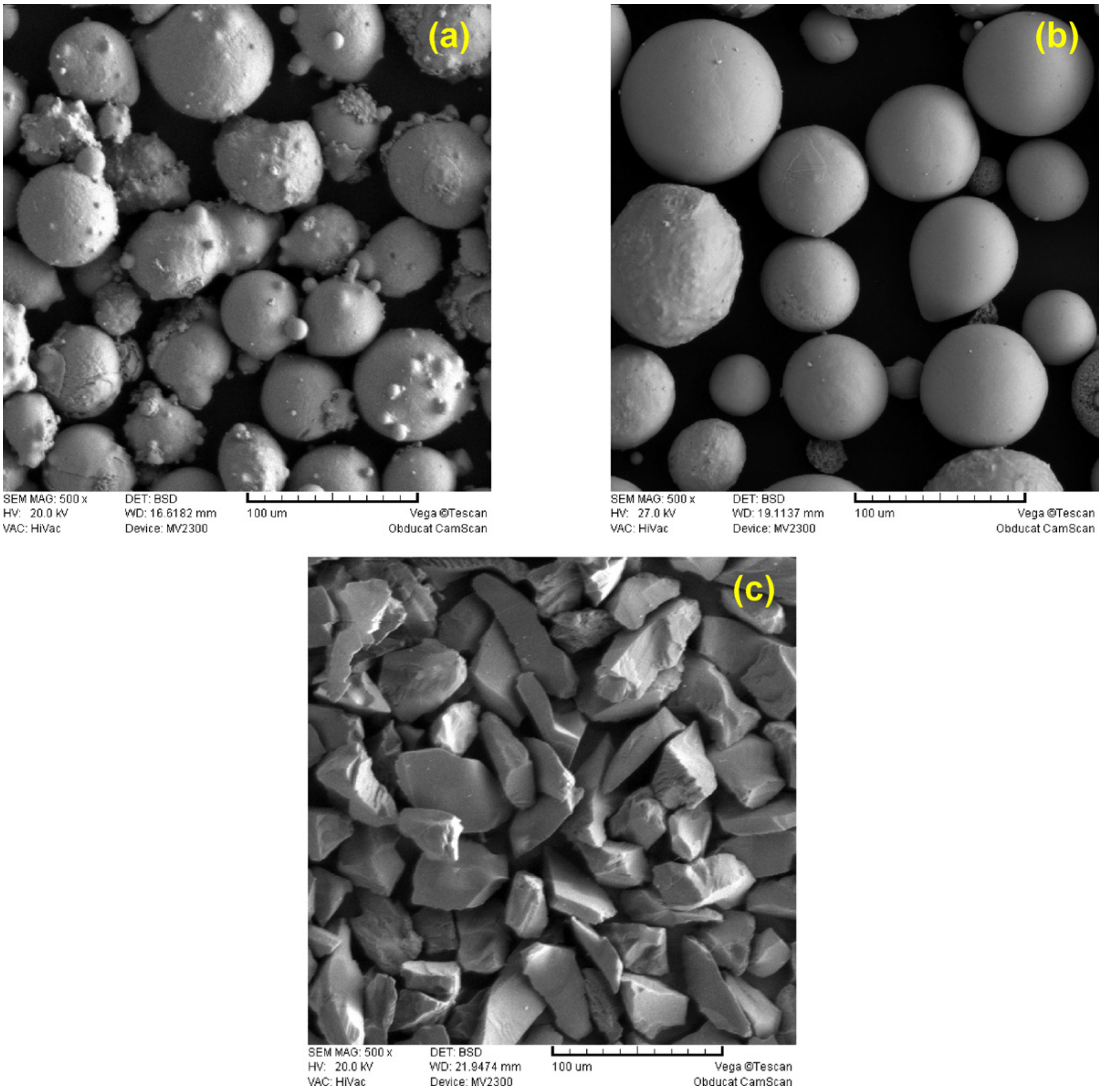


Fig. 1. The morphology of the powder: (a) NiCrAlY alloy; (b) YSZ; and (c) Al_2O_3.

the coatings is showed in Fig. 1. In Fig. 1a, spherical NiCrAlY particles, in Fig. 1b, spherical YSZ particles and in Fig. 1c pungent Al_2O_3 particles are observed. One can say that pungent Al_2O_3 particles are effective in bond strength among composite YSZ + Al_2O_3 coating particles and its particle size was near to other powders. We used three powders to keep the effect of morphology constant.

