A significant improvement in efficiency has been achieved by using thermal barrier coatings (TBCs) in gas turbines and diesel engines. A typical TBC is a multilayered coating system that comprises an oxidation-resistant metallic bond coating (BC) and a thermally insulating ceramic top coating (TC). Under service conditions an Al₂O₃ inter-layer, the thermally grown oxide (TGO), forms in the interface between the bond and the top coating, by a chemical reaction between the metallic aluminium from the BC material and the oxygen that comes from the environment through the pore channels of the TC. The aim of the present study is to describe the TGO formation on metallic bond coats deposited using the high-velocity oxygen fuel (HVOF) spraying technique. Therefore, TBCs that consist of a YSZ top (ZrO₂ + 8% Y₂O₃) and YSZ-Al₂O₃ double-layer systems with CoNiCrAlY bond coats were deposited on Inconel 718 super-alloy substrates. The bond coats were applied via HVOF, with the ceramic top coats being applied by atmospheric plasma spraying (APS) as well. The oxidation behaviors of the TBC systems were investigated. The oxidation tests were performed at 1000 °C in an air atmosphere for (8, 24, 50) h. The formation and growth of the TGO layers and the microstructural changes during the oxidation tests were scrutinized systematically. The results indicate that the TBC coating with the YSZ-Al₂O₃ double layer had a higher oxidation resistance and a lower TGO layer growth than that of the traditional TBC system. Likewise, the initial state of the porosity plays a critical role in enhancing or limiting the growth of the TGO scale in the TBC.

Keywords: thermal barrier coatings (TBCs), oxidation behavior, thermally grown oxide (TGO), high-velocity oxygen fuel (HVOF), atmospheric plasma spraying (APS)

Doseženo je bilo občutno izboljšanje učinkovitosti plinskih turbin in dieselskih motorjev z uporabo toplotnih zaščitnih prevlekov (TBC). Značilni TBC je večslojni varovalni sistem, ki vključuje prevleko, odporno proti oksidaciji, s kovinsko vezjo (BC) in toplotno izolativno keramično vrhnjo plastičo (TC). Pri obratovalnih razmerah vzemi sloj Al₂O₃ omogoča nastanek oksidov (TGO) na stiku med vezivnim in vrhnjim slojem, s kemijsko reakcijo kovinskega aluminija iz BC-materiala in kisika, ki iz okolice prodira skozi pore TC. Namen te študije je opisati nastanek TGO na kovinskem vezivu, nanesenem z nabrizgavanjem z kisikovim plamenom z veliko hitrostjo (HVOF). TBC, ki sestoji na vrhu iz YSZ (ZrO₂ + 8% Y₂O₃) ter z dvoslojnimo sistemom YSZ-Al₂O₃ z vezivno plastico CoNiCrAlY so bili naneseni na podlago iz superžlitine Inconel 718. Vezivna plast je bila nanesena z HVOF, keramični vrhnji sloj pa z atmosfersko plazmo (APS). Preiskovane so bili značilnosti oksidacije TBS-sistema. Preizkus oksidacije so bili izvršeni na zraku pri 1000 °C, za (8, 24 in 50) h. Med preizkusi oksidacije so bili sistematično preiskovani nastanek in rast TGO-plasti ter spremembe v mikrostrukturi. Rezultati kažejo, da ima TBC-prevelka YSZ-Al₂O₃ z dvomim slojem boljšo odpornost proti oksidaciji in manjšo rast TGO-plasti v primerjavi z navadnim TBS-sistemom. Videti je, da ima začetna poroznost ključno vlogo pri pripompevanju ali zaviranju rasti TGO-plasti na TBC.

