

**METHODS TO REDUCE THE THERMAL CONDUCTIVITY OF EB-PVD TBC's**

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**Abstract**

This paper reviews the advantages and disadvantages of various thermal barrier coatings (TBC) systems, with the aim of custom designing a TBC system to be both strain tolerant and have a low thermal conductivity.

Methods of heat transfer within zirconia based ceramics are discussed, including the influence of coating microstructure and ceramic composition. It is shown the addition of dopant atoms (colouring) is effective in reducing 'phonon' transport while that layered microstructures are effective in reducing 'photon' transport.

Advanced processing, using EB-PVD coating methods has allowed both coloured and layered ceramic coatings to be produced. Measured thermal conductivities of 1.0 W/mK have been achieved using these methods, much lower than current commercial EB-PVD coatings at 1.5-1.9 W/mK.

## **1. Introduction**

The need for coatings to protect hot section parts of gas turbines has evolved progressively since their first application on aerofoils in the early 1960's [1-3]. These early diffusion coatings were used to protect high-pressure turbine aerofoils against degradation by high temperature oxidation processes and hot corrosion. Since these early days, major steps have been made in the protection of hot path components culminating, at present, in the use of EB-PVD (electron beam physical vapour deposition) thermal barrier coatings on aerofoils of advanced aero-gas turbines [4-6].

This paper reviews the current status of thermal barrier technology and looks to methods capable of reducing the thermal conductivity in future generations of EB-PVD TBCs. Methods of heat transfer within zirconia based ceramics are discussed, focussing on the influence of the ceramic coating microstructure and ceramic composition in modifying the coatings thermal conductivity.

## **2. Thermal Barrier Coating Technology**

Plasma sprayed thermal barrier coatings Figure 1 have been used since the early 1950's and have been effective in protecting flare head and primary zone sections of combustors against the effects of hot spots within turbines, giving considerably improved component lives. Because of this success much attention has been directed towards the use of thermal

barriers on blades and vanes [4-9] but only within the last decade have they been used on highly stressed turbine components within commercial gas turbine engines [4, 5]. Figure 2 illustrates the strain tolerant columnar microstructure that is produced using electron beam physical vapour deposition (EB-PVD). It is this strain tolerant microstructure that has allowed TBC's to be successfully operate on highly stressed turbine components without spalling.

In addition to excellent strain tolerance [7, 8, 10-14], EB-PVD technologies result in an excellent surface finish [10] and good erosion resistance [15,16], but this is at the expense of the thermal conductivity which may be twice that of the best plasma sprayed thermal barrier coatings [10, 13, 17-19]. It is unfortunate that the microstructure (see Figure 2) which gives the EB-PVD thermal barrier coatings its high strain compliance and good erosion resistance leads to a relatively high thermal conductivity when compared to thermal sprayed coatings (Figure 3). Thus the challenge is to lower the thermal conductivity of EB-PVD TBCs to match that of plasma sprayed ceramic.

### **3. The Thermal Conductivity of Zirconia Based Coatings**

It is apparent (see Figure 3) that the thermal conductivity of zirconia based coatings strongly depends on microstructural features of the coating, introduced as a result of the chosen method of deposition. Plasma sprayed ceramics, Figure 1, at present, offer the lowest thermal conductivities (0.8-1.1W/mK) but at the expense of surface finish, strain tolerance and erosion resistance. EB-PVD ceramic coatings, Figure 2, have intermediate

values for thermal conductivity (circa 1.5-1.9 W/mK), between bulk yttria partially stabilised zirconia (YPSZ; 2.2-2.9 W/mK) and the values reported for plasma sprayed ceramics; but offer a high quality surface finish [10], better strain tolerance [7, 8, 10-14] and improved erosion resistance [15,16] over their plasma sprayed counterparts. Table 1 summaries the trade-off in properties between EB-PVD and plasma sprayed thermal barrier coatings: the properties cited have been measured at room temperature [10,15,17]. The elastic modulus data presented was measured using either a laser ultrasound method or a resonant technique [10]. Measurements using four point bending results generally in lower values of modulus for plasma sprayed TBCs typically 30 GPa [6]. Research is underway to understand the microstructural features that control thermal transport in zirconia based TBC's and thereby to reduce the thermal conductivity of EB-PVD thermal barrier coatings. Some aspects of this work are discussed in this paper, however, the degree of effort is much less than that currently spent on understanding the thermo-mechanical properties of these coatings [4, 5, 10-13, 20-25].

