Oxidation behavior of thermal barrier coating systems with Al interlayer under isothermal loading

I Ali1, P Sokołowski2, 3, T Grund1, L Pawłowski2 and T Lampke1

1 Institute of Materials Science and Engineering, Chemnitz University of Technology, Chemnitz, Germany
2 Institut de recherche sur les céramiques IRCER, University of Limoges, Limoges, France
3 Faculty of Mechanical Engineering, Wrocław University of Technology, Wrocław, Poland

Abstract. In the present study, the phenomena related to the Thermally Grown Oxides (TGO) in atmospheric plasma sprayed Thermal Barrier Coatings (TBCs) are discussed. CoNiCrAlY bond coatings were sprayed on Inconel 600 substrates. Subsequently, thin Al layers were deposited by DC-Magnetron sputtering. Finally, yttria-stabilized zirconia (YSZ) top coatings were deposited to form a three-layered TBC system. The thus produced aluminum interlayer containing thermal barrier coatings (Al-TBC) were subjected to isothermal exposure with different holding times at 1150 °C and compared with reference TBCs of the same kind, but without Al interlayers (R-TBC). The oxide film formation in the interface between bond coating (BC) and top coating (TC) was investigated by scanning electron microscope (SEM) after 100 and 300 h of high temperature isothermal exposure. The growth of this oxide film as a function of the isothermal exposure time was studied. As a result, the designed Al-TBC system exhibited better oxidation resistance in the BC/TC interface than the two-layered R-TBC system. This was lead back to the Al enrichment, which slows down the formation rate of transition metal oxides during thermal loading.

1. Introduction

Progress in gas turbines technology is largely associated with developments in the research area of Thermal Barrier Coatings (TBCs). Plasma spraying and electron beam physical vapor deposition methods have been used to produce TBCs since the 1960s and 1980s, respectively [1-5]. Recently, suspension plasma spraying (SPS), liquid solution precursor plasma spraying (SPPS), suspension high velocity oxy-fuel spraying and plasma-spray physical vapor deposition (PS-PVD) were introduced to modify the microstructure of the ceramic top coatings of the TBC systems. The recent generation of TBCs thus shows a smaller thermal conductivity and better performance under thermal loads in comparison to older generations [5-8].

The current design of a TBC system in turbine applications consists of two main coatings: (i) a metallic bond coating (BC), which is sprayed directly onto the base material and (ii) a ceramic top coating (TC), which insulates the coated component from high-temperature gas atmosphere [9-10]. The BC is composed of MCrAlY alloys (M=Ni, Co or NiCo alloy) and plays two important roles. Firstly, it provides an effective protection of the substrate against high-temperature oxidation. And secondly, it reduces thermal stresses that affect the ceramic TC material in thermal cycling loads due to CTE mismatches between the metallic and ceramic partners in the TBC system [11-12]. The TCs
are most frequently composed of phase-stabilized zirconia (rare-earth-doped zirconia, mainly with yttrium) [13-14]. The so-called TGO layer in TBC systems summarizes thermally grown oxides which develop and grow during high-temperature service in the BC/TC interface. Since TGO introduce additional stress into the TBC system and hence cause TBC failure, one possible way to increase the lifetime of TBCs is to control the formation of the TGO and minimize their growth rate [15-16].

In the present work, thin Al interlayers were applied between BC and TC obtained by atmospheric plasma spraying in order to improve the oxidation resistance of the BC by direct and fast formation of alumina films on top of this interlayer. TGO development and growth during isothermal loading was then analyzed and quantified. The obtained results were compared to those obtained with conventional reference TBC systems (R-TBC).

2. Experimental work

The single coating layers included in TBCs were prepared by air plasma spraying (APS) on Inconel 600 (DIN 2.4816, UNS N06600) substrates with rectangular dimensions of 30 x 10 x 3 mm. They included a CoNiCrAlY bond coating (CoNi32Cr21Al8Y0.5, 60.95.1, GTV GmbH) and an yttria-stabilized zirconia (YSZ) top coating (ZrO2 + 8 wt.-% of Y2O3, Oerlikon Metco 204NS). Substrate sheets were grit blasted and cleaned before spray coating application. BCs were sprayed with a thickness of 150 µm using a F6 plasma torch (GTV GmbH). Thin Al films of 2 µm thickness were sputtered on the as-sprayed BC surfaces using a non-commercial DC-Magnetron PVD coating unit B0 TSP. (working pressure: 8 x 10⁻³ mbar, Al target: Al 99.999 %, EVOCHEM Advanced Materials GmbH, sputtering gas: Ar 99.9999 %). Roughness measurements by contact stylus instrumentation and basing on statistical determination according to ISO 11562 were conducted on the raw as well as the Al-covered BC surfaces. Afterwards, YSZ TCs were sprayed using plasma torch SG-100 (Praxair S.T.) to a thickness of 150 µm. BCs and TCs were sprayed according to the given parameters in Table 1. The designs of TBCs used in the present study are shown in Figure 1. The microstructure of the as-sprayed TBC systems was investigated using laser scanning microscopy. The porosity content in the coatings was determined using digital image analysis.

