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PROCESSING, CHARACTERISATION AND TESTING OF EB-PVD THERMAL BARRIER COATINGS

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Summary

Thermal barrier coatings (TBCs) are increasingly applied to hot components in gas turbines. Contrary to plasma spraying, the electron-beam physical vapour deposition (EB-PVD) process offers the opportunity to generate coatings having a unique columnar microstructure. The main advantage of this structure is its superior tolerance against straining and thermoshock, thus giving it a major edge in lifetime. Furthermore, cooling hole closure will be prevented and the aerodynamic design of the blades will be maintained.

This paper will outline the advantages of EB-PVD for the production of TBCs on rotating gas turbine components like blades and vanes. The effect of EB-PVD processing parameters on the microstructural evolution and respective lifetimes of partially yttria stabilised zirconia (PYSZ) TBCs will highlight the potential of the evaporation process. Alternative stabilisers like Ce and La are looked at in terms of increase of application temperatures as well as life extention of the blades. An extended structural zone diagram for PVD is proposed incorporating the influence of substrate rotation on microstructural evolution. Finally, the limits of evaporation processing will be stressed.

1. INTRODUCTION

There is no single parameter to verify the competitiveness of an aircraft. However, it is commonly accepted that direct operating cost (DOC) is a useful indication of the potential of a given type of aircraft. If a new aircraft is introduced it has to show significant DOC benefits of at least 5 to 10% compared to the aircraft currently in service to make it an attractive proposition to an airline. For an aero engine manufacturer the DOC is primarily reduced by control of fuel costs through weight savings, drag reduction and specific fuel consumption. For a new engine a realistic picture would call for a 2-3% improvement in specific fuel consumption and for about 5% in weight reductions [1].

Apart from specific fuel consumption, the thrust of an engine is another design criterion, more precisely the specific thrust as expressed in the thrust-to-weight ratio. Both, specific fuel consumption and thrust-to-weight ratio have been significantly improved over the years accomplished through increased operating temperatures as well as improved structural efficiency [2]. It is very obvious that here advanced materials play a major role. In fact, modern aero engines represent some of the most demanding and sophisticated applications for structural materials in any engineering system manufactured today. This has been manifested by the steady increase in service temperature, product reliability and usage of lightweight materials [2].

But engines need not to be only reliable, economical on fuel and profitable, they also have to be environmentally acceptable. In terms of emission nitrogen oxides and carbon dioxide are of prime concern. NOx is particularly a problem since emission increases with increasing pressure ratio and process temperature - both are obvious ways to increase engine performance.

Blades and vanes of the high pressure turbine section of aero engines are among the most highly stressed parts in engineering components. Internally cooled aerofoils of state-of-the-art Ni-base superalloys operate at temperatures of about 1000°C with short-term peaks yielding even 1100°C which is close to 90% of the alloys' melting points. These temperatures are maintained in service due to a highly sophisticated cooling technology by which however thermal energy is withdrawn from the aerofoils in the order of 1 MW/m² thus reducing the overall fuel efficiency of the engine. The necessity of a close control of materials temperatures can be expressed by the simple rule that blade life on creep is halved for every 10 to 15°C increase in temperature [3].

But further increases in thrust-to-weight ratio of advanced aero engines will require even higher gas turbine inlet temperatures. Figure 1 shows how these temperatures have increased over the years. Today turbine inlet temperatures exceed 1400°C while 1760°C are aimed at within the next twenty years. There is no doubt that this ambitious goal can only be met by usage of uneconomically extensive cooling

techniques or by advanced high temperature materials [4] and in particular through the introduction of electron-beam physical vapour deposition (EB-PVD) thermal barrier coatings (TBCs) [5].
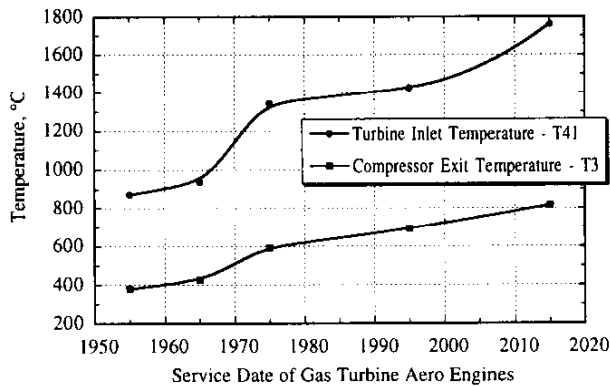

Figure 1: Increase of turbine inlet temperature of aircraft gas turbine engines [2]

2. THERMAL BARRIER COATINGS

TBCs consist of thin ceramic layers of low thermal conductivity - typically partially stabilised zirconia - which are applied on aerofoil surfaces that just have a metallic corrosion resistant coating. The coating imparts good adhesion of the ceramic to the substrate. Application of the TBCs enables increasing engine performance/thrust by either increasing the gas temperature or reducing the cooling air flow. Alternatively the lifetime of the turbine blades can be extended by decreasing metal temperatures as schematically outlined in Figure 2 [6, 7].
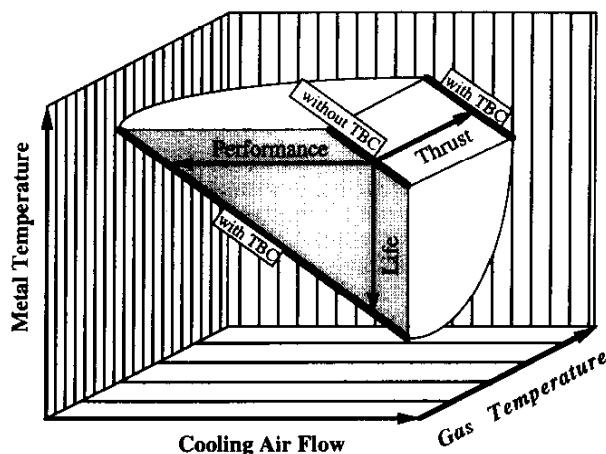

