Surface & Coatings Technology 245 (2014) 92–101

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Microstructure and cyclic lifetime of Gd and Dy-containing EB-PVD TBCs deposited as single and double-layer on various bond coats

Ahmed Umar Munawar [a,b,*], Uwe Schulz [b], Giovanni Cerri [a], Hendrik Lau [b]

[a] University of Roma Tre, Via Della Vasca Navale 79, Rome 00146, Italy
[b] German Aerospace Center (DLR), Linder Hoehe, Cologne 51147, Germany

A R T I C L E I N F O

Article history:
Received 1 January 2014
Accepted in revised form 21 February 2014
Available online 28 February 2014

Keywords:
Thermal Barrier Coatings
EB-PVD
Gadolinium zirconate
Dysprosia-stabilized zirconia

A B S T R A C T

Gadolinium zirconate (GdZ) and dysprosia stabilized zirconia (DySZ) are known for their lower thermal conductivity and higher thermal stability. In the present study, Electron Beam Physical Vapor deposited (EB-PVD) GdZ and DySZ are coated on different bond coats and the TBC systems are investigated for their lifetimes by thermal cycling at 1100 °C. Lifetime values of these new TBC systems are then compared with their standard 7YSZ counterparts. GdZ top coats on NiCoCrAlY bond coats show a longer lifetime than the standard 7YSZ systems. However, on the (Ni, Pt)–Al bond coat lifetimes are generally short and 7YSZ shows a longer lifetime than the GdZ based systems. On NiCoCrAlY bond coats, single layer TBCs show longer lifetimes than their double layer counterparts. During thermal cycling, a chemical reaction between GdZ and the thermally grown oxide occurs, however, it has not been found detrimental for the lifetime of TBC systems. Besides lifetime investigations of different TBC systems, their failure patterns, diffusion of elements, phase changes and sintering of the TBC materials due to thermal cycling are also discussed.

1. Introduction

Thermal Barrier Coatings (TBCs) refer to a multi-coating system which is extensively used in gas turbines to withstand high temperature, temperature cycling, stress, and oxidation and corrosion conditions. A TBC system consists of a metallic bond coat and a ceramic top coat applied on a substrate which is usually made up of a nickel or cobalt based superalloy. The purpose of the ceramic top coat is to cause a maximum temperature drop across its thickness thereby lowering the metal temperature. The metallic bond coat is incorporated into the system to provide oxidation resistance at high temperatures and to improve the lifetime of TBC systems by forming a suitable oxide layer. This oxide layer which forms during the deposition of TBC and grows continuously when the TBC system is in operation is called thermally grown oxide (TGO). So far, 7 wt.% yttria stabilized zirconia (7YSZ) has been the most widely used material for the ceramic top coat layer because of its suitable properties [1–3]. For the bond coat, (Ni, Pt)–Al or MCrAlY type overlay coatings (where M = Ni or Co or a combination of both) are commonly used. The bond coat determines structure, composition and growth rate of the TGO and that's why it plays a very important role in controlling the lifetime of the TBC systems. A substantial amount of literature covers the various aspects of TBCs [1–7].

The efficiency of a gas turbine is directly proportional to the Turbine Inlet Temperature (TIT) and therefore efforts have always been made to obtain the highest possible TIT. The adiabatic combustion temperature for most of the commonly used fuels is around 2000 °C, however, most of the super-alloys that constitute the engine components have their melting points in the range of 1300 °C. Therefore, the ceramic top-coat materials must have a low thermal conductivity so that they can cause a maximum temperature drop across the thickness. In addition, they should have the ability to withstand those high temperatures. The upper temperature limit for the state-of-the-art 7YSZ has been found to be approximately 1200 °C as long term exposure at this temperature causes some detrimental effects in 7YSZ [8–10]. Therefore, the combustion products are diluted with compressed air and turbine blades are heavily cooled to ensure their safe operation at the allowed service temperature of the materials. For the ceramic top coat material, new compositions are being searched for, which have a lower thermal conductivity and a higher thermal stability. This will ensure the operation of a gas turbine at a higher temperature or if utilized at the current operation temperature, the lifetime of the components can be improved.