The TBC systems were submitted to isothermal exposure tests. Samples were heated up in air from room temperature (RT = 20 °C) up to 1150 °C with a heating rate of 6 K/min, then held for 100 or 300 h at 1150 °C and finally cooled down to RT with cooling rate of 0.5 K/min. After thermal treatment, all specimens were metallographically polished and analyzed using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXS).

Table 1: Spraying parameters of BC and TC using atmospheric plasma spraying

| Spray powder | Co32Ni21Cr8Al0.5Y | YSZ |
|--------------|------------------|-----|
| Ar [slpm]    | 65               | 45  |
| H2[slpm]     | 14               | 5   |
| Plasma current [A] | 600   | -   |
| Plasma power [kW] | -       | 40  |
| Spray distance [mm] | 140  | 100 |
Figure 1: Schemes of the two TBC designs analyzed in the present study

3. Results

3.1. Microstructure of as-sprayed TBC
The microstructures of R-TBC and Al-TBC samples are shown in Figure 2. The BC in both systems reveals the typical microstructure of APS sprayed metal coatings showing oxide scales, pores, flakes and inter-lamellar delamination between molten splats. Porosity and oxide content are about 2 % and 22 %, respectively. The porosity of the YSZ TC is about 7 %. The TBCs show generally good contact between TC and BC by mechanical interlocking, anticipating a good adhesion. In the Al-TBC design, the Al interlayer was not influenced by application of the TC. The interlayer is, however, not homogeneously and continuously formed, that results in zones of direct contact between the BC and TC (Figure 2, right, regions marked by circles). This is either due to shadowing effects resulting from the roughness of the as-sprayed BC surface or due to inhomogeneous grain growth of the DC-sputtered aluminum on the rough and chemically inhomogeneous BC surface. Consequently, the sprayed YSZ particles could have removed some parts of the Al interlayers. In comparison to the uncoated BC, the surface roughness of the Al-covered BC is not altered by the 2 µm thick Al layer. Measurements revealed $R_a = 7 \, \mu m$ and $R_z = 49 \, \mu m$ for the uncoated BC surface, but $R_a = 7 \, \mu m$ and $R_z = 50 \, \mu m$ for the Al-coated BC surface.

Figure 2: Laser intensity images show the as-sprayed microstructures of the TBC systems, left: without Al interlayer, right: with Al interlayer; the marked zones highlight limited BC surface areas that have not been fully covered by the DC-PVD Al interlayer and reveal direct contact between BC and TC material.
3.2. Microstructure of as-sprayed TBC

The microstructures of the TBC after both 100 h and 300 h of isothermal exposure are shown in Figure 3. The Al-TBC system (Figure 3, right) exhibits a thinner TGO layer (dark grey region between BC and TC) in comparison to the R-TBC system. The difference is already visible after 100 h, but much more pronounced after 300 h, wherein the optically estimated reduction is about factor 3.

![Figure 3: Back-scattered electron SEM micrographs of the cross-sections of Al- and R-TBCs after isothermal exposure at 1150 °C, left: R-TBC without Al interlayer, right: Al-TBC with Al interlayer, top: after 100 h of exposure, bottom: after 300 h of exposure; arrows point to an area/diffusion front with heightened contents of “Al” and “O” on the BC facing side and in comparison to the BC material composition.](image)

EDXS mapping on the Al-TBC samples show, the semi-continuous dark zone into the BC material starting from the BC/TC interface is rich in aluminum and oxygen (Figure 4). This observation suggests that part of the Al diffuses during isothermal exposure into the bond coating material, and the non-continuous dark line hence represents the diffusion boarder. The diffusion is probably supported by interlamellar surface diffusion and hinders diffusion of oxygen and thus, consequently, improves the BC’s oxidation resistance.