Figure 2: TBCs allow increased engine performance and/or life extension

3. HISTORIC DEVELOPMENTS IN TBCS

Since the early sixties PS (plasma sprayed) calcia- and magnesia-stabilised zirconia TBCs have been used extensively as ceramic top coat on combustion chamber walls and on burner cans to prolong their

lives by avoiding hot spot formation and subsequent failure by thermal fatigue. These materials were broadly accepted for 20 years until their replacement by PYSZ (partially yttria-stabilised zirconia) coatings was initiated. The APS (air-plasma sprayed) PYSZ TBCs offer outstanding mechanical, chemical and thermal properties. Two generations of high temperature (>1000°C) TBCs were based on these unique ceramics (generation I is APS MCrAlY / APS PYSZ and generation II is LPPS (low-pressure plasma sprayed) MCrAlY / APS PYSZ) which allowed in the early eighties to introduce TBCs on highly thermally loaded parts like vane platforms and vane airfoils. The need for higher operating temperatures in turbines, however, inspired material scientists for half a decade to search for TBCs which could also be applied on blade platforms and airfoils which are subjected to high thermal and additional mechanical loads.

Here the electron-beam physical vapour deposition (EB-PVD) technology offered the opportunity to generate TBCs with vastly superior strain tolerance. This is due to their specific coating structure which grows from the vapour phase in a columnar form with individual ceramic columns being weakly bonded to their neighbour columns as e.g. shown in Figures 8a or 13.

Coating all these high performance parts with reliable TBCs would allow to alter the initial component design and to operate the TBC bearing components with the coatings as an integral part of them. The exploitation of strain-tolerant TBCs initiated a renaissance of industrial EB-PVD technology in 1987 which until then had been utilised for deposition of metallic MCrAlY-type coatings for 20 years. The novel EB-PVD PYSZ ceramic layers with advanced LPPS MCrAlY bond coat, designated now as generation III TBC, offered a roughly 3 times improvement in blade life or a surface temperature increase on the hot sections of airfoils of approximately 150K.

4. PROCESSING OF TBCS

Plasma-sprayed (PS) TBCs have been widely applied to hot components like burner cans since the sixties while in recent applications to more pretentious parts like turbine blades EB-PVD technology is favoured. Contrary to plasma spraying, EB-PVD processing offers the opportunity to generate coatings having a unique columnar microstructure with 2 to 25 μm in diameter. The main advantage of this structure is its superior tolerance against straining and thermoshock, thus giving it a major edge in lifetime [8]. Furthermore, cooling hole closure will be prevented and aerodynamic design of the blades is maintained. In Table 1 the two processing methods are compared as far as thermal barriers for turbine blades are concerned.

During EB-PVD processing a high energy electron beam melts and evaporates a ceramic source ingot in a vacuum chamber. Ingots are bottom fed into the crucibles during evaporation to ensure continuous

TBC growth. To achieve defined stoichiometry of the zirconia a controlled amount of oxygen is bled into the deposition chamber. Preheated substrates are positioned in the vapour cloud above where the vapour is deposited on substrates at deposition rates of 100 to 250 nm/s [9]. Typical columnar microstructures and aerodynamically smooth surfaces are obtained without the need for final polishing or conditioning of cooling holes. Due to the columnar microstructure the life time of the TBCs is prolonged and the damage tolerance improved. Typical characteristics and major advantages of thermally sprayed and on-evaporated TBCs are schematically outlined in Figure 3 [10]. Figure 4 shows a selection of EB-PVD TBCs on aero engine and stationary gas turbine blades produced at DLR on semi-commercial single-source 60kW Leybold and dual-source 150kW von Ardenne EB-PVD coaters.

Table 1: Plasma sprayed (PS) versus on-evaporated (EB-PVD) TBCs

	PS	EB-PVD
Surface Finish	good but extra polish	excellent
Bond Coat Roughness	grit blasted	smooth
Bonding Mechanism	mechanical	chemical
Alloy Flexibility	high	limited
Typical Thickness	0.2-3mm	0.1-0.3mm
Cooling Hole Closure	poor	excellent
Coating Source	movable	fixed
Large Parts predicable	favourable	costly
Parts per Charge	1	1-10
Investment Costs (%)	100	100-400

PS   EB-PVD

◄ TBC ►
◄ BC ►

Substrate   Substrate

* horizontal splat structure
* 0.2-3 mm coating thickness
* mechanical bonding /
  rough BC surface
+ flexible coating chemistry
+ low initial thermal conductivity
  in coating thickness direction

* columnar coating structure
* 0.1-0.3 mm coating thickness
* chemical bonding /
  smooth BC surface
+ smooth coating surface
+ low E in coating plane
+ cooling holes stay open
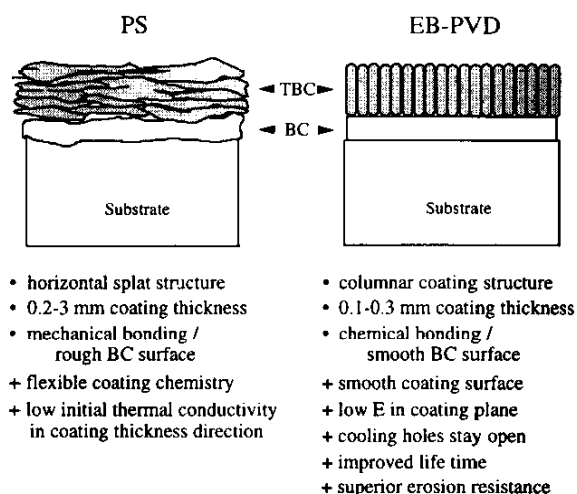+ improved life time
+ superior erosion resistance