The specimens were grit blasted by 50–80 grain mesh alumina particles under 0.28–0.34 MPa pressure, before applying coatings. The surfaces were cleaned using methyl ethyl kethon cleaner, and degreasing was performed under trichloro ethylene vapor and washed by distilled water. The samples were preheated at 65–95 °C before plasma spraying under parameters summarized in Table 2 and finally the coatings were sprayed onto the test specimens. Argon and hydrogen were the primary and the secondary plasma gases, respectively.

NiCrAlY coating with a thickness of 150 μm was plasma sprayed on the specimens. Having applied the NiCrAlY bond coating, the specimens were then plasma sprayed with the four following coatings:

(a) Normal YSZ with a thickness of 350 μm.
(b) Composite layer of 100 μm Al_2O_3 on bond coat and 250 μm YSZ top coat.
(c) Composite layer of 350 μm mixing Al_2O_3 and YSZ particles.
(d) Composite layer consisting 100 μm Al_2O_3 top coat on 250 μm YSZ.

Table 1
Chemical composition of IN738LC.

IN738LC	C	Al	Co	Cr	Mo	Nb	Ta	Ti	W	Ni
wt%	0.101	3.45	8.32	16.09	1.70	0.75	1.73	3.34	2.56	Balance

YSZ + Al_2O_3 composite powder was made by mixing 60 wt% of YSZ and 40 wt% of Al_2O_3 powder. In an earlier work it was shown that 60/40 mixture provides better results on thermal shock resistance and bond strength [10].

To produce composite YSZ + Al_2O_3 coating, 50 volume percent of each (were mixed to achieve an evenly distributed structure) or 60 wt% of YSZ powder ($\rho_{YSZ} = 5.9\,g/cm^3$) and 40 wt% of Al_2O_3 powder ($\rho_{Al2O3} = 3.9\,g/cm^3$) that were ball milled with alumina cup and balls and at a rotating speed of 150 rpm for 5 h and homogenized [10,11].

Oxidation tests were carried out in an electrical atmospheric air furnace at 1100 °C in 4 h cycling in which the samples were furnace cooled and the tests were continued until the appearance of the first crack. They were then inspected and their peripheral conditions were examined. If there were any crack or spallation in the coating edge the test was stopped and the time was recorded. The testing tempera-

Table 2
Plasma spray parameters for each coating.

Parameter	NiCrAlY	YSZ	YSZ + Al_2O_3	Al_2O_3
Current (A)	500	600	550	550
Voltage (V)	80	70	70	70
Primary gas flow, Ar (l/min)	55	40	40	40
Secondary gas flow, H_2 (l/min)	17	15	15	15
Powder feed rate (g/min)	42	37	37	37
Spray distance (mm)	130	120	100	100
Wheel rotation speed (rpm)	35	25	30	35