Table 1 Properties of TBC's at Room Temperature

Property/Characteristic	EB-PVD	Plasma Sprayed
Thermal Conductivity (W/mK)	1.5-1.9	0.8-1.1
Surface Roughness ( $\mu\text{m}$ )	1.0	10.0
Adhesive Strength (MPa)	400	20-40
Young's Modulus (GPa)	90	200 [7-30]*
Erosion Rate (Normalised to PVD)	1	7

\* Measured by four-point bending

Alperine and coworkers [13] in their recent review cited thermal conductivity measurements of zirconia TBC's from seven independent studies. Both air plasma sprayed (APS) and EB-PVD ceramics were examined. They concluded that the thermal conductivities for zirconia based coatings were significantly lower than bulk zirconia, the latter having values between 2.2 and 4.0 W/mK depending on the polymorph of the zirconia ceramic present. This can be seen from Figure 4, which plots the thermal conductivity data for zirconia ceramics and coatings as a function of the yttria content in the ceramic [the data are those cited in references 10, 13, 17, 18, 20, 26-35, or measured independently at Rolls Royce].

The observed differences in thermal conductivities reported in the above studies can be explained by the microstructures developed within the coatings, as apparent in Figures 1 and 2. The plasma sprayed TBC's (Figure 1) exhibit a two dimensional microcrack network; one oriented parallel to the coating surface and corresponding to poor contact between different splats; the second oriented perpendicular to the coating, which results from the microcracking of splats during cooling. It is the parallel oriented cracks which are particularly effective in reducing the thermal conductivity in the APS coating as the interfaces formed by such cracks are also perpendicular to the primary heat flux. In addition, dispersed spheroidal micro-porosity also lowers the conductivity of the zirconia ceramic. For the EB-PVD case, see Figure 2, the reduction in thermal conductivity reflects different microstructural features. It is the intra-columnar fine porosity that accounts for the reduced thermal conductivity over that of the bulk ceramic. This is generally perceived to be much less effective as its distribution is generally aligned

perpendicular to the coating surface, i.e. parallel to the direction of the primary heat flux.

From a comparison of these two basic microstructures, it is clear that microstructural features are important in controlling the thermal conductivity of zirconia thermal barrier coatings, particularly the beneficial effects that could be introduced through the inclusion of planar scattering centres (layered structures) such as those that result naturally through the plasma spray manufacturing processes.

As well as microstructural features, the thermal conductivity would also be expected to vary with the ceramic composition. This has already been demonstrated in Figure 4, where the change in thermal conductivity of zirconia ceramics and coatings, is plotted against yttria content. In each case, the thermal conductivity decreased as the yttria content increased, with the highest conductivities measured for the bulk ceramic and the lowest for the air plasma sprayed coatings.

### **3.1 Theory of Thermal Conduction in Zirconia Ceramics**

In crystalline solids heat is transferred by three mechanisms, (i) electrons (ii) lattice vibrations and (iii) radiation [35, 36]. 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 and thus conduction in zirconia is by lattice vibrations (phonons) or by radiation (photons).

The contribution to thermal conductivity from lattice vibration ( $k_p$ ), the quanta of which are known as phonons, is given by [35,36]:

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

where  $C_v$  is the specific heat,  $\rho$  the density,  $\bar{v}$  the phonon velocity and  $l_p$  the mean free path for scattering of phonons.