Figure 3: A simplified comparison of properties for plasma sprayed (PS) and evaporated (EB-PVD) TBCs (schematic)

5. FAILURE MECHANISMS AND PREVENTION

Pertinent usage of TBCs as a reliable component or future TBC applications as integral design elements of highly loaded engine parts need a more comprehensive understanding of the failure mechanisms of the coating systems. Failure in TBC systems almost always occurs by TBC spallation due to stresses in the ceramic or in the bond coat. But failure of EB-PVD processed TBCs happens, unlike those for PS based TBCs, at the ceramic - bond coat interface. There is a thermally grown oxide (TGO) of a few μm in thickness which plays a key role in the adhesion of EB-PVD TBCs since it is considered to be the weak link in the system. Its strength and adhesion to the bond coat governs the true location of failure whether first cracks will propagate within or along the TGO - bond coat interface. Here spallation is initiated by accommodation of stresses surmounting a critical value.

Figure 4: EB-PVD TBCs on turbine blades for use in stationary gas turbines, civil aero engines and helicopter engines (decreasing in size)

A way to minimise misfit stresses in TBC systems is to reduce the growth rate of TGOs. The early overlay bond coatings which were EB-PVD MCrAlYs were followed by PS MCrAlY families. Advanced MCrAlYs contain additional elements like Si and/or Ta, Hf for providing lower scaling rates and better hot corrosion resistance. These coatings with low vapour pressure elements (mostly refractory elements) are more easily deposited by LPPS techniques. TGOs grow more slowly and thus effectively prolong the lifetime of the TBCs on them.

Another route to minimise misfit stresses and improve spallation resistance is to make the bond coatings more creep resistant which will bring more stability to the TBC root area on thermomechanical cycling. This change in mechanical characteristics is successfully done in recent LPPS MCrAlY overlay coats by converting the former γ/β phase structure into a γ/γ' structure by appropriate alloying. Due to the introduction of a significant portion of refractory ele-

ments the modified high creep resistance phase structure offers further benefits which refer to a low diffusivity and a reduced coefficient of thermal expansion (CTE). The latter property is of uppermost importance for the amount of residual stresses accumulating in the TGO layer. They can be reduced if the differences between the CTEs of the respective ceramic and metallic partners of the whole system are minimised.

Finally the involvement of superalloy substrates in the interplay of the physical properties of the respective material components and their influence on the compositional behaviour of TBC systems has to be addressed. Ni-base superalloys have gained a high degree of technical maturity in the early nineties. They have passed a lot of development stages, e. g. hardening by precipitated γ' phases, extensive solid solution strengthening, directional solidification and finally single crystals to trust in more creep-resistant crystal orientations and continuous grain structures [11]. The most creep-resistant crystal orientation (001), however, provides the least Young's modulus of only 120 MPa. Obviously it is a drawback for the adhesion of TBCs as thin-walled airfoils can be bent more rigorously under same loads in service than the conventionally cast counterparts. Three generations of single crystal superalloy development, however, resulted in a reduction of the CTE which compares with the recent low expansion bond coats.

6. SURFACE TRAETMENT/ROUGHNESS

Another key issue for utilising the full potential of TBCs is their surface finish. Increasing roughness results in higher aerodynamic losses as well as increased heat transfer to the airfoil [12]. It also has an impact on TBC adherence. So the roughness of the TBCs needs to be closely controlled.

The processing steps before TBC deposition are essential for attaining the targeted surface characteristics of the final surface. For EB-PVD TBCs the bond coats have to have a finish on mechanical surfacing better than 1 to 1.5 µm Ra. Identical pilot sample parts are attached with thermocouples at representative locations in order to have a means to calculate in analogy the temperature distribution over time within real parts during a real deposition process as closely as possible. Optimal T-t histories for the thermal cycle during preheating and TBC deposition have to be assured. The TBC deposition must be performed within an operating window which takes care of a number of parameters, the most important of which are [13]

  component temperature during coating
  pressure in the coating chamber
  oxygen partial pressure in the coating chamber
  part rotation rate during coating.

The final coating will then have a 1 to 1.5 µm Ra roughness [14]. Further reductions of roughness may be advantageous.

7. INFLUENCE OF STABILISERS ON TBC PERFORMANCE

Partially yttria-stabilised zirconia (PYSZ) is the current state-of-the-art material for TBCs. Unfortunately, the material shows insufficient phase stability and accelerated sintering at temperatures above 1200°C. Therefore, further increases of gas inlet temperature require alternative stabilisers with improved phase stability. Another argument for new stabilisers in zirconia or for completely new ceramics is the insufficient resistance of current TBCs 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 stabilisers from parent zirconia. The degradation occurs by transformation of high temperature phases to monoclinic zirconia on cooling. This failure mode may be found mainly in heavy duty engines and off-shore service [15].

One alternative stabiliser for zirconia is CeO_2. The benefits of ceria-stabilized (CeSZ) TBCs are good corrosion resistance [16-17] and excellent phase stability at high temperature [18]. Furthermore, the thermal conductivity is found to be lower than for PYSZ and some benefits for lifetime and thermocyclic resistance are reported, too. La_2O_3 is another candidate for replacing Y_2O_3 in zirconia.