Ključne besede: termični varovalni sloj (TBC), vedenje pri oksidaciji, termična rast oksida (TGO), kisikov plamen z veliko hitrostjo (HVOF), atmosfersko plazemsko nabrizgavanje (APS)

1 INTRODUCTION

Many attempts have been made to understand the role of TGO, formed at the interface between the bond coat and the top coat during elevated-temperature service conditions, which strictly governs the lifetime of the TBC. The thickness, the roughness of the TGO, the adherence quality of the bond coat to the substrate, the type and shape of the oxides present in the vicinity of the TGO during oxidation are the main issues in controlling the degradation of the TBC.1–5 Likewise, the oxidation behavior of the TBC is strongly linked to the bond coat properties, which affect the durability of the TBC. The bond coat is deposited conventionally by LPPS, HVOF, plasma and also cold gas dynamic spray: a method recently preferred to avoid complex oxide formation as well.5–8

Generally, the forming of a dense, homogeneous, α-Al₂O₃ oxide scale is preferred as it is relatively stable, chemically and thermally, which means the degradation of the α-Al₂O₃ is negligible and also has a low ion diffusivity, which causes a slow growth rate and prevents further oxidation.9–11 Oxidation-based damage, which is the result of stresses developed at the interface of the top coat and the bond coat during TGO growth, is a common failure of TBC since these stresses result in the
spallation-induced failure of the topcoat. In order to retard or avoid such a failure in the TBC, i.e., better oxidation resistance, any methods employed should facilitate the slow growth of the TGO scale, which favors good adherence of the TGO. To achieve this, apart from using several kinds of methods to deposit the bond coat, a thermal barrier thin film deposited by EB-PVD, CVD, etc. was employed over the bond coat in order to inhibit the formation of undesirable mixed oxides as they have a fast growth rate leading to accelerated TBC failure.

In addition, the introduction of alumina powders to the YSZ might possibly reduce the inward diffusion of oxygen from the topcoat and thus make it difficult to have rapid growth of the TGO. It was claimed in studies that Al2O3 present in the topcoat exhibited better oxidation resistance compared to the YSZ without Al2O3 powders. In this work, the YSZ topcoat with a conventional composition and with YSZ/Al2O3 double-layer systems were applied on Inconel 718 super-alloy substrates to investigate and compare their oxidation behaviors. The oxidation results for the traditional TBC that has the YSZ system was compared with the YSZ/Al2O3 double-layer TBC system. The microstructural differences and the formation and growth of the TGO layers in the isothermal oxidation resistance of these TBC systems are discussed.

2 EXPERIMENTAL METHODS

2.1 Materials and coating-deposition methods

The Inconel 718 Ni-based super-alloy, in disc-shaped coupons, was used as the substrate. CoNiCrAlY, ZrO2–8% Y2O3, and Al2O3 powders were used as the starting materials. A Microtrack S3500 laser particle-size analyzer was used to determine the powder size distribution. The mean diameters were determined to be d0 = 33 μm, 38.52 μm, 33.36 μm for the CoNiCrAIY, ZrO2–8% Y2O3, and Al2O3 powders, respectively. Half of the TBC samples consisted of a CoNiCrAIY BC and a ZrO2–8% Y2O3 TC and the other half of the TBC samples were composed of a CoNiCrAIY BC, a ZrO2–8% Y2O3 TC and an Al2O3 top coat over the YSZ. The HVOF technique was used to produce bond coats and the ceramic top coatings were produced by the APS method using a fully automated MultiCoat System from Sulzer Metco. All the spraying parameters are shown in Table 1.

2.2 Microstructural Characterization

The microstructures of the TBC systems were investigated by scanning electron microscopy (SEM, Tescan VEGA II, SBU Bruker EDX, Czech Republic). The porosity of the bond coatings was measured using optical image-analysis software (Olympus a4i). The coating microhardness (HV0.3) was determined using a microhardness tester (Shimadzu, Japan) with a load of 300 g for 15 s from the bond coats and the top coats. The oxidation tests of the TBC system produced were conducted by means of a high-temperature furnace (Nabertherm, Germany) with an air atmosphere.