As an example, consider the data plotted in Figure 4, one may conclude that increasing the yttria content decreases the thermal conductivity. Thus, yttria must shorten the intrinsic mean free path in zirconia by increasing phonon dispersion. This is most probably due to the combined effect of alloying, local strain fields and the introduction of vacancies into the lattice, and will be discussed further later in this section.

As well as phonon conductivity, zirconia is susceptible to radiation conduction (photon transport) at high-temperatures. Partially stabilised zirconia commonly used for TBC's, becomes significantly transparent to thermal radiation at wavelengths between  $0.3\mu\text{m}$  and  $5\mu\text{m}$ , as illustrated in Figure 5. At  $1250^\circ\text{C}$ , 90% of the incident radiation lies in the range  $0.3\text{-}2.8\mu\text{m}$  with some 10% of the heat flux through the zirconia due to radiation [17]. This contribution due to radiation can be written as [37]:

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

where  $k_r$  is the thermal conductivity due to radiation,  $\sigma$  is the Stephen-Boltzmann's constant,  $n$  is the refractive index,  $T$  is the absolute temperature, and  $l_r$  the mean free path for photon scattering.

The total theoretical thermal conductivity of zirconia-based systems is the sum of these two terms:

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

At temperatures below 1200°C, phonon transport dominates the heat conduction through zirconia. However, as the temperature is increased radiation becomes more significant (a 10% contribution at 1250°C) and thus is expected to be a significant factor in the performance of future, high powered, high efficiency engines. Higher powers and improved efficiencies are achieved by raising the turbine entry temperatures (TET) which would result in a higher fraction of heat conducted through the EB-PVD TBC due to photon transport (radiation). One may expect radiation to be attenuated within the TBC and this would act to reduce the radiation contribution to total conductivity. The splat boundaries of APS-TBC's are particularly effective in this context, as these boundaries are perpendicular to the primary heat flux [33]. Even so as the operating temperature increases the contribution to thermal conductivity from radiation becomes increasingly important.



#### 4. Methods to Reduce the Thermal Conductivity of EB-PVD Thermal Barrier Coatings

To lower the intrinsic thermal conductivity of a material, reductions in the specific heat capacity, phonon velocity, mean free path, density or refractive index are needed (equ. 1 and 2). The specific heat capacity at constant volume ( $C_v$ ) for any system is constant at a value of  $3.kbN \approx 25 J/(K.mol)$  [38] when above the Debye temperature (380K for zirconia [38]). 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 may 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 ( $l_p$ ). This approach has been used by several workers, for which the phonon mean free path is defined by:

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

where  $l_i$ ,  $l_{vac}$ ,  $l_{gb}$  and  $l_{strain}$  are the contributions to the mean free path due to interstitials, vacancies, grain boundaries and lattice strain respectively.

Of these the grain boundary term has the least effect on the phonon mean free path in conventional materials, but may provide a significant effect in nanostructured coatings [18,39] , whilst the intrinsic lattice structure and strain fields have a significant effect in both conventional materials and coated structures. Figure 4 demonstrates that the thermal conductivity of zirconia ceramics can be reduced by alloying addition, irrespective of the gross microstructure. Microstructural effects are also important as can be seen by comparing the data for bulk zirconia-yttria, with that for the EB-PVD (columnar microstructure) and plasma sprayed (lamellar microstructure) thermal barrier coatings. The reduction in thermal conductivity with yttria addition, illustrated in Figure 4, is commensurate with a shorter intrinsic mean free path with increasing yttria additions due to local modifications to the lattice structure, introduction of vacancies and local strain fields generated by incorporating large dopant atoms. 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.