To get more insight into single-source EB-PVD processing of new compositions for TBCs a feasibility study was performed on four differently stabilised zirconias (Table 2) using identical substrate alloys and EB-PVD NiCoCrAlY bond coat compositions [19].

Table 2: Differently stabilised zirconias investigated

	ZrO_2 +
PYSZ	6.5 wt% Y_2O_3
FYSZ	20 wt% Y_2O_3
LaSZ	8 wt% La_2O_3
CeSZ	25 wt% CeO_2 - 2.5 wt% Y_2O_3

A columnar structure of the TBCs of about 250µm thickness was found for all four chemistries with some noticeable differences between the various ceramics. FYSZ and CeSZ posses a larger column diameter and a higher degree of ordering compared to PYSZ and LaSZ. On the other hand, LaSZ has the most nonuniform shape of the terminal section of columns. The microstructure of standard PYSZ lies between these two extremes with more irregularities than CeSZ and FYSZ but not as many as with LaSZ.

One possible explanation for the variations in morphology are the differences of the respective homologous temperatures $T_{deposition} / T_{melting}$ which have a strong relation to diverse microstructural zones within common structural zone diagrams [20-21]. Although the deposition temperature was nearly the same for all four zirconia, their melting points differ widely, thus resulting in different microstructures according to the structure zone models mentioned

above. Other effects that affect the microstructure include variations in phase composition, ion radii, and surface energy aspects during condensation [22].

Phase analyses by X-ray diffraction (XRD) revealed that the compositions of the three binary TBCs, PYSZ, FYSZ, and LaSZ, were close to the ingot compositions. For PYSZ exclusive tetragonal (t') phase was identified while FYSZ only contained cubic (c) phase and LaSZ exhibited a mixture of mainly tetragonal, minor cubic, and substantial amounts of monoclinic (m) phase. In the case of the ternary composition ZrO_2-CeO_2-Y_2O_3, however, analysis showed no constant but fluctuating compositions across the TBC thickness. Due to these variations the surface content of ceria varied among test pieces of different deposition runs between 13 and 38 wt%. For CeSZ a mixture of cubic, tetragonal, and occasionally monoclinic phases was found [22].
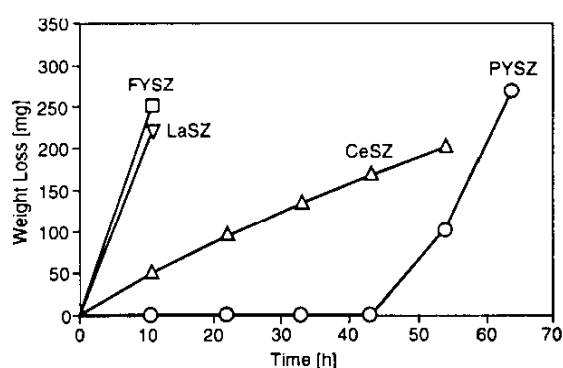
Figure 5: Weight loss of cyclically burner rig tested samples versus time

These four differently stabilised TBCs were subjected to cyclic burner rig testing at Mach 0.35 gas velocity with cyclic heating up to 1150°C for 57 minutes and forced air cooling to room temperature for 3 minutes. The results are summarised in Figure 5. Rapid spallation of FYSZ and LaSZ TBCs was observed as characterised by high weight losses after short testing times. PYSZ proved to be the most stable coating system over long times, followed by sudden spallation of TBC.

CeSZ exhibited a different behaviour. 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 visible in Figure 6: a step-wise degradation in layers was observed instead of spallation of the whole TBC in a single event as noticed in all other cases. A thin layer of ceramic was still present on top of the bond coat after the tests.

Considering the lifetime of the TBCs a similar ranking was also found in cyclic furnace tests between 150°C and 1100°C. Here, however, for all stabilisers the main failure location was found between the thermally grown oxide (TGO) and the bond coat rather than between TGO and TBC.

Burner rig tests as well as furnace tests revealed that composition and phase structure of the variously stabilised zirconias are closely related to the cyclic lifetime of the coating system. The only phase found in PYSZ was metastable non-transformable t'. The equilibrium phase diagram [23] predicts a two-phase mixture consisting of t containing 4 % Y_2O_3 and c containing 16 % Y_2O_3 at deposition temperature. The c phase, however, can only be maintained at RT under the preconditions that a very low critical grain size of c is established and/or the c particles are subjected to high compressional stresses by the surrounding t matrix. Both mechanisms would cause the half widths of the XRD peaks to be broadened which, however, is not observed. Therefore, formation of the t' phase is considered to be caused via rapid quenching on PVD processing as can similarly be assumed for solidifying TBCs during PS deposition.
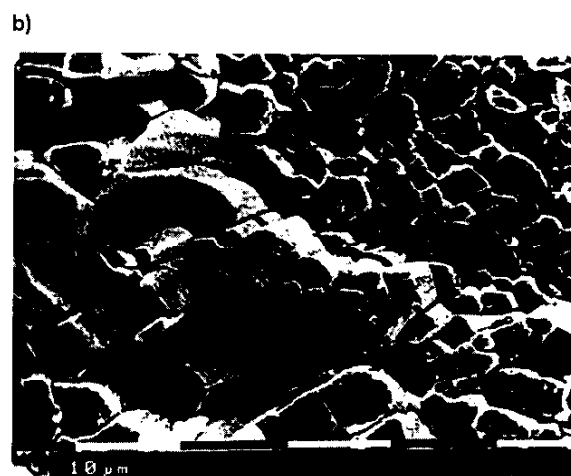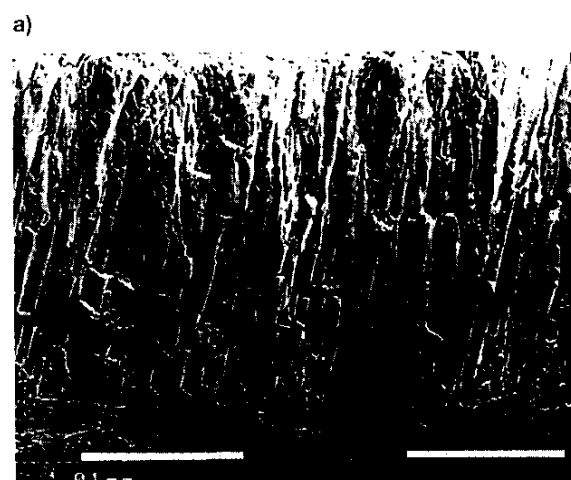
a)

