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## Advanced Processing of TBC's for Reduced Thermal Conductivity

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### ABSTRACT

Zirconia-8wt% yttria thermal barrier coatings (TBC's) provide the potential to increase the operating temperatures within the modern aeroengine gas turbine.

Of particular interest are the columnar, strain tolerant thermal barriers produced by electron beam physical vapour deposition which can be applied to rotating components and can reduce the metal surface temperature by up to 150°C. Measured thermal conductivities for this columnar microstructure are typically 1.8-2.0 W/m.K. Should it be possible to reduce this value to that observed for plasma sprayed ceramics (0.9-1.0 W/m.K) then further benefits from the use of such a ceramic layer could ensue including either a further increase in operating temperature or a reduction in cooling air requirements.

This paper examines the advanced processing of TBC's with the aim of reducing thermal conductivity. The role of coating thickness is reviewed, where it is shown that for thin coatings, circa 100µm thermal conductivities of 1.0 W/m.K can be achieved. This is thought to be due to increased scattering of thermal waves close to the early confused growth region. The possibility of further reducing thermal conductivity by using layered structures is examined. These structures have been manufactured by control of rotation, controlled dwell and through the use of plasma assistance during the deposition process. The benefits of such layers in scattering thermal waves is discussed.

### LIST OF SYMBOLS

$x$  total coating thickness  
 $x_1$  thickness of inner "nucleate" zone  
 $k$  thermal conductivity for the complete TBC.  
 $k_1$  thermal conductivity of the inner "nucleate" zone  
 $k_2$  thermal conductivity of the outer columnar structure  
 $k_p$  is the phonon thermal conductivity,  
 $k_r$  is the contribution to thermal conductivity due to radiation,  
 $C_v$  is the specific heat capacity at constant volume,  
 $\rho$  is the density of the material,  
 $\bar{v}$  is the mean velocity of phonons in the material (speed of sound)

$l_p$  is the phonon mean free path.

$\sigma$  is Stefan Boltzmann's constant =  $5.67 \times 10^{-8}$  W/(m<sup>2</sup>.K),

$T$  is the thermodynamic temperature (K),

$n$  is the refractive index of the material,

$l_r$  is the photon mean free path

$l_i$  is the intrinsic mean free path of phonons due to the lattice and differing ion masses,

$l_{vac}$  is the mean free path of phonons due to vacancies in the lattice,

$l_{gb}$  is the mean free path of phonons due to grain boundaries,

$l_{strain}$  is the mean path of phonons due to local strain centres within the lattice.

### 1. INTRODUCTION

The drive to improve engine performance and fuel efficiency, while reducing emissions, has meant that the operating temperatures of the turbine section of aero-engines has increased significantly over the last 20 years. This has been achieved by novel material design, improved cooling technologies and better manufacturing methods [1]. The latest development in this drive for improved performance is to apply thermal barrier coatings to turbine aerofoil surfaces. Thermal barrier coatings offer the potential of increasing turbine operating temperatures by up to 150°C, without any increase in metal operating temperatures (Figure 1), or alternatively permits a reduction in the mass of cooling air required while maintaining the turbines operating temperature giving improved specific fuel consumption.

Thermal barrier coatings (TBC's) have been used in the gas turbine engine since the 1970's [2-4] to lower mean metal temperatures. These coatings, based on partially stabilised zirconias, are deposited using thermal spray processing and have performed well in service, extending the lives of combustion chambers and annular platforms of high pressure nozzle guide vanes within the turbine section of the engine [5]. However, the use of thermal sprayed TBC systems have not generally been