3 RESULTS AND DISCUSSION

3.1 Microstructure of the powders and the coatings

Two types of TBC were prepared using the HVOF method to produce bond coats that included CoNiCrAIY. The APS method was used to produce ceramic top coats, which included traditional YSZ and a double layer of YSZ and Al2O3 in which the Al2O3 was a top coat over the YSZ in a second system. The thickness of the bond and the top coats of both systems were about 100 μm and 300 μm, respectively. The YSZ top coat used in the first system was 300 μm. The YSZ and Al2O3 ceramic top coatings used in the second system were both 150 μm. The type, components, thicknesses and spray systems of the coating layers are shown in Table 2.

Table 2 shows the morphology of the as-received ZrO2+Y2O3, Al2O3 and CoNiCrAIY powders. As can be seen from this figure, the CoNiCrAIY powder has a spherical morphology, while the Al2O3 is angular. Figures 2a and b show the cross-sectional microstructure of
traditional TBC and Al₂O₃-YSZ gradient double layer TBC system. The HVOF-CoNiCrAlY bond coats have relatively less porosity and cracks in the TBCs.

The ceramic top coats contain porosity and some crack-like discontinuities during the spraying process. A smaller amount of porosity for the BC of both TBC systems was measured to be approximately 1.0 %. On the other hand, like for the top coat the porosity values were not significantly different from each other. The porosity level of the top coat was found to be approximately 5.0 % in both TBC systems. But as is clear from Figure 2, the size and distribution of the porosity in the TC of the two-layer YSZ/Al₂O₃ TBC are quite different from the traditional values.

3.2 Oxidation tests

The TBC specimens were subjected to oxidation tests. These oxidation tests were carried out in an air atmosphere at 1000 °C for (8, 24 and 50) h. Typical SEM microstructures of the whole TBC-systems are shown in Figures 3 and 4.

As shown in these figures, the TGO was formed at the ceramic/bond-coat interface due to oxygen penetration through the ceramic layer. Various formations of
discontinuities between the bond layer and the ceramic top layer can be clearly seen in Figures 3 and 4.

When the oxidation properties of the two different TBC systems are compared, it was clear that the oxidation in the conventional TBC system (CoNiCrAlY bond layer with YSZ top coat) developed faster than that of the YSZ/Al₂O₃ double-layer TBC system, and the TGO growth rate in the former system was found to be higher. As seen from the interface microstructures given in Figure 5, the TGO structure in the YSZ/Al₂O₃ double-layer TBC system is more uniform and is mainly composed of Al₂O₃, which was confirmed by an EDX analysis. In the conventional YSZ system, due to the increasing oxidation process, complex oxides developed in the TGO layer and affected the growth behaviors of the TGO. This was caused by the prevention of the oxygen penetration to the bond coat from the surface due to the Al₂O₃ layer and hence a slowing down of the oxygen attack in YSZ/Al₂O₃ coating systems. As a result, the decrease of the Al₂O₃ content in the TGO layer caused by bond-coat oxidation is delayed, the degradation of the uniform structure is retarded and in this way an increase in the volume of the TGO occurs at a lower rate. Similar results showing an increase in the oxidation resistance of the coatings due to the Al₂O₃ layer depending on the temperature and the time exist in the literature²⁰–²⁵.

Figure 6 indicates that the thickness of the TGO layer increased with increasing exposure time for both
kinds of TBC specimens. The specimens with the YSZ top coatings with CoNiCrAlY bond coatings show a higher rate of TGO thickness growth than the samples with YSZ/Al₂O₃ top coatings with CoNiCrAlY bond coatings. This difference could be attributed to the initial porosity state of the as-sprayed TBC samples and/or the Al₂O₃ layer acting as a diffusion barrier due to its low diffusion coefficient for oxygen ions. This effect has been observed in many other studies 20-25.

Therefore, the greater the increase of the TGO thickness of the specimen with traditional YSZ top coatings with CoNiCrAlY bond coatings at the same exposure time compared to the specimen YSZ/Al₂O₃ top coatings with HVOF-BC could be attributed to this mechanism. After increasing the exposure time the TGO layer thickness increased to higher values.

