Thermocyclic Behavior of Variously Stabilized EB-PVD Thermal Barrier Coatings

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Abstract

The demand for increasing gas inlet temperatures in modem gas turbines up to 1500°C and above is the main reason for the need for more reliable thermal barrier coatings. New ceramics should provide higher phase stability and better resistance against chemical attack by pollutants in the combustion gas.

Electron-beam physical vapor deposition (EB-PVD) processed, ZrO_2-based TBCs were generated on bond-coated superalloy directionally solidified (DS) samples. Common yttria-stabilized zirconias of two different compositions, as well as novel stabilizers like CeO_2 and La_2O_3 were investigated. A columnar structure was established during high-rate deposition in all cases. Diameter, degree of ordering of the columns and phase composition depended on stabilizer oxide and content. The role of differences of vapor pressures is addressed with regard to chemical homogeneity of the coatings.

The performance of the TBCs having various stabilizers was investigated in a cyclic oxidation furnace test and in a burner rig at Mach 0.3. The results were correlated to the type and content of stabilizer with special emphasis on phase analyses.

Evaporation of new ceramic compositions necessitates special precautions because the vapor pressures of the components may differ too much. A new dual-source evaporation coater allows the production of these innovative TBCs with close control of chemistry. The potential of the equipment will be discussed.

1. Introduction

Thermal barrier coatings (TBCs) on components in the high pressure turbine allow the essentially increase in gas inlet temperature. They are an integrated part of the design of blades and vanes in the new generation of high bypass aero engines as well as in the latest generation of gas turbines for power generation. A further increase of gas inlet temperature is intended for future developments to increase the engine efficiency. Higher gas temperatures will cause higher thermal load on the components, mainly of those in the combustion chamber and in the high pressure turbine. This necessitates materials that are capable of operations at temperatures much higher than currently acceptable.

There are two preferential methods to apply TBC-systems on airfoils: Plasma Spraying (PS) and Electron-Beam Physical Vapor Deposition (EB-PVD). It is well known that the EB-PVD processed TBCs offer significantly extended lifetimes, smooth aerodynamically attractive surfaces and only minor cooling hole closure. PS coatings, on the other hand, offer economic advantages and provide slightly better thermal isolation /1/.

The superiority of EB-PVD TBCs is related to their columnar microstructure /2, 3/. They consist of densely packed 2 to 25 μm diameter columnar crystals. This specialty gives EB-PVD TBCs outstanding resistance against thermal shocks and strains.

Partially yttria-stabilized zirconia (PYSZ) is the current state-of-the-art material for thermal barrier coatings. Unfortunately, the material shows insufficient phase stability and accelerated sintering at temperatures above 1200°C. Therefore, the increase of gas inlet temperature up to 1500°C and above is the main reason for the search for alternative stabilizers which should provide improved phase stability. Another argument for new stabilizers in zirconia or for completely new ceramics is the insufficient resistance of current thermal barrier coatings against

chemical attack by pollutants in the combustion gas. Hot corrosive decay of TBCs by Na_2SO_4 and vanadates are reported which involves leaching out of stabilizers from parent zirconia. The degradation occurs by transformation of high temperature phases to monoclinic on cooling. This failure mode may be found mainly in heavy duty engines and off-shore service as referenced elsewhere /4/.

An alternative composition for TBCs is ZrO_2-25wt.% CeO_2-2.5%Y_2O_3 (CeSZ). The benefits of Ce-stabilized TBCs are good corrosion resistance /5, 6, 7/ and an excellent phase stability at high temperature /8, 9/. The mechanisms of vanadium attack on zirconia are not fully understood. Therefore the discussion in literature is controversial /10, 11/. The thermal conductivity is found to be extremely low and some benefits for life time and thermocyclic resistance are reported too. This or similar Ce-containing compositions, however, were investigated only as plasma sprayed TBCs. Two short contributions on EB-PVD TBCs are excepted: one which mentions the provision of ZrO_2 - 45wt.% CeO_2 /7/ TBCs, the other presents preliminary random burner rig test results and phase analyses (100% tetragonal) of ZrO_2 - 23wt% CeO_2 /12/.