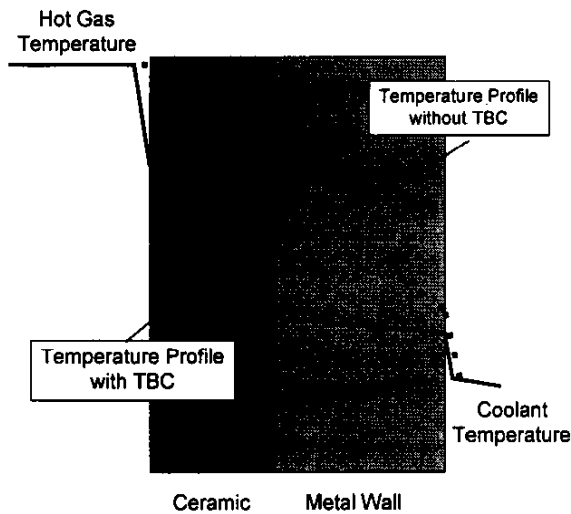


Figure 1 Schematic of thermal barrier coating systems showing thermal gradient subtended across the ceramic layer

extended to high-pressure turbine aerofoils, due to their poor surface finish, high heat transfer coefficient, low erosion resistance and poor mechanical compliance. Success in coating turbine aerofoils has been achieved by adopting electron beam physical vapour deposition (EB-PVD) technology to coat these parts. Thermal barrier coatings deposited by EB-PVD processes have a good surface finish [5], columnar microstructures with high strain compliance [5,6] and good resistance to erosion [5,7] and foreign object damage [7]. EB-PVD thermal barrier coatings have been used in production since 1989 [8].

Unfortunately, the microstructure which gives the EB-PVD TBC system its high strain compliance and good erosion resistance leads to a relative high thermal conductivity when compared to thermally sprayed coatings (Figure 2). Table 1 compares the properties and performance of commercially produced thermally sprayed and EB-PVD deposited PTSZ thermal barrier coatings. Previous work in the development of ceramic alloy compositions indicated that there is opportunity to reduce the thermal conductivity of the zirconia-based

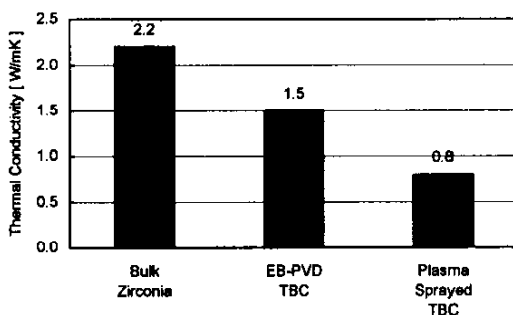


Figure 2 Thermal conductivities of bulk, EB-PVD and thermally sprayed zirconia-yttria materials at room temperature.

systems by alloying with ceria and yttria [9]. This paper discusses the theoretical models of heat transfer in solids with regard to the reduction of the thermal conductivity, and reviews these against the measured values on TBC coatings engineered for low conductivity.

Table 1 Properties of TBC's at Room Temperature

Property/Characteristic	EB-PVD	Plasma Sprayed
Thermal Conductivity (W/mK)	1.5	0.8
Surface Roughness ( $\mu\text{m}$ )	1.0	10.0
Adhesive Strength (MPa)	400	20-40
Young's Modulus (GPa)	90	200
Erosion Rate (Normalised to PVD)	1	7

## 2. THEORY OF CONDUCTION

The theory of thermal conductivity in solids is fully described elsewhere and will only be briefly reviewed here [10-12]. In crystalline solids heat is transferred by three mechanisms, (i) electrons, (ii) lattice vibrations and (iii) radiation. As zirconia and its alloys are electronic insulators (electrical conductivity occurring at high-temperatures by oxygen ion diffusion), electrons play no part in the total thermal conductivity of the system.

The contribution to thermal conductivity from lattice vibrations (the quanta of which are known as phonons) is given by:

$$k_p = \frac{1}{3} \int C_v \rho \bar{v} l_p \quad [1]$$

Whilst equation [1] describes the phonon conductivity, the total thermal conductivity of the material is higher than this figure due to the contribution to the thermal conductivity by radiation. Zirconia is susceptible to radiation transport (photon transport) at high-temperatures (Figure 3). The contribution to the total thermal conductivity due to radiation can be written;

$$k_r = \frac{16}{3} \sigma n^2 T^3 l_r \quad [2]$$

Therefore the total theoretical thermal conductivity of zirconia-based systems is merely the sum of the two terms :

$$k = k_p + k_r \quad [3]$$

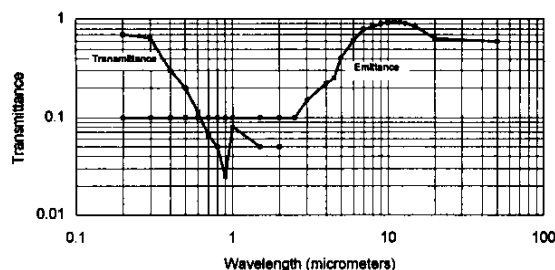


Figure 3 Emittance and transmittance of zirconia as a function of wavelength.