#### **4.1. Reduction of the Thermal Conductivity for EB-PVD TBC's by the Addition of Dopants (Colouring)**

Tamarin and co-workers [40] examined the addition of divalent transition metal oxides to reduce the thermal conductivity of zirconia-yttria TBC's and reported reductions of 30-40%. Such dopant additions give rise to two effects; firstly to reduce the phonon transport in the material and secondly to reduce the radiative transport mechanism. The

use of a divalent transition metal oxide will introduce vacancies as well as strain centres into the lattice, both of which will reduce the phonon mean free path as discussed above. In addition, this doping changes the colour of the TBC material to dark green/grey, reducing radiation transport in the visible range, and by inference in the near infra-red.

Following this concept, but concentrating on the role of high mass additions, which theoretically will provide more effective scattering centres [35], a number of alternative dopant additions have been examined with the aim of further reducing the phonon thermal conductivity. Five dopant additions have been examined; Erbium, Nickel oxide, Neodymium, Gadolinium and Ytterbium, with the aim of maximising lattice strains and lattice anharmonicity [41]. The ternary additions were introduced by custom manufacturing evaporation rods with known dopant levels, 2.0, 4.0 and 8.0 mole %. All rods evaporated well, resulting in coating thicknesses between 120-400 $\mu$ m. The thermal conductivity of each doped TBC was measured. The data are presented in Figures 6 and 7. Figure 6 demonstrates the benefits of Erbium and Neodymium additions, at various mole fractions, where it can be seen that up to 8 mole % results in a significant drop in thermal conductivity for both additions, with Neodymium more effective. For example, an 8% Erbium addition lowered the thermal conductivity (measured at 500°C) by 32% and coloured the ceramic pink, while Neodymium at 8 mole % lowering the thermal conductivity (measured at 500°C) by 46% and coloured the ceramic blue; achieving comparable thermal conductivities to plasma sprayed TBC's for an EB-PVD ceramic. Figure 7 compares the performance of various additions at 4 mole %. As can be seen from Figure 7, the most effective additions examined to date were Gadolinium, Neodymium and

Ytterbia, which resulted in a thermal conductivity of 0.88, 1.00 and 1.02 W/mK, calculated for a 4 mole % addition at a coating thickness of 250 $\mu$ m, when measured at 500°C

In this study, the addition of divalent metal ions, as suggested by Tamerin et al [40] was much less beneficial. The addition of 4 mole % NiO, which coloured the ceramic dark green/grey, only reduced the thermal conductivity of an EB-PVD TBC by some 3%, for a 250 $\mu$ m thick coating, measured at 500°C.

#### **4.2 Reduction of Thermal Conductivity by Varying the Coating Nano-structure**

Although for conventional materials, the grain boundary contribution to phonon scattering is thought to be small it has been shown [18,39] that within thermal barrier coatings (both plasma sprayed and EB-PVD) grain boundaries can have a significant effect, particularly when the grain size is of the same order as the mean free path for phonon scattering. Figure 8 presents a calculation by Kabacoff [39] of the influence of nano-grain size on the phonon conductivity of zirconia-7wt% yttria as a function of temperature. This demonstrates that the thermal conductivity is drastically reduced for fine grained materials, particularly when the grain size is of nanometer dimensions. For a 5nm grain size a value of 0.7 Wm<sup>-1</sup>K<sup>-1</sup> is predicted, virtually independent of temperature, for temperature above 200°C.

For EB-PVD thermal barrier coatings, the thermal conductivity has been observed to vary with coating thickness [18]. For the early stages of deposition (<100 $\mu$ m) a value of 0.8-

1.0 Wm<sup>-1</sup>K<sup>-1</sup> has been reported, however, by the time the coating is 250µm thick, the mean thermal conductivity is between 1.5-1.9 Wm<sup>-1</sup>K<sup>-1</sup>, when measured at room temperature. This behaviour has been modelled by using a two layer coating approximation consisting of an inner (100µm) fine-structured zone, overcoated with a layer with thermal conductivity close to bulk zirconia (2.2 Wm<sup>-1</sup>K<sup>-1</sup>). The two layer model provides a close approximation to the thermal conductivity of variable thickness EB-PVD thermal barrier coatings. Measurements of the inner, fine-structured grain size gives value of 3-4 µm, although within each grain is a ultrafine fibrous structure of nanometer dimensions.