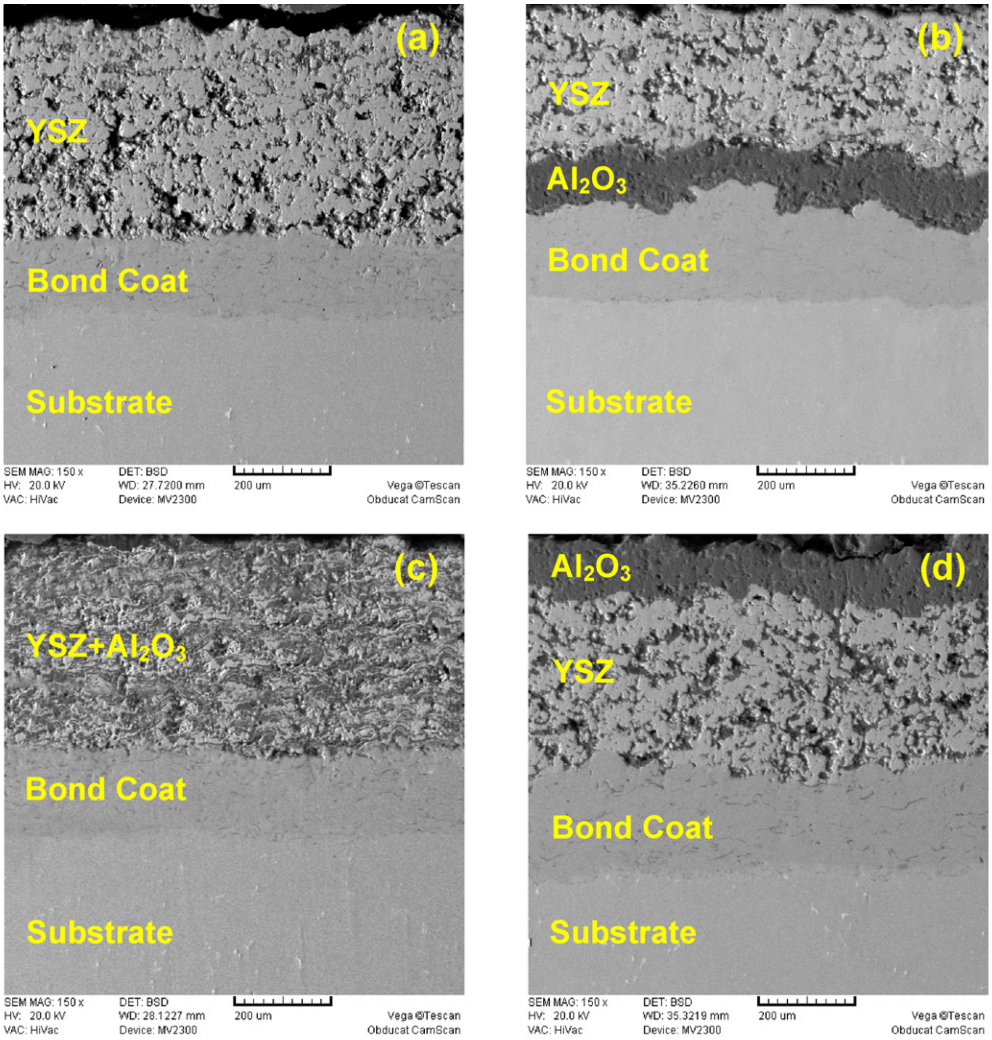


Fig. 2. SEM microstructural images of TBC section (as-sprayed): (a) YSZ/NiCrAlY; (b) YSZ/Al_2O_3/NiCrAlY; (c) YSZ + Al_2O_3/NiCrAlY; and (d) Al_2O_3/YSZ/NiCrAlY.

ture was selected according to inlet temperature zirconia phase transformation and the real engine.

For conducting the oxidation tests at 1100 °C in every status, five specimens were used simultaneously to ensure the reproducibility. The average time to spallation was recorded. For instance, 20 specimens were tested to attain useful life span of the four coatings of the specimens at 1100 °C. Therefore the average life spans of five specimens were recorded for each coating. As another example to measure the TGO thickness at 20, 40 and 100 h, 15 specimens were tested for each time-duration. Therefore 60 specimens were tested for the 4 types of coatings.

The failure of TBCs takes place primarily within the top ceramic coat, near the YSZ/TGO interface.

Scanning electron microscopy (SEM, CAMSCAN-MV2300) equipped with energy dispersive spectrometer (EDS) was used for microstructural and microanlysis of the surface.

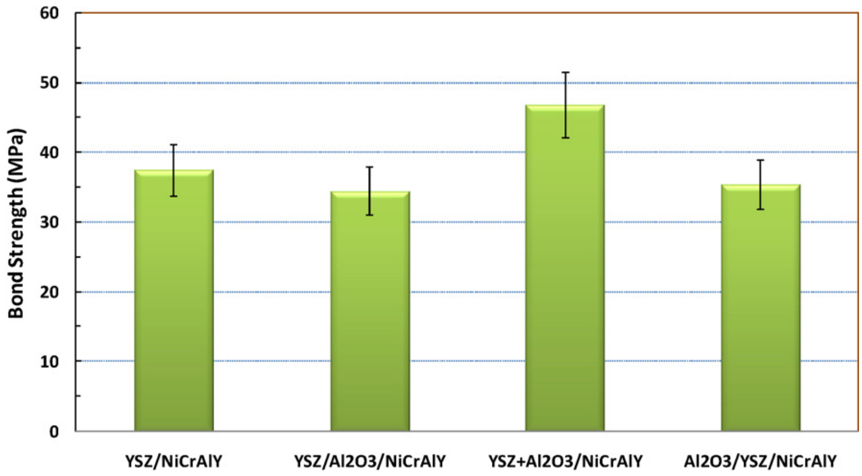


Fig. 3. Comparison of the coatings bond strength.

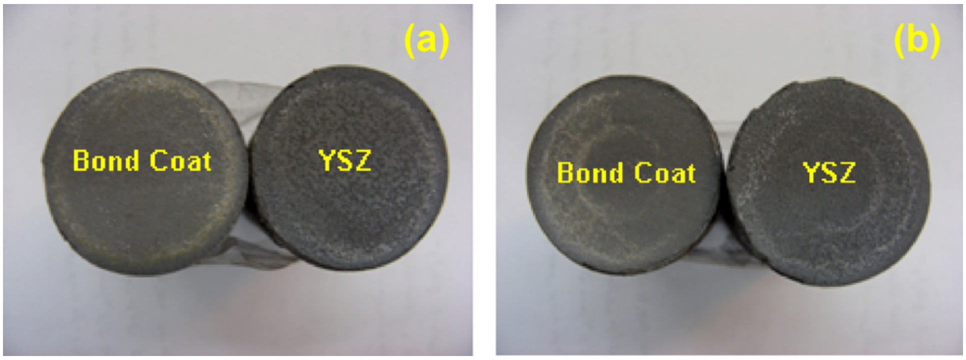


Fig. 4. OM images of specimens surface after spallation during bond strength test: (a) normal YSZ; (b) YSZ + Al_2O_3.