b)

Figure 6: SEM micrographs of burner rig tested TBCs after 65hrs at 1150°C:
a) PYSZ (cross section); b) CeSZ (surface)

A major drawback of PYSZ is the lack of high temperature phase stability as 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 into three phases suggests a sequential mechanism consisting of yttrium cation diffusion out of t' and destabilisation of t' into c and t with subsequent phase transformation to m during cooling. At temperatures below the stability point t' is still the most effective phase for durability in thermal barrier coatings as can be seen in Figure 5. The t' microstructure is characterised by outstanding bending strength, high crack propagation energy, high fracture toughness and highly tolerant thermoshock behaviour. Lattice distortion due to tetragonality, a domain structure and the well-described tweed microstructure inside the t' grains [25] are supposed to be responsible for the excellent performance of PYSZ.

The formation of a single cubic phase for FYSZ TBCs is in accordance with all findings on EB-PVD as well as PS TBCs known from literature. FYSZ suffers from low thermal shock resistance and poor fracture properties of the equilibrium c phase. Earlier reports on PS TBCs [26-27] have shown that FYSZ possesses poor thermocyclic behaviour. However, some inconsistency in the literature on TBCs of this composition must be recognised. The present results support findings [28] that the columnar EB-PVD structure is not able to overcome the intrinsic problems of FYSZ leading to poor integrity of such coatings after cyclic testing (Figure 5).

Monoclinic phases that undergo a phase transformation during temperature variation will cause rapid spallation of EB-PVD TBCs. The volume change associated with the phase transformation m ´ t creates high stresses. Even strain tolerant structures like columnar EB-PVD ones are unable to accommodate these stresses on transformation. Early spallation of LaSZ gives clear evidence for such a failure mechanism. It has to be taken into account that high rate condensation from a vapour phase is not necessarily a process that stabilises equilibrium phases. Therefore, phase diagrams do not allow a safe prediction of the phases of real coatings.

CeSZ showed the most interesting behaviour. The condensing matter is evaporated from a ceramic ingot source material at approximately 3500°C [29]. The presence of ceria considerably lowers the melting interval of the ingot. Selective processes are facilitated which cause the preferential evaporation of high vapour pressure components and enrichment of low vapour pressure elements in the melting pool. Vapour pressures are $8 \cdot 10^2$ Pa for ZrO_2 and $9 \cdot 10^5$ Pa for CeO_2 at 3060°C [30] and thus differ more than three orders of magnitude. This difference is probably even higher at the evaporation temperature which is indeed too much for viable single-source EB-PVD processing. As a matter of fact the evaporation process becomes instationary resulting in the compositional fluctuations observed. However, burner rig results of CeSZ were promising (Figure 5). 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' [24]. Apparently, the coating will first break in weaker regions. Lattice misfits between the various layers may further contribute to reduced adhesion between the layers. Higher erosion rates of CeSZ found for PS TBCs [28, 31] 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 offers some potential in thermal barrier coatings especially if a columnar microstructure can be utilised. Multiple source evaporation is however required to bring about reproducible CeSZ TBCs of stable composition.

8. INFLUENCE OF MORPHOLOGY ON TBC PERFORMANCE

The microstructure of EB-PVD layers is essentially influenced by four basic processes:

> shadowing,
> surface diffusion,
> volume diffusion and
> desorption.

Their evolution is roughly predicted in structural zone diagrams [20-21]. Rotation of substrates during deposition, however, is not regarded as an essential contribution to the growth process so far. Nevertheless, it causes an additional microstructural feature in zirconia-based TBCs. A beaded or "c-shaped" structure of the columns is formed due to the continuous change of vapour impact angle and amount of vapour particles that adhere on the surface during each revolution [32-33]. Elevated substrate temperatures during EB-PVD cause a higher density of the TBCs and a higher hardness as well [34]. In addition to stabiliser type and content the degree of ionisation of the vapour cloud, gas pressure, surface roughness, deposition rate and vapour impact angle are other parameters that influence the columnar microstructure of EB-PVD thermal barrier coatings [22].

EB-PVD TBC production upon 3-D coated parts like vanes and blades necessitates substrate rotation during deposition. Therefore, the influence of rotational speed on microstructural evolution of the coatings has been investigated in more detail. The differences in microstructure between TBCs deposited under two separate process parameter sets are illustrated in Figure 7. SEM pictures of the surface of TBCs display that microstructures of EB-PVD TBCs strongly depend on process parameters, particularly substrate temperature and rotation.