A different possibility to meet the above mentioned requirements of phase stability at higher temperatures is to stabilize the cubic equilibrium phase in the ZrO_2 - Y_2O_3 system. In this case, the content of yttria must be increased to near 20wt%.

Several alternative stabilizers have been investigated, namely candidates from rare earth oxides like scandia /13/, ytterbia /14/ or india /15/.

In this study, four EB-PVD processed ZrO_2-based TBC systems on IN100 substrates covered with a NiCoCrAlY bondcoat were examined. Samples were thermocycled in a furnace and in a high velocity burner rig. Common yttria-stabilized zirconias of two different compositions as well as zirconias with novel stabilizers like CeO_2 and La_2O_3 were investigated. This work was intended to study the feasibility of novel TBC compositions by EB-PVD and to trace the potential of these coatings for future applications in turbines.

2. Experimental procedure

Directionally solidified IN 100 pin samples of 6mm diameter and 100mm length were coated with a 75 to 90μm thick NiCoCrAlY bond coat by EB-PVD. Table 1 gives the compositions of substrate and bond coat.

Table 1: Average composition of substrate and bond coat (wt%)

	Ni	Co	Cr	Al	others
IN 100	64,1	14,1	8,6	5,1	5 Ti-2,3 Mo-0,8 V
NiCo-CrAlY	46	22	20	12	0,1...0,15 Y

Samples were EB-PVD coated with variously stabilized TBCs after peening at an Almen intensity of 12N to 14N and a vacuum heat treatment at 1080°C for 4h.

The coating equipment used in this study for both metallic and ceramic deposition was a 60kW EB-PVD single source coater with preheating chamber, facilities for rotating and moving the specimens on a 27° tilted axis, and an automated control system for power, electron beam movement and gas flow (for detailed description see /16/).

The compositions of the 50 mm diameter ceramic ingot sources for evaporation and the respective designations of the TBCs are listed below:

PYSZ   6,5 wt% Y_2O_3
FYSZ   20 wt% Y_2O_3
CeSZ   25 wt% CeO_2 - 2,5 wt% Y_2O_3
LaSZ   8   wt% La_2O_3

The substrates were rotated on a planetary drive to achieve a uniform thickness distribution around the circumference of the pins. Temperature of the substrate pins was adjusted between 1000°C and 1050°C during thermal barrier coating deposition. Condensation rate was between 5 and 7 μm/min. The total pressure in the coating chamber was adjusted to 0,2 Pa by permanent oxygen bleed in during TBC deposition. For more details see /17/.

Two alternative cyclic tests were used to quantify the lifetime of the coating systems: a burner rig and a furnace test. Cyclic burner rig tests were carried out on samples that are mounted on a rotating carousel (1000min^{-1}) under high velocity clean fuel gases of Mach 0.3-0.4 . One cycle consisted of 57 min heating at 1150°C metal temperature and 3 min quench to RT in a Mach 0.1 air stream. Optical inspection and weighing of the samples were done every 11 hours. A local spallation of ceramic coating greater than 3mm length in one direction was considered as failure. The furnace tests consisted of 9,3 min heating at 1100°C (temperature was reached within

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90 sec) and 6 min cooling in forced air down to 130°C. After each collective of 25 cycles stereo microscopic inspection was undertaken /18/. The number of samples of each type was 3 for each test.

Specimens were investigated before and after testing by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and optical microscopy. Chemical contents were measured by XRF. Oxides were calculated from measured values of elements assuming normal stoichiometry. Phases were determined from XRD measurements using copper radiation.

3. Results

The surface image of the four TBCs in the as coated condition is shown in Fig. 1.

A columnar structure is apparent in all cases with some noticeable differences between the various ceramics. FYSZ and CeSZ posses a larger column diameter and a higher degree of ordering as well. LaSZ, on the other hand, has the most nonuniform shape of the terminal section of columns which can be seen in Fig. 1d). Here many small protrusions on top of larger crystals can be found. The standard material PYSZ lies between these two extremes with more irregularities than CeSZ and FYSZ but not as many as with LaSZ. Some differences in the symmetry of the terminal faces must be considered. Because of the 27° tilted rotational axis all columns were also not perpendiculare to the surface.