3. Results and discussion

Fig. 2 shows the SEM images of the cross section of the four TBC layers microstructure. The YSZ layer is some how porous but the alumina and bond coat layers are less porous and all layers are in good adhesion together and to the substrate. The specimen's bond strength was attained based on ASTM C633-79 [12].

Bond strength results indicate that YSZ + Al_2O_3 coating is stronger than YSZ (Fig. 3). Since the spallation of both the YSZ and YSZ + Al_2O_3 coatings take place in the interface of NiCrAlY/YSZ (Fig. 4), one can say that YSZ particles cohesion are stronger than adhesion with NiCrAlY layer [13].

The thickness of the bond coats are around 150 μm, YSZ is 250 μm and alumina layer is 100 μm. The YSZ + Al_2O_3 composite is less porous because part of the porosities are filled with alumina powder.

The time to failure of each sample during oxidation at 1100 °C in atmospheric furnace is indicated in Table 3 in which the most

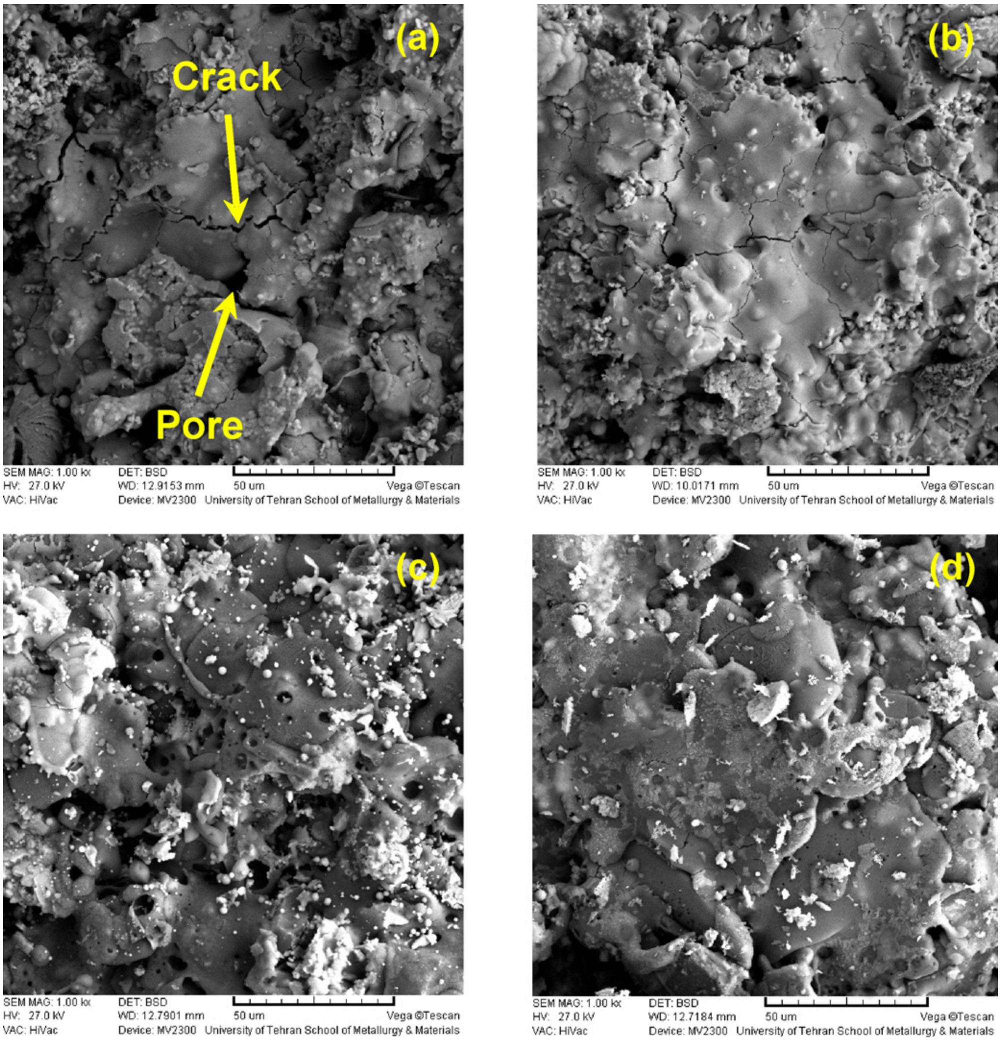


Fig. 5. Coating outer surface morphology after oxidation tests: (a) YSZ/NiCrAlY (192 h); (b) YSZ/Al_2O_3/NiCrAlY (112 h); (c) YSZ + Al_2O_3/NiCrAlY (244 h); and (d) Al_2O_3/YSZ/NiCrAlY (356 h).