#### **4.3. Reduction of the Thermal Conductivity for EB-PVD TBC's by Layering**

The foregoing discussion would suggest that to reduce the thermal conductivity of EB-PVD TBC's further one should introduce additional phonon scattering centres into the coating. Further, from equation 2, reducing the mean free path from 250µm (of the order of the thickness of the coating) to 1-2µm would cause a reduction in the radiation contribution to the total thermal conductivity from 1 to 0.005 W/mK [17]. Thus, layering of the ceramic offers a most promising route to lower the thermal conductivity of an EB-PVD TBC, by modifying both the phonon and photon transport within the coatings.

For photon scattering, the periodicity of the layers should be chosen to act as a quarter wavelength filter (between  $\lambda$  and  $\lambda/4$  of the incident radiation). With radiation wavelengths between 0.3-5.0µm, the layer periodicity should lie between 0.2-2.0µm, centred around 0.7µm. This concept of layering within each column of an EB-PVD

coating is illustrated schematically in Figure 9; the principle being to introduce interfaces into each column structure which are essentially parallel to the ceramic/bondcoat interface, but without disrupting the columnar structure that provides the EB-PVD coating with good strain tolerance and erosion resistance. This concept is the subject of a European patent [42].

The method of obtaining such structures in practice uses a glow discharge plasma to vary the density of the ceramic during deposition. Figure 10 illustrates a typical micrograph of the morphological changes that can be introduced [19]. 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 10 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  $0.1\text{mA/cm}^2$  are required to achieve a significant density change [17,42].

The measured thermal conductivity for this microstructure is significantly lower than that for a coating produced without ion bombardments (Figure 11). Reductions of the order of 37-45% compared to state-of-the-art EB-PVD TBC's have been measured for these layered structures, approaching the values for thermally sprayed TBC systems. Clearly, the combination of layering at micron dimensions and the introduction of density change from layer to layer work in combination to reduce the thermal conduction of the coating.

The layering periodicity is selected to significantly reduce photon transport, while local changes in layer density act to scatter phonons and thus reduce thermal conduction by lattice vibration as well.

## 5. Conclusions

In this paper. Methods capable of lowering the thermal conductivity of EB-PVD thermal barrier coatings have been reviewed. Four significant factors have been identified that may lower the coating thermal conductivity by modifying either phonon and/or photon transport.

These factors are:-

- 1) **The introduction of atomic level defects**, such defects include atoms of differing mass, vacancies and interstitials and can be introduced by adding dopant, or by ion bombardment. These defects are effective in reducing phonon conduction (heat transfer by lattice vibrations).
- 2) **Colouring** of the thermal barrier coatings can be used to increase the coatings opaqueness to infra-red radiation. This is achieved through the addition of dopant materials and reduces the radiative transport through the coating.

- 3) **Nano-grained structures** act to scatter both phonons and photons. The fine, micro-crystallite zone observed within the nucleation region of EB-PVD thermal barrier coatings behaves in this way. Re-nucleation of the EB-PVD coating growth at periodicities less than 100 $\mu\text{m}$  would lower the ceramic coatings thermal conductivity.
  
- 4) **Layering** involves the introduction of interfaces/density changes parallel to the ceramic bond coat interface. These layered structures are effective in reducing both radiative and phonon transport.

This paper has shown that a 4 mole % addition of a tertiary dopant will reduce the thermal conductivity of zirconia-7wt% yttria (4 mole %). Ytterbia, Neodymia and Gadolinia have been shown to be particularly effective, achieving thermal conductivities of 0.88 and 1.02  $\text{Wm}^{-1}\text{K}^{-1}$  (calculated for a 250 $\mu\text{m}$  coating at 500 $^{\circ}\text{C}$ ).