If the mean free path for radiative transport is assumed to be the thickness of the coating then, for an application where the surface of the TBC is operating at 1473K and the interface operates at 1323K the contribution to total thermal conductivity due to radiation could be as high as 1 W/m.K. In this case the heat flux which could arise through radiation is of the order of 80-90 kW/m<sup>2</sup> out of typical total values of 800 kW/m<sup>2</sup> seen in high heat flux regions in engines. Clearly the mean free path of photons is not the thickness of the coating and therefore radiation is attenuated within the TBC structure reducing the contribution to the total conductivity from the value listed above. However, as the operating temperature increases the contribution to thermal conductivity from radiation becomes more important.

Therefore to lower the intrinsic thermal conductivity of a system, reductions in the specific heat capacity, phonon velocity and mean free path, density or refractive index are needed. The specific heat capacity at constant volume for any system is constant at a value of  $3.kbN \approx 25 \text{ J/(K.mol)}$  [13] above the Debye temperature (380K [13] for zirconia). Therefore to engineer a lower thermal conductivity in zirconia-based ceramics, the only options are to lower the mean free paths of the heat carriers, to lower the velocity of the heat carriers, or to lower the density of the material.

In real crystal structures scattering of phonons occurs when they interact with lattice imperfections in the ideal lattice. Such imperfections include vacancies, dislocations, grain boundaries, atoms of different masses and other phonons. Ions and atoms of differing ionic radius also scatter phonons by locally distorting the bond length and thus introducing elastic strain fields into the lattice. The effects such imperfections cause can be quantified through their influence on the phonon mean free path. This approach has been used by several workers, for which the phonon mean free path ( $l_p$ ) is defined by:-

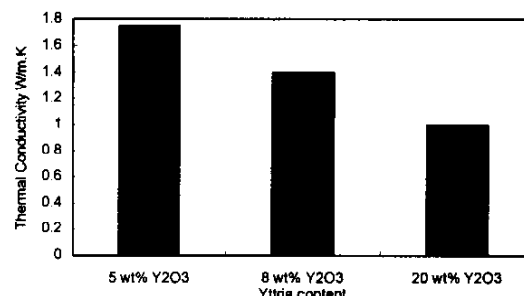


Figure 4 Theoretical conductivity of EB-PVD zirconia ceramics as a function of yttria content.

$$\frac{1}{l_p} = \frac{1}{l_i} + \frac{1}{l_{vac}} + \frac{1}{l_{gb}} + \frac{1}{l_{strain}} \quad [4]$$

Of these the grain boundary term has the least effect on the phonon mean free path, whilst the intrinsic lattice structure and strain fields have the most significant effect. For example, the addition of NiO has a marked effect on the intrinsic mean free path in MgO, reducing the mean free path by a factor of 10 [14]. However, the addition of alloying oxides has the largest effect on simple systems, the zirconia-yttria crystal system is more complex than MgO and the effect of alloying additions is less. For zirconia based systems, workers in the field have demonstrated that increasing the level of yttria in the alloy, decreases the thermal conductivity [15,16] which is commensurate with shorter intrinsic mean free paths with increasing yttria content (Figure 4).

Further to the reduction in the intrinsic mean free path due to alloying, local strain fields and vacancies can be generated in the lattice. These strain fields and vacancies act to scatter phonons directly increasing phonon dispersion in the lattice. With increased dispersion, there is a high probability that phonon-phonon interactions will occur whereby the mean free path will be further reduced. The benefit of a 20-30% lower thermal conductivity by adding divalent transition metal dopants, as reported by Tamarin et al [17] is attributed to this effect and in part to the dopants ability to attenuate radiation within the ceramic layer.