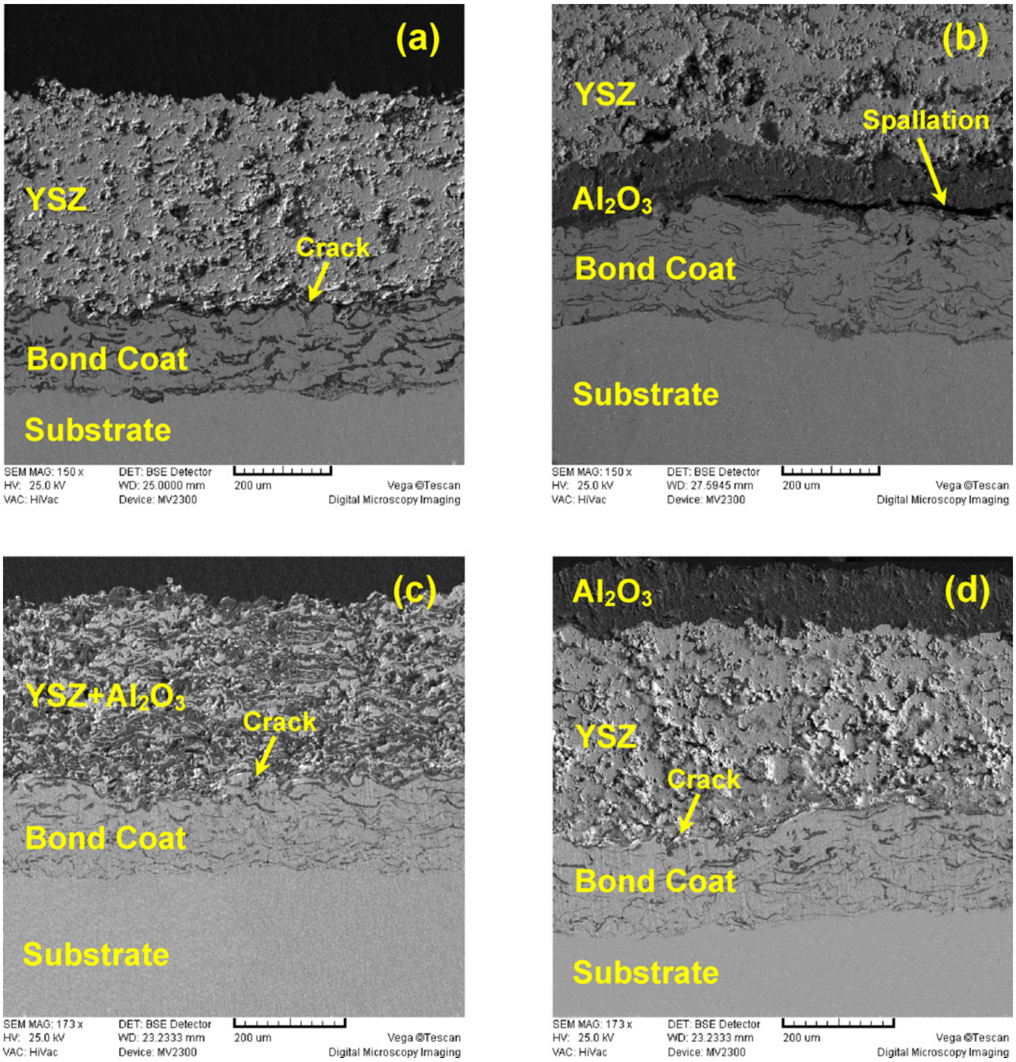


Fig. 6. TBC section microstructure after oxidation test: (a) YSZ/NiCrAlY after 192 h; (b) YSZ/Al_2O_3/NiCrAlY after 112 h; (c) YSZ + Al_2O_3/NiCrAlY after 244 h; and (d) Al_2O_3/YSZ/NiCrAlY after 356 h.

resistant sample was Al_2O_3/YSZ composite coating with no cracking before 356 h and the least resistant was YSZ/Al_2O_3 composite coating with appearing spallation after 112 h of oxidation. Many factors may have caused the low resistance of the latter coating. The most important one is the mismatch of thermal expansion of alumina layer with the bond coat and YSZ layer. But weak adhesion may have also caused the separation.