Aiming at customising microstructures of TBCs for specific performance it is noteworthy that substrate temperature and rotational speed are alternative process parameters that cause the same microstructural features in the TBCs within certain limits. At low temperature and low rotational speed columns

often vary in diameter from root to top or from one column to the other. Columns at the root section are much thinner than at the top and are enlarging discontinuously from root to top conically. Increasing both temperature and rotational speed improves the regularity and parallelity of the microstructure and enlarges the column diameter. After competitive selection of favoured crystal orientations in the thin root area during the first stages of coating growth, columns start immediately to grow in width to their terminal diameter. Although the coating density measured is higher for high temperature/high rotational speed TBCs than in low temperature deposited TBCs, the columns appear to be less densely packed.

a)
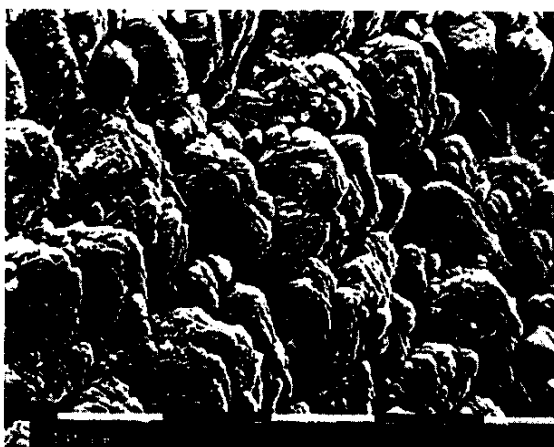
b)

Figure 7: Surface of YPSZ TBCs: a) 980°C; 12rpm; b) 1050°C; 30rpm

The microstructure can be varied without altering the deposition temperature by different rotational speeds. At low rotational speed the beaded structure is formed within the columns while it disappears immediately after changing to a higher speed. An increase of column diameter was also found.

This processing tool allows to manufacture microstructurally graded TBCs that can be adapted to the

need of appropriate column features in particular TBC thickness zones. Several aspects may contribute to the observed effects including surface temperature fluctuations, change of diffusion kinetics and enlarged shadowing due to rotation. For instance, measurements of actual surface temperatures on flat samples during deposition gave temperature differences of 60 to 80°C for a low rotational speed compared to 15 to 25°C for a three times higher speed.
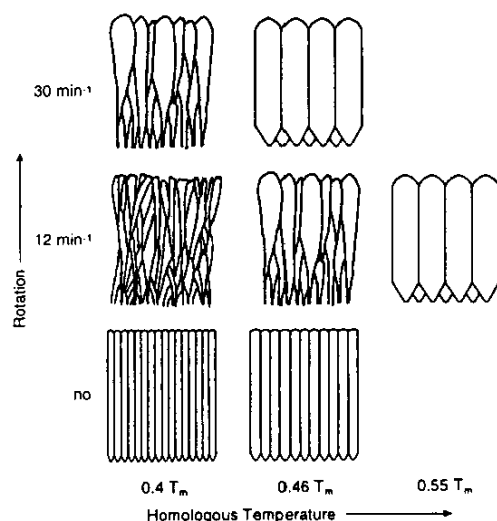

Figure 8: Schematic representation of the influence of substrate temperature and rotational speed on columnar microstructure evolution of EB-PVD TBCs

These observations suggest that structural zone diagrams should be modified when substrates are rotated during deposition. It is therefore proposed to incorporate a second axis in the models as a further degree of freedom similar to sputtered coatings where e.g. the role of argon pressure was considered. To give a first idea of a potential model extension, the observed microstructures for the interval of homologous temperature investigated are summarised in Figure 8 [35].

9. INFLUENCE OF DEPOSITION ANGLE ON TBC STRUCTURE

Another processing parameter of interest for EB-PVD component coating is the angle under which the vapour cloud hits the substrate. This is of particular practical importance since usually substates like turbine vanes and blades irregularly shaped.

First it was shown that for both single source and dual source evaporation morphology and texture of PYSZ TBCs produced under a perpendicular vapour incline angle were nearly identical for [35]. In all cases a {100} plane nearly parallel to the surface was found, an example of which is given in Figure 9 [36].

The good performance of TBCs on highly loaded parts in severest environments, achieved in less than a decade of development, is a good indication for the versatility of the columnar structure concept of TBCs. The unfavourable crystallographic relations between the columns and the direction of highest straining in service, hypothetically addressed before, stand for a positive view into the future of TBCs: they still bear a potential for further improvements.

11. STRUCTURE PROPERTY RELATIONSHIPS

Some representative microstructures of TBCs produced by single source evaporation were chosen for cyclic furnace testing (Figure 12). All samples had the same EB-PVD NiCoCrAlY bond coat and surface treatments. Samples with a microstructure consisting of tapered and discontinuous columns due to multiple branching on growth exhibit the longest cyclic lifetime (12rpm/1020°C). TBCs with more regular columns of larger diameters appear less tolerant against thermo-cyclic loading. Burner rig tests confirm these results. Obviously, microstructure of TBCs and thermocyclic lifetime are closely interlinked. Figure 12 evidences the superiority of TBCs with a non-regular micro-structure consisting of columns with variable diameters over TBC with large uniform column diameters and a regular microstructure.
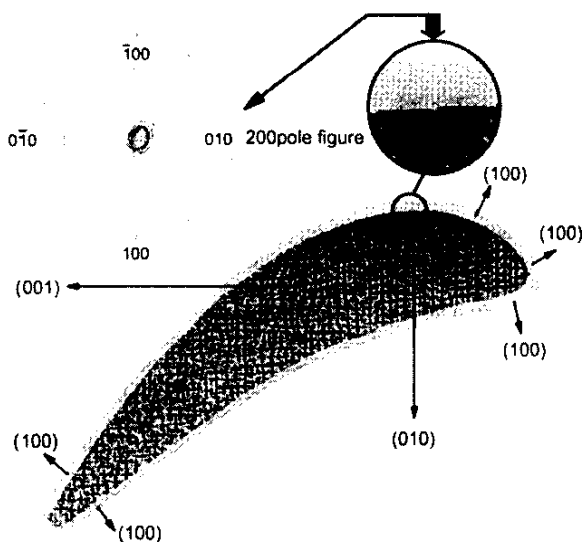