For thermally sprayed TBC's the typical grain size is of the order of 1  $\mu\text{m}$  and for EB-PVD TBC's the grain size varies from c.a.  $\ll 1 \mu\text{m}$  at the interface whilst the column length is 100-250  $\mu\text{m}$  in the bulk of the coating. These dimensions have little effect on the mean free path of phonons. However, these dimensions can have an effect on the radiative transport in the ceramic, where a reduction in the mean free path for photons from 250  $\mu\text{m}$  to 1  $\mu\text{m}$  would cause a reduction in the radiation contribution to total thermal conductivity from 1 to

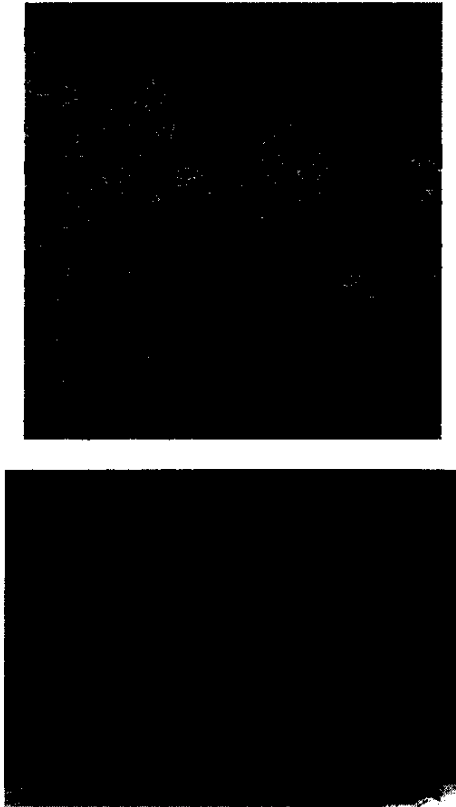


Figure 5 photomicrographs of thermally sprayed (top) and EB-PVD TBC's (bottom), showing the differences in microstructure.

0.005 W/m.K from equation [2].

In real coating systems grain boundaries are associated with air-gaps (inter-splat boundary porosity and inter-column porosity in thermally sprayed and EB-PVD TBC's respectively - Figure 5) and these have a significant effect on the thermal conductivity. The alignment of the inter-splat boundaries in the case of the thermally sprayed coatings has by far the larger effect reducing the conductivity of zirconia-yttria TBC materials from theoretical values of 2.2-2.6 W/m.K to values in the range 0.7-0.9 W/m.K (refer to Table 1). This behaviour is well documented and is due to the reduction of mean free paths of photons (radiative heat transfer) by scattering at the splat boundaries, but more importantly, by the reduction in the composite thermal conductivity due to the air-gaps [18].

### 3. THERMAL CONDUCTIVITY IN EB-PVD TBC's

Whilst the thermal conductivity of air plasma sprayed

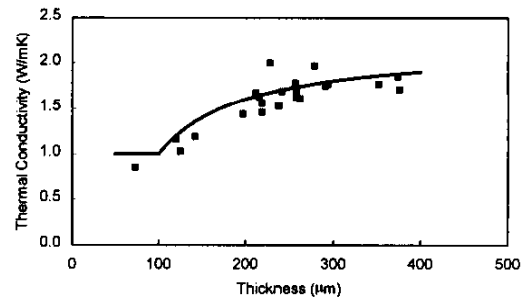


Figure 6 Effect of coating thickness on thermal conductivity of EB-PVD at room temperature.

PYSZ ceramic and bulk zirconia are essentially insensitive to coating thickness this is not the case for EB-PVD ceramics [19]. This behaviour is illustrated in Figure 6.