3.3 Mechanical properties

The microhardness value for the bond and top coats were taken from the average value of all the measurement points. Figures 7 and 8 present the Vickers microhardness measurements before and after the oxidation tests for the bond and the top layers. The bottom and top limit lines in the graph show the maximum and minimum hardness values. The microhardness of the substrate Inconel 718 super-alloy was in the range 310–340 HV.

The mean values of the bond and top-coat microhardness changed before and after the oxidation tests with increasing time. The microhardness of the bond coats decreased with increasing time at 1000 °C for traditional and two-layered coatings. The decline in microhardness of the bond coatings was possibly linked to the decrease in the density of the bond coats. The decrease of the microhardness in the HVOF bond coats is related to the thermal relaxation of the residual stress present in the as-sprayed coating due to the high temperature. The fact that the decrease in microhardness after 8 h is higher while the decrease after 24 h is lower and no change is observed after 50 h should support this theory, i.e., thermal relaxation occurs very quickly, and since almost no change in microhardness is observed after 8 h it can be concluded that this initial change is due to thermal relaxation.

The microhardness of the top coats increased with increasing time at 1000 °C for the traditional and two-layered ceramic coatings. According to the literature, the situation mentioned above is caused by the decreasing density of the porosity and the increasing density of the ceramic top coating depending on increasing time 26.

4 CONCLUSIONS

Traditional YSZ and YSZ/Al₂O₃ double-layer TBCs were produced using the APS technique and bond coats were deposited using the HVOF spraying technique. The following results were obtained:

During oxidation of the TBCs, the TGO layer was formed along the interface of the BC/TC layer. The thickness of the TGO in the traditional YSZ coating is higher in comparison with the YSZ/Al₂O₃ coating after oxidation at 1000 °C for different oxidation times. According to the TGO growth in both TBC systems, the TGO thickening became steady state in the YSZ/Al₂O₃ two-layer system and, on the other hand, the TGO
thickness in the traditional TBC system was still increasing. The different formations of the discontinuities between the bond and the ceramic top layers were observed. The ceramic top coats contained porosity and some crack-like discontinuities for both kinds of TBC. After a prolonged oxidation time the number of cracks was much larger in the traditional YSZ ceramic top coat with the CoNiCrAlY bond coating system. The initial porosity state of the as-sprayed TBC samples and/or the acting of the Al2O3 layer as a diffusion barrier at high temperatures have a great influence on determining the TGO growth, since they change the penetration behavior of the oxygen from the surface. In the conventional YSZ system, due to the increasing oxidation process, complex oxides developed in the TGO layer and affected the growth behaviors of the TGO. The mean values of the bond and top-coat microhardnesses changed before and after the oxidation tests with increasing time. The microhardness of the bond coats decreased and that of the top coats increased with increasing time at 1000 °C for the traditional and two-layered coatings.

5 REFERENCES

6 Y. Li, C. J. Li, G. J. Yang, L. K. Xing, Thermal fatigue behavior of thermal barrier coatings with the MCrAlY bond coats by cold spraying and low-pressure plasma spraying, Surface and Coatings Technology, 205 (2010), 2225–2233
10 P. Richer, M. Yandouzi, L. Beauvais, B. Jodoin, Oxidation behaviour of CoNiCrAlY bond coats produced by plasma, HVOF and cold gas dynamic spraying, Surface and Coatings Technology, 204 (2010), 3962–3974

18 M. Sarem, A. Afsariabi, A. Kobayashi, Microstructural analysis of YSZ and YSZ/Al2O3 plasma sprayed thermal barrier coatings after high temperature oxidation, Surface and Coatings Technology, 202 (2008), 3233–3238
23 J. Müller, M. Schierling, E. Zimmermann, D. Neuschütz, Chemical vapor deposition of smooth a-Al2O3 films on nickel base superalloys as diffusion barriers, Surface and Coatings Technology, 120–121 (1999), 16–21