The mismatches of the coatings are attributed to cracking or spallation. In some coatings like Al_2O_3/YSZ we only observed cracking while in coatings that Al_2O_3 was between NiCrAlY and YSZ we had spallation which is the worst situation.

The normal YSZ coating cracked after 192 h of oxidation, while YSZ + Al_2O_3 composite coating resisted for 244 h of oxidation at 1100 °C.

The SEM images of the coatings surfaces after oxidation at 1100 °C are illustrated in Fig. 5, in which large cracks are observed on normal YSZ coating while very small cracks were visible on Al_2O_3/YSZ composite coating after 356 h.

The stability of this coating could be explained under oxidation mechanism and process. Oxygen can diffuse from the pores or cracks in molecule from but it can also diffuse as O^{2-} through zirconia crystal layer which is transparent to O^{2-} at above 1200 °C temperatures [14–21]. In both cases oxygen molecules or ions can react with Al, Cr or Ni of the bond coat at the bond coat/YSZ interface to form TGO (thermally grown oxide). The TGO may grow gradually and exert excessive stress normal to the zirconia or the TBC layer causing its separation or creating microcracks.

Presence of alumina layer on the top prevents oxygen diffusion through the aluminum and consequently protects YSZ layer and bond coat [19,20].

Fig. 6 shows the SEM images of microstructures of layers after oxidation. It is quite visible thatalumina is separated from the bond

Table 3
The results of oxidation test at 1100 °C.

YSZ ordinary coating	Layer composite YSZ/Al_2O_3 coating	Particle composite Al_2O_3+YSZ coating	Layer composite Al_2O_3/YSZ coating
48 cycles (192 h) Cracking	28 cycles (112 h) Spallation	61 cycles (244 h) Cracking	89 cycles (356 h) Cracking