The explanation for this increase in thermal conductivity with thickness relates to the unique columnar microstructure which characterise PVD ceramics when grown from the vapour phase. During deposition, competitive growth occurs, as illustrated in Figures 7 and 8. This results in a decrease in the number of oblique columnar boundaries in the outer part of the coating as grains with "less favoured" growth directions are eliminated from the coating structure. The number

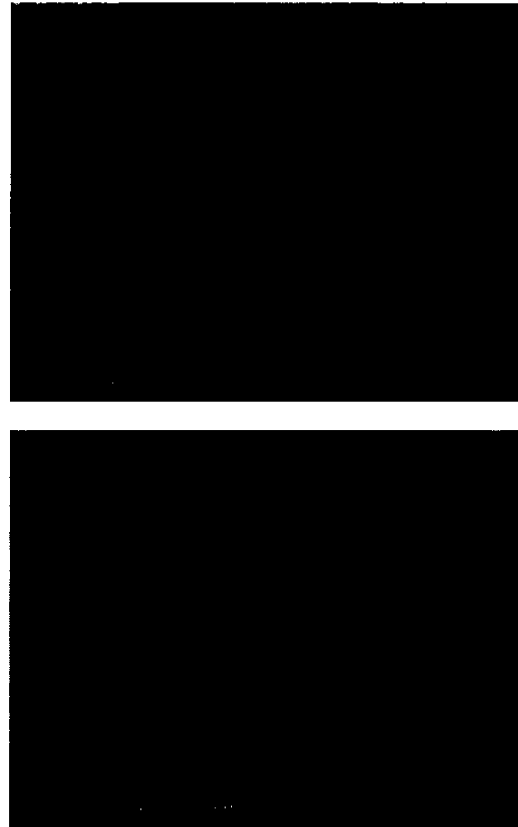


Figure 7 Differences in the column density for the nucleate zone (top) and the steady state region (bottom)

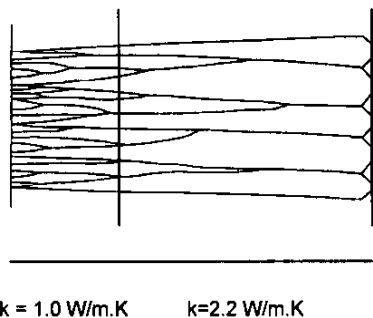


Figure 8 Schematic of an EB-PVD TBC and the associated variation of thermal conductivity for the two-layer model

and distribution of columnar boundaries is responsible for the reduction in thermal conductivity. More boundaries mean additional centres capable of scattering thermal waves. Thus the thermal conductivity of an EB-PVD TBC can be modelled successfully using a two-layer model, shown schematically in Figure 8 [19]. The inner "nucleate" zone is dominated by defect/grain boundary scattering and this results in a lower conductivity of around 1.0 W/m.K. With increasing thickness, the structure is characterised by a dominant crystallographic texture and the thermal conductivity increases as the outer part of the coating becomes more perfect. In this outer zone the thermal conductivity approaches that of bulk zirconia at circa 2.2 W/m.K. The overall coating thermal conductivity results from the combined effect of these two layers and can be predicted using a rule of mixtures. For coating thicknesses ( $x$ ) less than  $x_1$  (100 $\mu$ m for the schematic illustrated in Figure 8) then

$$k = k_1 \quad [5a]$$

while for coating thickness ( $x$ ) greater than  $x_1$

$$k = \frac{x_1 k_1}{x} + \frac{(x - x_1)}{x} k_2 \quad [5b]$$

Figure 9 provides a comparison between predicted and measured thermal conductivities for EB-PVD zirconia thermal barrier coatings, illustrating the good agreement to experiment of this two layer thermal conductivity model.

It should be expected that the thermal conductivity of chemical vapour deposited (CVD) ceramic should show a similar thickness dependence to EB-PVD zirconia as both coating morphologies are grown from the vapour phase. A study on the thermal conductivity of CVD deposited synthetic diamond confirms this hypothesis [19,20].