The results of phase analyses can be summarized as follows:

PYSZ fully metastable tetragonal t' phase
FYSZ fully equilibrium cubic phase
CeSZ mixture of cubic, tetragonal, and occasional monoclinic phases
LaSZ mixture of mainly tetragonal, minor cubic, and substantial amounts of monoclinic phases.

Phase analysis is described in more detail in /17/.

The compositions of the three binaries TBCs PYSZ, FYSZ, and LaSZ were close to the ingot compositions. In the case of the ternary composition ZrO_2 - CeO_2 - Y_2O_3, however, analyzes show no constant but fluctuating compositions on traversing the cross section of the TBCs. Due to these variations the surface content of ceria varied among test pieces of different deposition runs between 13 and 38 wt%.

Results of burner rig testing are summarized in Fig. 2.

10 μm

Fig. 1: Morphology of EB-PVD processed thermal barrier coatings: PYSZ, FYSZ, CeSZ, LaSZ (from top to bottom)
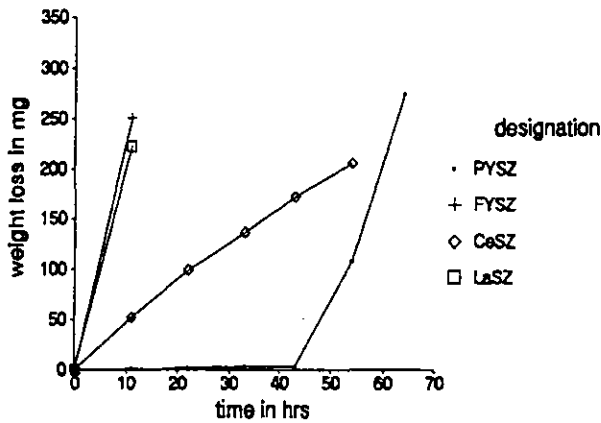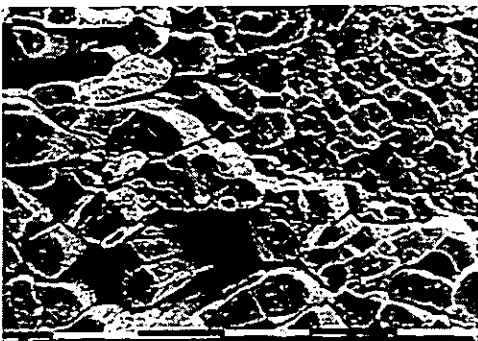
3

Fig. 2: Weight loss of cyclically burner rig tested samples versus time

0,1mm

10μm

Fig. 3: SEM pictures of burner rig tested TBCs after 65hrs at 1150°C: PYSZ (cross section, top),
CeSZ (surface image, bottom)

Rapid spallation of FYSZ and LaSZ TBCs was observed as characterized by high weight losses after short testing times. PYSZ proved as most stable coating over long times, followed by sudden spallation of TBC. CeSZ exhibits a different behavior. Here a quasi-continuous weight loss was observed after each inspection cycle. The different failure mode of CeSZ in comparison to "standard" failure by spallation of PYSZ is shown in Fig. 3.

A step-wise degradation in layers is established for the CeSZ TBCs instead of spallation of the whole TBC in one single event as shown in all other cases. A thin layer of ceramic was still present on top of the bond coat after the tests .
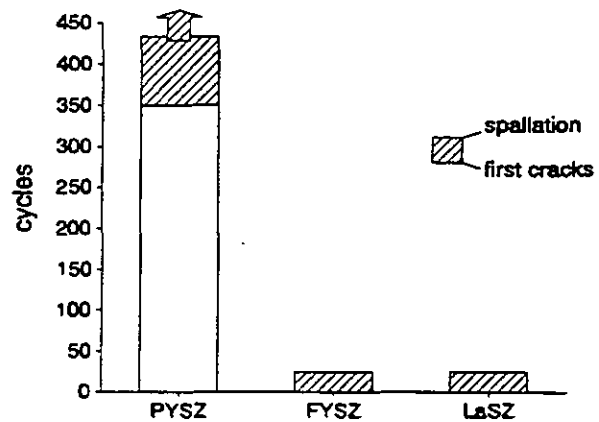