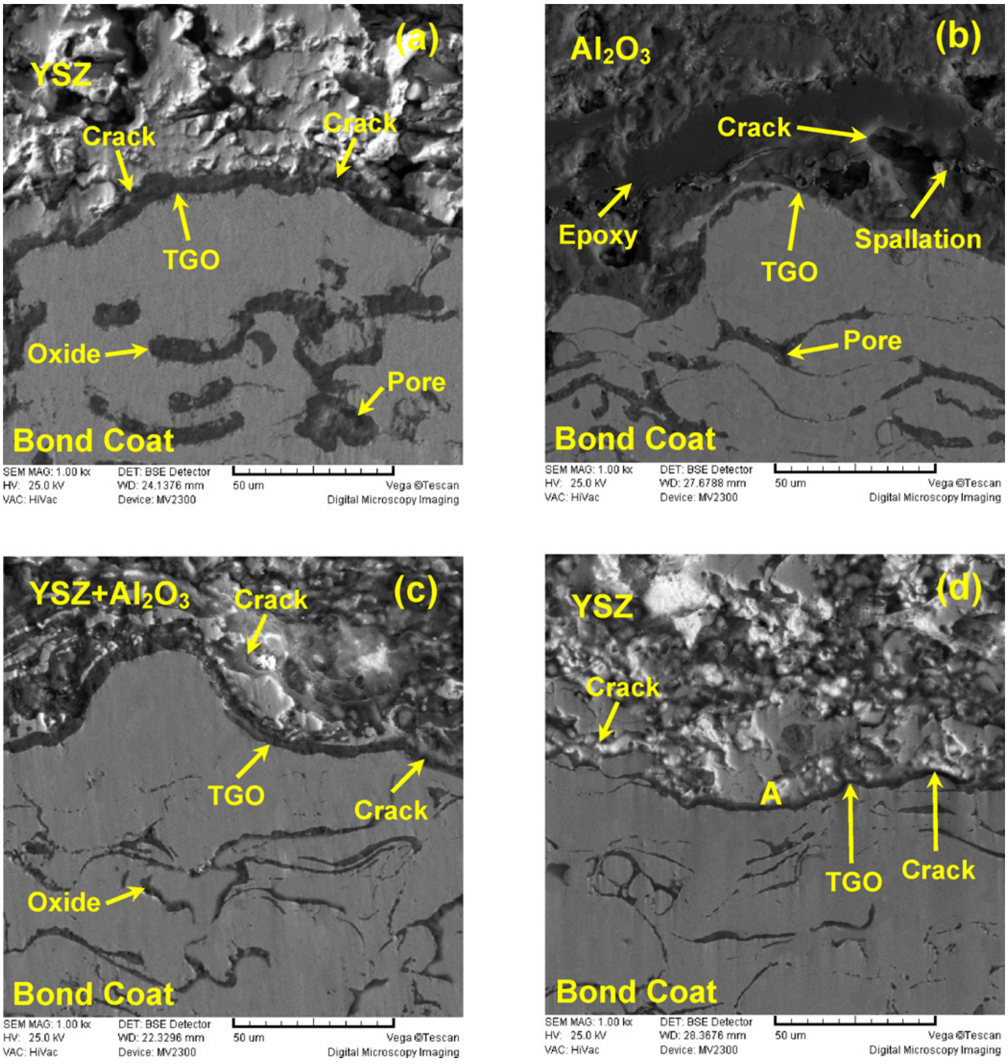


Fig. 7. TBC section microstructure containing TGO layer after oxidation test: (a) YSZ/NiCrAlY after 192 h; (b) YSZ/Al_2O_3/NiCrAlY after 112 h; (c) YSZ + Al_2O_3/NiCrAlY after 244 h; and (d) Al_2O_3/YSZ/NiCrAlY after 356 h.

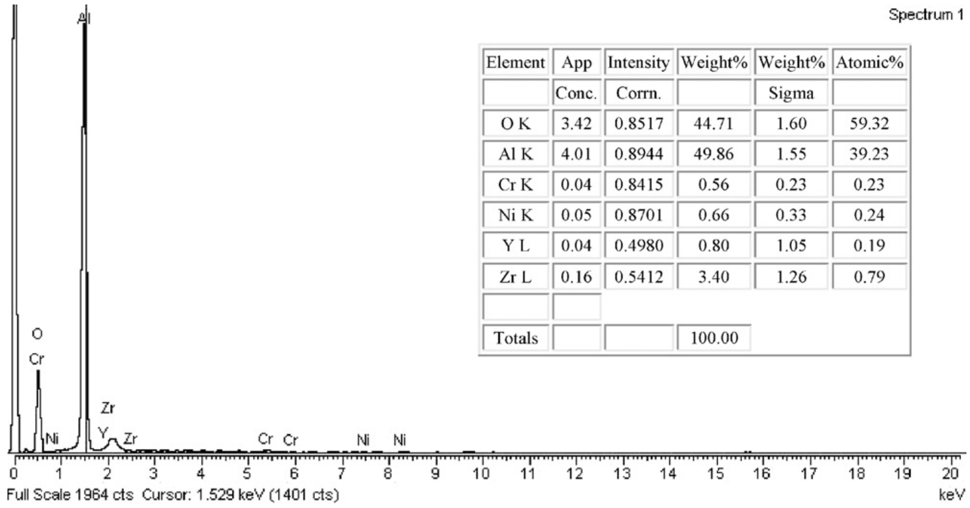
coat. Higher magnification of the microstructures (Fig. 7) clearly illustrates the TGO formed at the bond coat surface while thinner TGO layer is observed in Al_2O_3/YSZ composite interface with the bond coat.

Fig. 8 illustrates the EDS analysis at point A in the TGO region of Fig. 7d. It shows the presence of Al, Cr and Ni with plenty of oxygen which can be deduced to be oxides of the above elements. More over oxygen has also diffused through interconnected porosities of the bond coat [14] and resulted in formation of oxide layers (dark points) which may be named as internal oxidation of bond coat [15]. This phenomenon is due to lamellar structure and existence of porosity among splats of mentioned layer. The actual existence of porosities in TBCs involves two important advantages [16], i.e. increase in strain endurance during thermal cycles and decrease in thermal conductivity, yet diffusion of oxygen through porosities is one of its draw-backs.

Variation of TGO thickness after 20, 40 and 100 h of oxidation at 1100 °C is shown in Fig. 9. First of all the rate of TGO formation is higher in normal YSZ in comparison to composite layers. In the first 20 h of oxidation a fast increase in thickness is observed which is due to the formation of alumina because of high affinity of aluminum with oxygen based on thermodynamics theories [17]. The rate is slowed down until 40 h after which the increase is slow and reaches to a constant rate. The least and the most TGO layer growth occurred in Al_2O_3/YSZ and YSZ/Al_2O_3, respectively.

The TGO layer growth for Al_2O_3/YSZ coating is less than others after first 20 h of oxidation but it is then increased considerably so that after 100 h of oxidation reaches to thickest layer. Cracking occurs at the bond coat/YSZ interface (Figs. 6 and 7). The difference in thermal expansion between the mentioned layers could be responsible for this spallation. The interface of dissimilar layers which differs in mechanical and physical properties is a critical crack initiation site. As mentioned before, the TGO layer is the origin of stresses which cause crack formation and separation of ceramic coating. Various mechanisms have been proposed for this failure. As there are usually asperities in the TGO/YSZ interface and the peak in these asperities is stress concentration site. The crack initiation and spallation of ceramic layer/TGO occurs therefore in the surroundings of these peaks [18]. It has been also proposed that due to difference in thermal expansion between TGO and the bond coat can develop residual compression stresses [16] which are freed as tensile stresses parallel to TGO/YSZ interface after the next thermal cycles leading to interface spallation [15]. The increase in TGO layer thickness certainly corresponds to the development of larger stresses.