From the foregoing, it is evident that the manufacturing

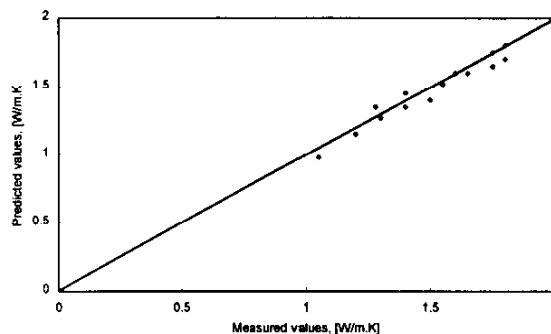


Figure 9 Comparison between predicted and measured thermal conductivities of EB-PVD TBC's of varying thickness.

process used to produce the thermal barrier coating strongly affects the coatings resultant thermal conductivity. Lamellar interfaces, parallel to the coating/substrate interface as produced in plasma sprayed ceramic, act to strongly scatter thermal waves reducing the coatings thermal conductivity. This behaviour is observed to a lesser extent in the inner growth zone of EB-PVD deposited coatings due to the inclined nature of many of these inner boundaries. Defect scattering must also play a role in this early deposition zone of EB-PVD ceramics. However, due to the competitive nature of coating growth for vapour deposited coatings a dominant growth texture is developed. This vertically aligned microstructure of the outer layer of an EB-PVD coating results in thermal conductivities close to that for the bulk ceramic.

These observations would suggest that to further reduce the thermal conductivity of EB-PVD TBC's one should introduce layers and/or additional phonon scattering centres into the coating.

#### 4. REDUCTION OF THERMAL CONDUCTIVITY IN EB PVD COATINGS BY LAYERING

The former section discussing heat transfer into and through the ceramic has highlighted a number of methods capable of reducing the thermal conductivity of the zirconia ceramic. To reduce radiative transport 'colouring' and 'layering' are possibilities, while introducing 'atom dimension defects', 'local changes in ceramic density' and 'local variation in ceramic elastic modulus' may be effective in reducing phonon conduction.

As indicated earlier the plasma sprayed TBC structure is such that the contribution to total thermal conductivity by radiation is minimised by the lamellar splat boundaries at a typical spacing of 1  $\mu$ m. If this attenuation of the radiative transport mechanism could be applied to EB-PVD it could make a significant contribution to the reduction of the thermal conductivity,

especially at high temperatures. Thus layering of the ceramic appears a most promising route to lower the ceramics thermal conductivity, especially if it can be coupled with changing the local density or elastic modulus of the material. A suitable periodicity of the layers should be  $0.2\text{-}2.0\mu\text{m}$  (between  $\lambda$  and  $\lambda/4$  for an incident radiation of  $0.5\text{-}5.0\mu\text{m}$ ), which is able to scatter photons and thus reduce radiative transport. This concept of layering within each column of an EB-PVD coating is illustrated schematically in Figure 10.

To reduce phonon conduction layer periods would have to be of near atomic dimensions ( $0.3\text{-}2.0\text{nm}$ ) and this is not considered feasible, although it should be possible to locally change either the elastic modulus or density of the ceramic by introducing atomic level defects into the lattice.

The PVD process offers a number of ways to tailor coating microstructures and thereby introduce multi-layers, since both the column angle and morphology may be influenced by variations in the flux density and the direction this flux subtends to the substrate surface [21].

Three alternative EB-PVD processing routes could be used to generate layering within the columns.

- Route 1 varying the speed of rotation of the parts during coating
- Route 2 rocking the substrate between two fixed tilt angles.
- Route 3 varying the degree of ion bombardment to change the density of the ceramic.

The principle behind each of these routes is to introduce interfaces into each of the column structures which are essentially parallel to the ceramic/bond coat interface, but without disrupting the overall columnar structure that provides the coating with its good strain tolerance and erosion resistance. Thus, these layered structures should offer the best of the properties currently available from commercial EB-PVD coatings and thermally sprayed ceramic coatings, namely low thermal conductivity, good strain tolerance and good erosion

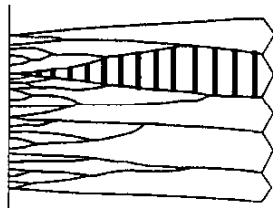


Figure 10 Schematic of layering within an EB-PVD column to reduce radiative heat transfer within the coating.

resistance. The concept is the subject of a European patent [22].

This paper focuses on the use of ion bombardment to create layers in the EB-PVD structure with varying density.