Fig. 4: Cyclic lifetime in furnace test between 1100°C and 130°C

Fig. 4 summarizes the results of cyclic furnace testing. Here a distinction is made between the time to first cracking as visible in stereo microscope and the time to spallation. CeSZ was not examined in furnace test because of the uncertainty of the composition (see above). The lifetime of PYSZ was much higher than that of FYSZ and LaSZ. Both these two thermal barrier coatings showed spallation after the first 25 cycles. Testing of PYSZ which still adhered to the bondcoat has to be stopped after 500 cycles. Termination was due to total consumption of IN 100 substrate material in the uncoated root area that is needed for fastening. EDS analyses give evidence that the main failure location was between thermally grown oxide (TGO) and bond coat with some areas of failure between TGO and TBC in all three cases.

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4. Discussion

The use of different source compositions like PYSZ, FYSZ, CeSZ, and LaSZ for the deposition of EB-PVD thermal barrier coatings bring about severe variations of the columnar structure (Fig. 1). A possible explanation for this observation is the following. Variations can be assumed to be mainly caused by differences of the respective homologous temperatures $T_{deposition}$ / $T_{melting}$ which have a strong relation to diverse microstructural zones within common structural zone diagrams /19, 20/. Although the deposition temperature was nearly the same for all four versions of TBCs their melting points differ widely. Thus, the "actual point" in these structure models for PVD processes will change, and consequently the structure will vary. CeSZ with a comparably lower melting point, for instance, comes closer to zone 3 according to its homologous temperature value of 0.47 compared to PYSZ which is centrally located in zone 2 with reference to its homologous temperature value of 0.43. This shift in the structural diagrams results in a larger column diameter and in a more regular structure for CeSZ than for PYSZ. Some other effects that may also affect the microstructure arise from variations in phase composition, ion radii, and surface energy aspects during condensation /17/.

Analyses of composition and phase structure of the variously stabilized zirconias provide some help for understanding of the respective cyclic lifetimes. The only phase in 6.5 wt% Y_2O_3 stabilized zirconia EB-PVD TBCs is metastable nontransformable t'. This observation agrees with findings in literature /21, 22/ and with our previous investigations /18, 23/. The lack of high temperature phase stability of PYSZ is supported by annealing experiments. Whereas EB-PVD TBCs are stable at temperatures up to 1150°C, they transfer after 100 hrs annealing at 1400°C to a mixture of 48% tetragonal + 48% cubic + 4% monoclinic (Mol%) phases /24/. The transformation processes to these three phases suggests the operation of a sequential mechanism which consists of yttrium cation diffusion out of t' and destabilization of t' into c and t with subsequent phase transformation t ---> m during cool down. At temperatures below the stability point t' is still the most effective phase for durability in thermal barrier coatings as can be seen in Fig. 2 and 4 respectively. Outstanding bending strength, high crack propagation energy, high fracture toughness values and highly tolerant thermoshock behavior represent the microstructure of t'. Lattice distortion due to tetragonality,

a domain structure and the well-described tweed microstructure inside the t' grains /21/ are supposed to be responsible for this excellent performance of PYSZ.

Formation of single cubic phase for FYSZ TBCs is in accordance with all findings on TBCs of EB-PVD and also PS origin. {112} pole figure measurements confirmed the absence of any t' phases. FYSZ suffers from low thermal shock resistance and poor fracture properties of the equilibrium cubic phase. Earlier reports on PS thermal barrier coatings /25, 26/ have shown that FYSZ posses poor thermocyclic behavior. Some inconsistency in the literature on EB-PVD TBCs of this composition must be recognized. The present study supports findings in /12/ that the columnar structure is not able to overcome the intrinsic problems of FYSZ. The result is poor integrity of these coatings in both cyclic tests (Fig. 2 and 4). It must be pointed out that there is still a potential to improve the adherence of FYSZ EB-PVD thermal barrier coatings on top of latest generation bond coats. This potential may lead to a substantial increase of lifetime.