Figure 11: Crystallographic orientation of single crystal blades and EB-PVD TBC

Changes in stress state, elastic moduli, and adhesion between contacting columns that possess high numbers of protrusions may be responsible for this different behaviour. On the other hand, in the regular microstructure, crack propagation paths were provided along the parallel columns that cover the whole thickness of the TBC. Indeed early crack formation was found for these microstructures.

In hot corrosion testing of EB-PVD TBCs no evidence was found for hot corrosion of the bond coat and for a chemical reaction between the TBC and corrosion accelerators like molten salts and sulphur compounds [37, 38]. However, TBC failure can be initiated by mechanical attack of solidified salt compounds. Spallation of small areas of TBC in a funnel-shaped manner with some thinner coating still adherent on the bondcoat indicate this failure mechanism. For columns that posses larger voids between the interior column faces, salts may penetrate deeper into the coating than in denser columnar microstructures. Consequently, the weight loss is higher for a coarser microstructure deposited at higher rotational speed compared to a microstructure deposited at lower temperature and rotational speed [37].
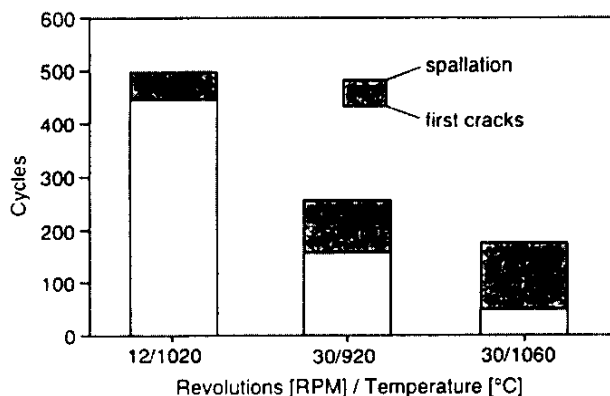

Figure 12: Cyclic lifetime in furnace test between 1100°C and 130°C

12. OUTLOOK AND CONCLUSION

To exploit the full potential of TBCs on highly stressed rotating turbine components further work has in particular to be directed to efforts which determine critical stresses more accurately based on detailed understanding of failure mechanisms of entire TBC systems with more confidence. The progress in the manufacture of more reliable TBC systems on single crystal materials will address the design of conveniently microstructured TBCs with superior strain tolerance on advanced bond coats with predictable TGO formation. The tailoring of respective microstructures to differing substrates with regard to optimal adaption of their "porosity" and of the thermal expansion mismatch has to be taken into account. Here the disposal of appropriate EB-PVD technologies will enable to manufacture unique microstructures for service-tolerant TBCs.

Future applications of TBCs aim at surface temperatures of 1250°C and above where aero engines as well as industrial gas turbines will operate. Today's state-of-the-art PYSZ ceramics, however, exhibit destabilisation of the tetragonal t' phase to monoclinic and cubic on extended exposure at temperatures above 1150°C, and sintering phenomena become predominant. Alternative ceramics will be needed with reduced sintering rates, improved phase stability and lower thermal conductivity. The need for ad-

In Figure 10 two EB-PVD PYSZ coatings are compared with vapour incline angles of 25-40° (Figure 10a) and < 10° (Figure 10b) deposited under constant rotating conditions. It is obvious that the columnar structure closely follows the incline angle of the vapour cloud to the substrate surface. This shows that the angle of the columns is directly related to the vapour incline angle, which is, however, different for the crystallographic orientation. Texture measurements have revealed that the deposition conditions clearly influence the type of texture of EB-PVD TBCs [36]. For rotated substrates a four-fold symmetry with {100} planes nearly parallel to the surface evolves independent of vapour incline angle, as indicated in Figure 10. The technical importance of textures in TBCs is related from the fact that the associated anisotropy in elastic moduli as well as thermal expansion within the t' phase may very well have a profound influence on the lifetime of the coating systems.
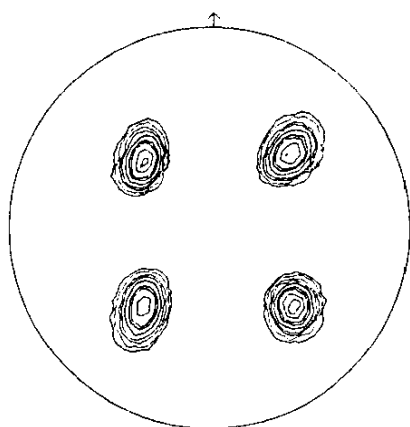
Figure 9: Characteristic texture of EB-PVD processed PYSZ TBCs indicated by {111} pole figure [36]

10. SINGLE CRYSTAL SUBSTRATES

As discussed before, the columns of EB-PVD TBCs exhibit a preferred {100} texture in perpendicular direction to the substrate. How does this reflect on advanced substrate material which more and more tends to be of single crystal nature? The technical advantage may be twofold, namely a slightly higher thermal expansion (CTE) in in-plane direction for a better fitting to the bond coat and a hypothetically lower Young's modulus (note: the Young's modulus is highest in {100} orientation for zirconia monocrystals) which provides more stress relief at the interface on mechanical loading.