#### 4.1 Layering by Plasma Assisted Deposition

This method uses a glow discharge plasma to vary the density of the ceramic during deposition. Figure 11 illustrates a typical micrograph of the morphological changes that can be introduced.

The layers were produced by switching the D.C. bias applied to the substrate between high and low levels during deposition. This has the effect of periodically changing the degree of ion bombardment and thus altering the density of the layers produced. The micrograph illustrated in Figure 11, was produced by switching between a D.C. bias with a peak voltage of 2500V and ground. The degree of bombardment that is attained depends on the applied bias and local current density, current densities typically greater than  $0.1\text{mA}/\text{cm}^2$  are required to achieve a significant density change [22].

The measured thermal conductivity for this microstructure is significantly lower than that for a coating produced without ion bombardments (Figure 12). Reductions of the order of 37-45% compared to state-of-the-art EB-PVD TBC's have been measured for these layered structures that are approaching the values for thermally sprayed TBC systems.



Figure 11 Layered structures introduced by PAPVD processing of the ceramic. Top general view, bottom detail of a boundary region.

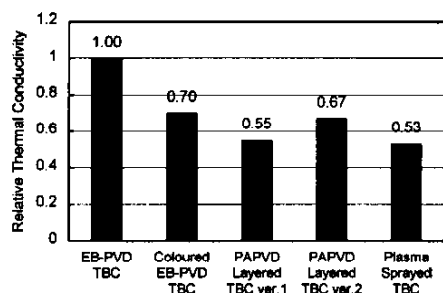


Figure 12 Relative thermal conductivity of modified EB-PVD TBC systems compared to state-of-the-art EB-PVD and thermally sprayed TBC's.

Clearly, the combination of layering at micron dimensions and the introduction of density change from layer to layer work in combination to significantly reduce the thermal conduction of the coating. As discussed earlier the layering periodicity has been selected to significantly reduce photon transport, while local changes in layer density act to scatter phonons and thus reduce thermal conduction by lattice vibrations.

Using this process route it has been possible to introduce layers into individual columns, without change the overall vertical columnar microstructure required for good strain, tolerance and good erosion resistance. For example, it can be seen from Figure 13 that layering produces no significant deterioration to the erosion performance of an EB-PVD thermal barrier coating.

Also it is possible by programming the sequencing of bias application to tailor the position of the layers in the coating. This potentially has benefits in allowing the properties of the coating to be varied from the surface to the interface. For example more erosion resistant structures could be generated at the outer surface of the coating with the application of bias in this region, whilst the inner zone of the coating is layered to lower the thermal conductivity. To demonstrate this a coating was produced where the early deposition has no bias applied,

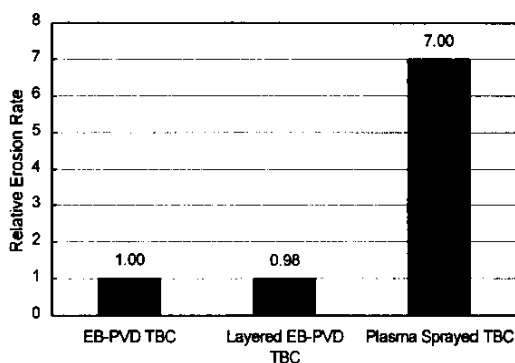


Figure 13 Erosion performance of various modified EB-PVD coatings.

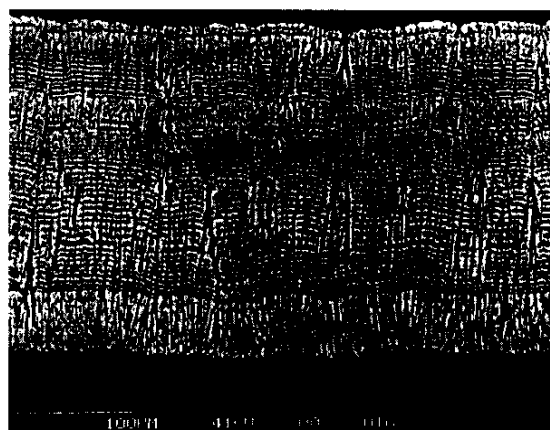


Figure 14 An example of a tailored EB-PVD layered structure.

followed by a region with bias and high ion current density to produce maximum density changes between layers. This was followed by a region of low current density giving low density differences between layers and finally a region of high current density giving a denser structure. (Figure 14).