Monoclinic phases that undergo phase transformation during temperature variation will cause rapid spallation of EB-PVD TBCs. The volume change that is connected to the phase transformation m <---> t creates high stresses. Even strain tolerant structures like columnar EB-PVD ones are not able to accommodate these stresses on transformation. Early spallation of LaSZ gives clear evidence of this mechanism. It must be noticed that phase composition depends strongly on the respective technique of manufacture. Above 7,5 wt% La_2O_3 in ZrO_2 exclusive cubic phase was reported for bulk materials /27/. In this study, however, mixtures of mainly tetragonal, minor cubic, and substantial amounts of monoclinic phases were identified for EB-PVD thermal barrier coatings of similar composition. It has to be taken into account that high rate condensation from a vapor phase is not necessarily a process that stabilizes equilibrium phases. Therefore, phase diagrams do not allow a safe prediction of phase structure of real coatings.

The most interesting behavior in the present study was exhibited by CeSZ. It was found that constant composition of this quality can not be obtained by single source evaporation. The reason for that is the preferential evaporation of high vapor pressure components and an enrichment of low vapor pressure compounds in the pool. Unfortunately, it is not possible to solve the problem of

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too low evaporation escape of the low vapor pressure components by overrepresenting them in the liquid pool. The provision of a "starter" composition that balances the vapor pressure differences proved infeasible because of small thickness of melt due to high melting point and low thermal conductivity of the ceramic, although the pool depth is larger in case of CeSZ compared to PYSZ.

In order to understand the problem of composition control the respective vapor pressures at 2500K were compared: 5×10^{-2} Pa for ZrO_2, 10^{+3} Pa for CeO_2 /28/. They differ by a factor of 20000 and probably even more at evaporation temperature which indeed is too much for viable single-source EB-PVD processing.

Burner rig results of CeSZ, however, were promising (Fig. 2). Quasi-continuous weight loss and a degradation of the CeSZ TBCs in thin layers were found but no spallation. One reason for a step-wise loss is, of course, the fluctuation of composition across the thickness of the TBC. This may cause alternating layers of "weak" phases including monoclinic and "strong" phases like t'. Apparently, the coating will first break in weaker regions. Lattice misfits between the various layers may further contribute to less adhesion between the layers. Higher erosion rates of CeSZ that were found for PS TBCs /5, 9/ may also account for this failure mode. The partial loss of this TBC may act as a strain/stress relief mechanism that allows the remainder part of the coating, which is thinner due to partial spallation, to adhere longer.

CeSZ apparently offer some potential in thermal barrier coatings specially if a columnar microstructure can be utilized. Single source EB-PVD proved unsuccessful so far. Two-source evaporation, however, may bring about reproducible CeSZ TBCs of stable composition. First tests of dual source evaporation of ceramics, powered by one 150kW gun using a "jumping beam technology", are promising. By adjusting dwell time and power distribution of the electron beam over each pool independently the intended mixing of components in the vaporized state can be established.

Conclusions

Common yttria-stabilized zirconias of two different compositions as well as two innovative coating compositions with CeO_2 and La_2O_3 as stabilizers were produced by reactive high-rate EB-PVD. The results allow following conclusions.

1. Lifetime of thermal barrier coating systems in a cyclic burner rig and in a cyclic furnace test can be correlated with phase content. PYSZ TBCs exhibit the longest lifetime, LaSZ and FYSZ are characterized by early spallation. CeSZ show a failure mode consisting of continuous weight loss on step-wise degradation in thin layers. Thus no total spallation occurred.

2. Crystal habit and phase content strongly depend on chemistry. The phases formed on EB-PVD do not confirm to equilibrium diagrams.

3. For CeSZ TBCs remarkable compositional fluctuations across coating thickness were found. They are due to overcritical differences in the vapor pressures of the components which become apparent during single source EB-PVD processing. TBCs which are composed of components of widely differing vapor pressures require a dual source evaporation process.

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