Some controversy may arise on the appropriate definition of the "right" Young's modulus which becomes effective as a stress depressant in in-plain direction. Is the effective Young's modulus the intrinsic physical property of an individual crystal column, or is it the - much lower - overall Young's modulus of the whole stack of TBC constituents composed of columnar and wedge shaped crystals, grain boundaries, loosely adherent interfaces and some free space e.g. at abandoned crystal positions?

This question in mind the habit morphology and orientation of a TBC will be detailed first. EB-PVD TBCs form a preferred {100} texture not only in normal but also in in-plain direction which will establish along the main axis of rotation and perpendicular to it (Figure 11). This axis usually coincides with the main axis of a turbine blade which also is most heavily subjected to mechanical stressing in service. In essence, the in-plain {100} texture orientation of TBCs is the most heavily strained one. Any other crystal orientation should be better. A look over a TBC in lateral direction (Figure 7b) clearly shows the longitudinal and often diamond-shaped cross section of crystals which spread with their elongated main diagonals in {100} direction. So less stress-depressant boundaries will accumulate in this direction compared to all others.
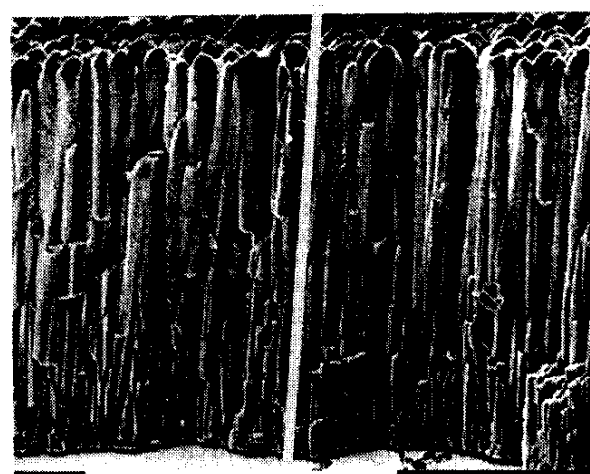
⟨113⟩   ⟨100⟩
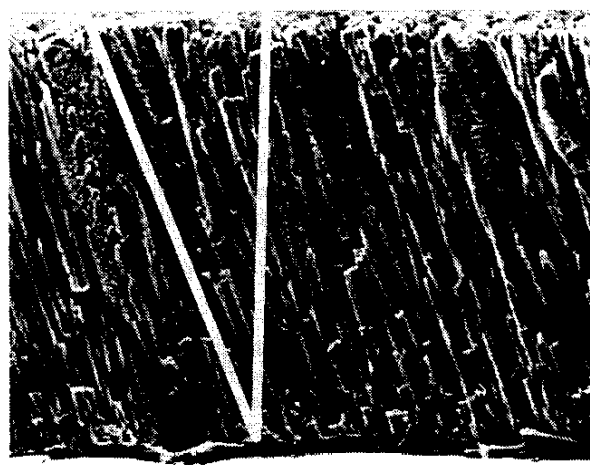
⟨100⟩

Figure 10: PYSZ EB-PVD coatings deposited under vapour incline angles of 25-40° (a) and < 10° (b)
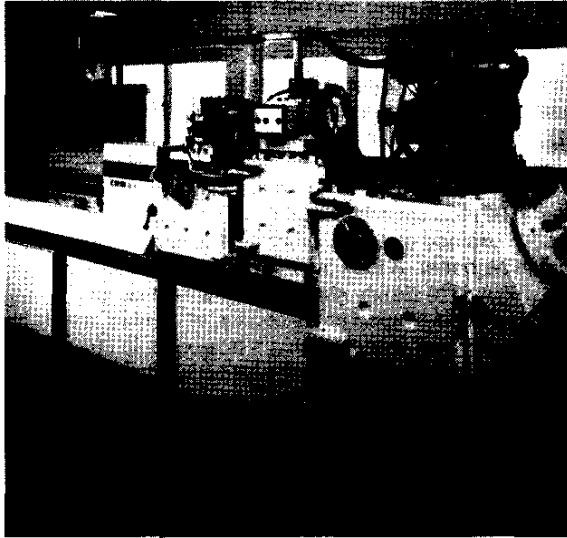
Figure 13: DLR's 150 kW dual-source EB-PVD laboratory coater (von Ardenne Anlagentechnik) for the production of novel TBCs and bond coats on aeroengine and stationary gas turbine components

vanced ceramic materials will force EB-PVD processing development to overcome pertinent materials restrictions. Multiple-source high rate coaters will be a valuable tool to enable the production of TBCs which are composed of low and high vapour pressure components (Figure 13).

Advanced electron beam gun design allows the use of only one gun in combination with jumping electron beam technology for dual source evaporation [39]. Fast to and fro movements of the electron beam from one pool to another and provides a quasi-continuous evaporation from multiple sources. Such equipment also allows to produce advanced bond coat compositions which may attribute their share to the manufacture of safer TBC systems.

New microstructures encompass compositionally graded, density graded and multilayered arrangements where, especially in the last case, a reduced heat conduction may allow the application of thinner overlays. CVD techniques can attribute their particular thin layer virtues. Basic and applied research capabilities have to focus on alternative materials and processing routes while earnestly guarding all cost requirements. Non-destructive testing and life-prediction methodologies for TBC systems have to be furnished. Finally, research and development efforts have to be combined to fully exploit the temperature potential of TBCs in aeroengine gas turbines and at the same time make TBCs mature for extensive usage for rotating components also in stationary gas turbines for energy conversion purposes [6].

13. ACKNOWLEDGEMENTS

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