#### 4.2 Addition of dopants to reduce thermal conductivity

Tamarin and co-workers [17] have examined the addition of divalent transition metal oxides to reduce the thermal conductivity of zirconia-ytria TBC's. As eluded to earlier this has two effects, firstly to reduce the phonon transport in the material and secondly a reduction in the radiative transport mechanism. The use of a divalent transition metal oxide introduces vacancies as well as strain centres into the lattice both of which will reduce the phonon mean free path. In addition this doping changes the colour of the TBC material to dark grey, reducing radiation transport in the visible range and by inference in the near infra-red.

Following this concept of dopant additions, further reduction in phonon thermal conductivity could be achieved by the selection of low levels of dopant which maximise lattice strain and lattice anharmonicity. This is best achieved by the addition of transition metal ions with high mass and large ionic radii.

## 5. SUMMARY OF REMARKS AND CONCLUSIONS

This paper has examined the factors that control the thermal conductivity of thermal barrier coatings and has highlighted the significance of three factors capable of lowering the coating thermal conductivity.

1) **Colouring** of the coating by addition of dopant materials can be used to increase the opaqueness to infra-red radiation and therefore radiative transport through the coating.

2) **Atomic level defects**, such as atoms of differing mass, vacancies etc. can be introduced by adding dopants or by ion bombardment. These are effective in reducing phonon conduction, i.e. heat transfer by lattice vibrations (Figure 15). A recent patent by Strangman [23] describes a TBC system with stabilised porosity wherein the pores are coated with a noble metal (Figure 16). This stabilised porosity along with the noble metal coating is claimed to reduce the thermal conductivity and improve its sintering behaviour at high temperatures.

3) **Layering**, can be used to introduce interfaces parallel to the ceramic bond coat interface and is effective in reducing both radiative and phonon transport. The layer periodicity when set at levels between 0.5 and 2.0 $\mu\text{m}$  is effective in reducing photon transport, when coupled with a significant change in layer density from one layer to another. These local changes to the ceramic density are also believed to be effective in reducing phonon conduction. Thus layering has been shown to be a most effective method of modifying the thermal conductivity of EB-PVD thermal barriers (Figure 16).

By using a switched D.C. bias, applied to the substrate it is possible to introduce these layers during the deposition processes. The degree of ion bombardment controls the density changes achieved, thus allowing tailoring of the ceramic microstructure to engineer the most appropriate mechanical and thermal properties in the coating for the operational requirements placed on it.

## 6. ACKNOWLEDGEMENTS

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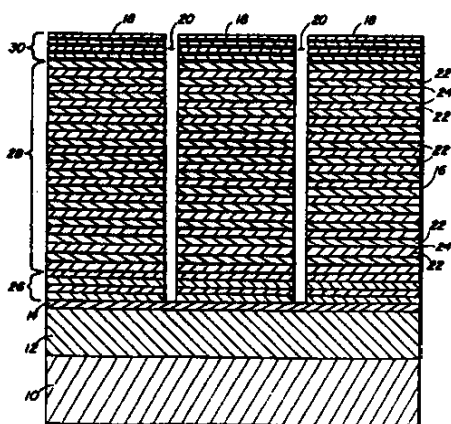


Figure 15 Schematic of EB-PVD TBC systems with stabilised porosity after Strangman

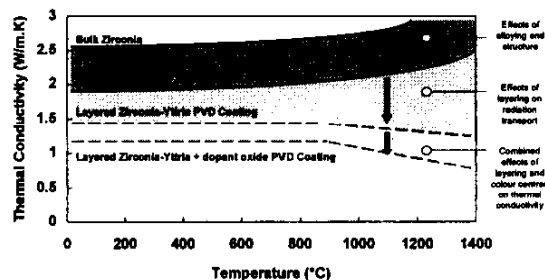


Figure 16 Summary of the reductions achievable in thermal conductivity in zirconia thermal barriers as a result of alloying and layering the structure.

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