Two of the relatively new compositions which have a lower thermal conductivity and high thermal stability are gadolinium zirconate (GdZ) and dysprosia stabilized zirconia (DySZ) [11–16]. Recently, some studies have shown excellent resistance of GdZ against CMAS [17–20] and volcanic ash [21,22]. However, incompatibility between GdZ and TGO due to the formation of a perovskite phase has also been reported [23] which is assumed to result in a lower lifetime. To overcome these

* Corresponding author at: German Aerospace Center (DLR), Linder Hoehe, Cologne 51147, Germany. Tel.: +49 2203 601 2560; fax: +49 2203 696480.
E-mail address: ahmedumar.munawar@uniroma3.it (A.U. Munawar).

http://dx.doi.org/10.1016/j.surfcoat.2014.02.047
0257-8972/

problems, double-layer structures, where a thin layer of 7YSZ is used between the new top coat compositions and bond coats, have been studied by some groups [24,25]. Another reason for using 7YSZ as the interlayer is its higher fracture toughness compared to GdZ and DySZ which is assumed to provide excellent adhesion of the TBC system.

In this study, the lifetimes of single layer and double layer EB-PVD GdZ and DySZ TBCs on IN100 super alloy substrates with different bond coat materials are investigated by furnace cyclic testing (FCT). The main focus has been on NiCoCrAlY bond coats with a variation in the yttrium content while (Ni, Pt)–Al bond coats have been included with GdZ top coats for comparison. In addition, several factors that are known to influence the lifetime were studied. These include phase changes during thermal cycling, diffusion of elements, changes in the microstructure and TGO growth. It is well known that conventional 7YSZ TBCs are highly textured [26,27]. The preferred <100> orientation of the column axis leads to strongly anisotropic mechanical properties that may further influence failure of these TBCs. For new TBC compositions information on texture is rather scarce. Therefore, phase formation and texture of GdZ and DySZ are investigated as well.

2. Experimental procedure

The samples consist of cylindrical rods of IN100 superalloy substrates with a diameter of around 6 mm and a length of around 60 mm. Two different versions of NiCoCrAlY bond coats of 75–100 μm thickness have been coated, one of the versions by a 60 kW EB-PVD coater and the other one by using a 150 kW EB-PVD coater. The main difference between the two NiCoCrAlY bond coats is their yttrium content, and to a lower extent their Cr and Al content. These two compositions are denoted by NiCoCrAlY-1 & NiCoCrAlY-2 and are presented in Table 1. The (Ni, Pt)–Al bond coats are obtained from a commercial supplier and consist of an approximately 50 μm thick two-phase outer zone consisting of the $PtAl_2$ and NiAl phases, an intermediate single phase beta zone, and the inter-diffusion zone close to the substrate. These bond coats have been manufactured by electroplating a Pt layer, followed by diffusion heat treatment and Al-diffusion. The concentration of aluminum at the top of the bond coat has been slightly above 50 at.%. For the NiCoCrAlY bond coats, peening and vacuum annealing at 1080 °C for 4 h have been done before deposition of ceramic top coat layers. For the (Ni, Pt)–Al bond coats, grit blasting is performed before any further deposition. Four different variants of the ceramic top coats in addition to the reference 7YSZ are deposited, namely single layers of GdZ and DySZ, and their corresponding double layers where an approximately 25 μm thick 7YSZ layer has been deposited between the bond coat and the new top coat composition (see Table 1). The deposition of ceramic top coats has been done in the 150 kW EB-PVD coater by using commercial ingots of 62.5 mm diameter. All samples are preheated in the same manner in a separate chamber before deposition. During deposition the samples have been rotated on a horizontal axis at 12 rpm. All top coat depositions have been carried out at a substrate temperature of around 1000 °C by using single source evaporation.