In both systems - Al-TBC and R-TBC - the investigated microstructures during isothermal exposure reveal the so-called “isothermal failure mode”. Crack paths run across the TGO as described in [17-19]. Since the R-TBC samples show thicker TGO in comparison to Al-TBC ones, crack paths initiate and follow the TGO layer in higher density within these standard TBC systems. This is in accordance with the state-of-the-art. It has been reported that the growth of TGO is correlated with long delamination cracks along the YSZ TC and near the BC/TC interface [20-23]. Consequently, the use of Al interlayer in TBC systems can effectively slow down TGO growth and is hence a useful approach to increase the lifetime of TBC systems.
4. Conclusion

The Al-TBC design, showing DC-PVD Al interlayers between BC and TC, form a TGO less intensively at isothermal exposure than R-TBCs. The reason is the presence of Al at BC/TC interface, which results in the diffusion of Al into the BC material and enable a steady TGO growth, probably by reducing oxygen diffusion. This may may lead to an increased service time of Al-TBC in comparison to R-TBC systems. The investigated microstructures of both TBC systems revealed the so-called “isothermal-failure mode”, however in different intensities.

![Figure 4: Back-scattered electron SEM micrograph and respective EDXS mapping of Al-TBC cross-section showing BC/TC interface with former Al interlayer and oxidation status after 100 h of isothermal exposure at 1150 °C.](image)
5. References

[1] Peters M, Leyens C, Schulz U, Kaysser W 2001 Adv. Eng. Mater., 3/4 pp 193–204
[2] Gleeson B, Sordelet D 2014 US Patent 8,821,654 B2
[3] Trunova O, Beck T, Herzog R, Steinbrech R, Singheiser L 2008 Surf. Coat. Technol., 202 pp 5027–32
[4] Jones R 1997 J. Therm. Spray Technol., 6/1 (1997) pp. 77–84
[5] Darolia R 2013 Int. Mater. Rev., 58/6 pp 315–48
[6] Bakan E, Vassen R 2017 J. Therm. Spray Technol., 26 pp 992–1010
[7] Sokolowski P, Pawlowski L, Dietrich D, Lampke T, Jech D 2015 J. Therm. Spray Technol., 25 (1-2) pp 94–104
[8] Podlesak H, Pawlowski L, Haese R, Laureyns J, Lampke T, Bellayer S 2010 J. Therm. Spray Technol., 19/3 pp 657-64
[9] Miller R 1987 Surf. Coat. Technol. 30/1 pp 1-11
[10] Padture N, Gell M, Jordan E 2002 Science, 296/5566 pp 280-84
[11] Jarvis E, Carter E 2002 Comput Sci Eng, 4/2 pp 34-41
[12] Spitsberg I, Mumm D, Evans A 2005 J. Mater. Sci. Eng. A., 394/1–2 pp 176-91
[13] Zhu D, Miller R 2008 Proc., of the 35th Int., Conf., on Metallurgical Coatings and Thin Films (ICMCTF), [Editors: Pauleau Y and Mayrhofer P et al], American Vacuum Society, (San Diego, CA)
[14] Sokolowski P, Latka L, Pawlowski L, Ambroziak A, Kozerski S, Nait-Ali B 2015 Surf. Coat. Technol. 268 pp 147–52
[15] Ali I, Grund T, Lampke T, Wett D, Nestler D and Wagner G 2015 Proc., of the Int., thermal Spray Conf., ASM Int., [Editors: McDonald A and Agarwal A et al]. (Long Beach, CA)
[16] Evans A, Mumm D, Hutchinson J, Meier G, Pettit F 2001 Prog. Mater. Sci. 46 pp 505-53
[17] Herzog R, Trunova O, Steinbrech R, Singheiser L 2006 First Japanese-German workshop on properties and performance of thermal barrier coating systems and factors affecting it., Darmstadt, Presentation
[18] Trunova O, Beck T, Herzog R, Steinbrech R, Singheiser L 2008 Surf. Coat. Technol. 202, pp 5027-32
[19] Herzog R, Warnken N, Steinbach I, Hallstedt B, Walter C, Mueller J, Hajas D, Muenstermann E, Schneider J, Nickel R, Parkot D, Bobzin K, Lugscheider E, Bednarz P, Trunova O, Singheiser L 2006 Adv. Eng. Mater. 8/6 pp 535-62
[20] Karaoglanli A, Altuncu E, Ozdemir I, Turk A, Ustel F 2011 Surf. Coat. Technol. 205 pp 369-73
[21] Kwon J, Lee J, Gil Y 2006 Surf. Coat. Technol. 201 pp 3483-90
[22] Munawar A, Schulz U, Cerri G, Lau H 2014 Surf. Coat. Technol. 245 pp 92-101 (doi: 10.1016/j.surfcoat.2014.02.047)
[23] Tsai P, Tseng C, Yang C, Kuo L, Chou Y, Lee J 2013 Surf. Coat. Technol. 228 pp 11-14