As it is observed in Fig. 9, the TGO layer thickness is much less in Al_2O_3/YSZ in comparison to ordinary TBC coating.



Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
O K	3.42	0.8517	44.71	1.60	59.32
Al K	4.01	0.8944	49.86	1.55	39.23
Cr K	0.04	0.8415	0.56	0.23	0.23
Ni K	0.05	0.8701	0.66	0.33	0.24
Y L	0.04	0.4980	0.80	1.05	0.19
Zr L	0.16	0.5412	3.40	1.26	0.79
Totals			100.00		

Fig. 8. Spot analysis from TGO layer at point A in Fig. 7d.

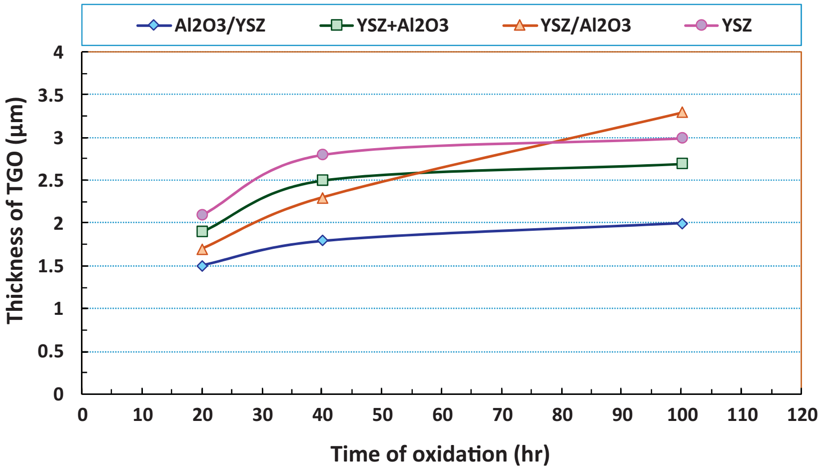


Fig. 9. TGO layer thickness versus oxidation time diagram at 1100 °C.

Hence alumina topcoat in Al_2O_3/YSZ coating plays an important role in decreasing oxygen diffusion into zirconia ceramic layer. Since Al_2O_3 is a stochiometric oxide, oxygen ions diffusivity from alumina particles is much less than zirconia particles [20]. The oxygen permeability of the Al_2O_3 coatings was found to be lower than that of zirconia coatings. This may be attributable to the lower porosity of the alumina coatings, but also suggests a lesser degree of micro-cracking or improved intersplat contact in Al_2O_3 coatings [21].

Basically the oxygen diffusion into bond coat and its internal oxidation through the existence of TGO protection layer arises from the following factors: (i) The existence of interconnected porosities due to the plasma spray process; (ii) Connection of these porosities from ceramic coating with TGO and NiCrAlY layers; (iii) Cracking in TGO layer due to its thickening and exerting compressive and tensile stresses during thermal cycles; (iv) Formation of nano-scale width crack within zirconia crystals [21].

However it should be mentioned that the Al_2O_3 layer on top of YSZ spalled and was separated after 356 h of oxidation, though the YSZ and bond coat remained unaffected because of Al_2O_3 presence.

The failure of TBCs occurs generally within ceramic layer near TGO/YSZ interface and is composed of the following steps [22]: (i) The growth of thermally grown oxide, which will induce the tensile stress normal to the YSZ/TGO interface within the ceramic top coat; (ii) The propagation of lateral cracks within the ceramic top coat with thermal cycling due to the tensile stress normal to the YSZ/TGO interface; (iii) When the length of the lateral cracks reaches a certain critical value, the coating fails by delamination or buckling.

It should be noted that at high temperatures the cracks do not travel to NiCrAlY bond coat which is due to its ductility. By the way the voids near the ceramic and intermediate layers act as suppressers of crack propagation [23].

4. Conclusions

Based on the experimental results, it could be concluded that presence of alumina as a top coat or as mixed oxide with YSZ can improve the durability of YSZ coating towards oxidation at 1100 °C presumably by oxygen diffusion slowdown. This improvement is partly due to infiltration through the pores or via the oxide crystal structure. The thickness of the TGO which is an indication of diffused oxygen through the TBC layer was reduced when Al_2O_3 was used as a top layer on YSZ.

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