Furnace cyclic testing (FCT) of the samples has been done by holding them in a pre-heated furnace at 1100 °C for 50 min and then cooling down close to room temperature by forced air cooling for 10 min. There has been no thermal gradient in the samples, in opposite to the burner-rig tests. Failure of the TBC systems is defined as the spallation of top coat of an area with one of the dimensions greater than 5 mm. A minimum of three samples has been tested for each TBC version.

For the cross-sectional investigations, cylindrical samples were mechanically cut and prepared by standard metallographic techniques. The microstructural analysis has been done in an analytical SEM (LEO Gemini 982) equipped with EDS (energy dispersive X-ray spectroscopy) system. Texture analysis is performed on flat samples using a Siemens D5000HR diffractometer with Ni filtered Cu-K_α radiation. The pole figures are plotted with an orientation such that the rotational axis is oriented vertical. Phase analyses was done with the same radiation in a Siemens D5000 powder diffractometer equipped with a secondary graphite mono-chromator and by using the EVA/Topas software package of Bruker AXS. To overcome the strong texture, several TBCs have been detached from the substrate and milled prior to the XRD measurement.

3. Results

3.1. Morphology of the columns

All coatings possess a coarse columnar structure as common for EB-PVD TBCs. However, the GdZ columns have an increasing diameter from bottom to top which is less pronounced for 7YSZ and DySZ. When the GdZ TBCs are cut in a direction perpendicular to the rotational axis, it has been observed that the columns are not straight but they are slightly curved which has never been found in the 7YSZ and DySZ coatings [42]. The direction of curvature of the columns has been found to be the same as the direction of rotation of samples during the deposition and this curvature of the columns has been found on both cylindrical and flat samples.

Fig. 1 shows the tips of a) as-coated GdZ columns, b) GdZ columns after 2000 cycles and c) DySZ after 4000 cycles. It can be clearly seen that GdZ columns, in the as-coated condition, have inter-columnar porosity which can be observed by a boundary between the columns. There are also several column-branches and feather arms which go quite deep inside the columns. However, after thermal cycling the column tips show considerable signs of sintering that looks like if the branches are reduced and the columns seem to be more connected at their tips. DySZ columns, on the other hand, are separate from each other even after thermal cycling for 4000 cycles. Column tips for the 7YSZ layer, after thermal cycling, have been found to be similar to DySZ i.e. the columns remain separate to each other.

Fig. 2 shows the transition region between 7YSZ and GdZ in a double layer TBC in the as-coated state and after thermal cycling for 635 cycles. The as-coated columns of GdZ grow on already existing 7YSZ columns such that the continuity of the columns is not disturbed. From a performance point of view, such a structure will be more strain-tolerant than forming of new columns in the second ceramic layer. The EB-PVD systems contain inter- and intra-columnar porosity and feather arms which (marked in Fig. 2a) are useful in reducing the thermal conductivity and in accommodating the stresses in the system. These features can be directly compared before and after thermal cycling to determine the extent of sintering in the ceramic layers that leads to coarsening of intra-columnar pores, disappearing of inter-columnar pores, and reduction in the sharpness of the feather-arms. GdZ in the lower and middle regions of its column thickness is characterized by more feather-arms

Table 1
The composition of different materials used in the study.

Layer	Material	Composition in wt.%
Substrate	IN100	14% Co, 9% Cr, 5% Al, 2.3% Mo, 5% Ti, 0.18% C, 0.015% B, 0.05% Zr, 1% V, balance Ni
Bond coat	NiCoCrAlY-1	47% Ni, 21% Co, 20% Cr, 11% Al, 0.19% Y
Bond coat	NiCoCrAlY-2	49% Ni, 21% Co, 17% Cr, 12% Al, 0.42% Y
Ceramic topcoat	7YSZ	7% Y_2O_3 in ZrO_2
Ceramic topcoat	DySZ	30% Dy_2O_3 in ZrO_2
Ceramic topcoat	GdZ	60% Gd_2O_3 + 40% zirconia