By layering, thermal conductivities of 0.9-1.1  $\text{Wm}^{-1}\text{K}^{-1}$  are possible for a 250 $\mu\text{m}$  EB-PVD zirconia-7wt% yttria TBC.

In combination, colouring plus layering, one should expect a significant further reduction in thermal conductivity; possibly achieving a value of 0.5  $\text{Wm}^{-1}\text{K}^{-1}$  for a 250 $\mu\text{m}$  EB-PVD TBC. Colouring plus layering is planned in a future extension of this research.



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## **7. References**

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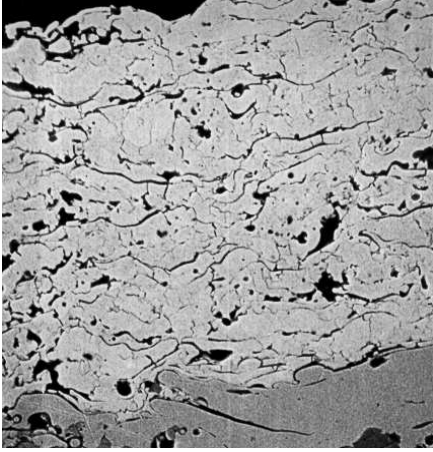


Figure 1 A plasma-sprayed TBC

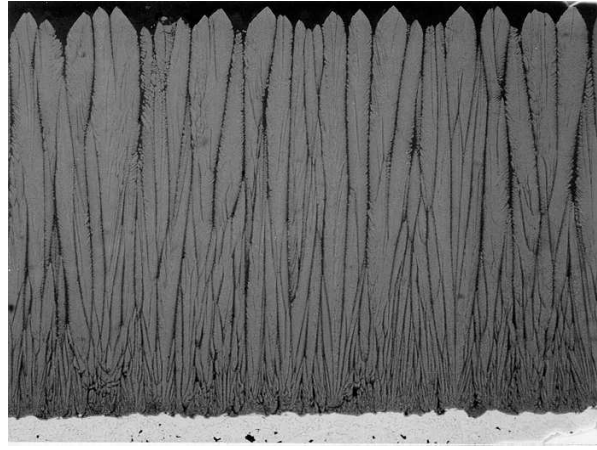


Figure 2 An EB-PVD TBC

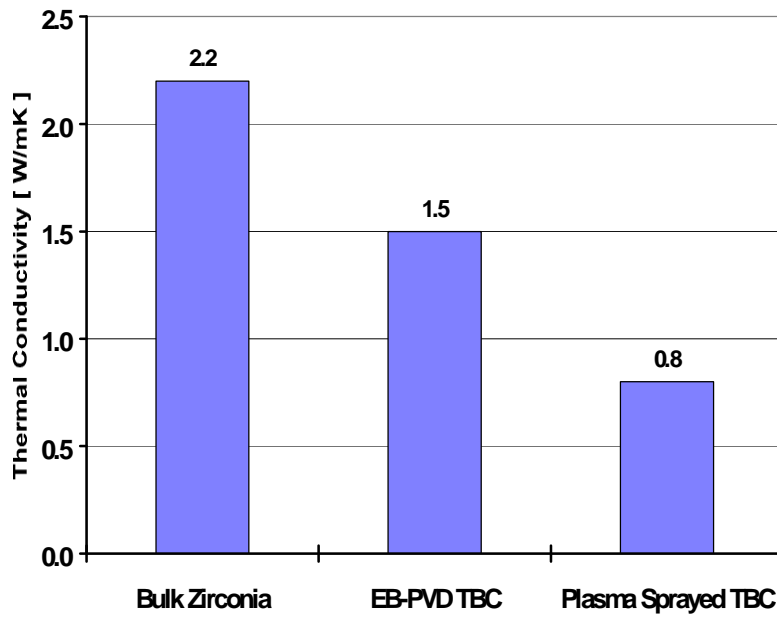


Figure 3 Thermal conductivities of bulk, EB-PVD and thermally sprayed zirconia yttria materials [17].

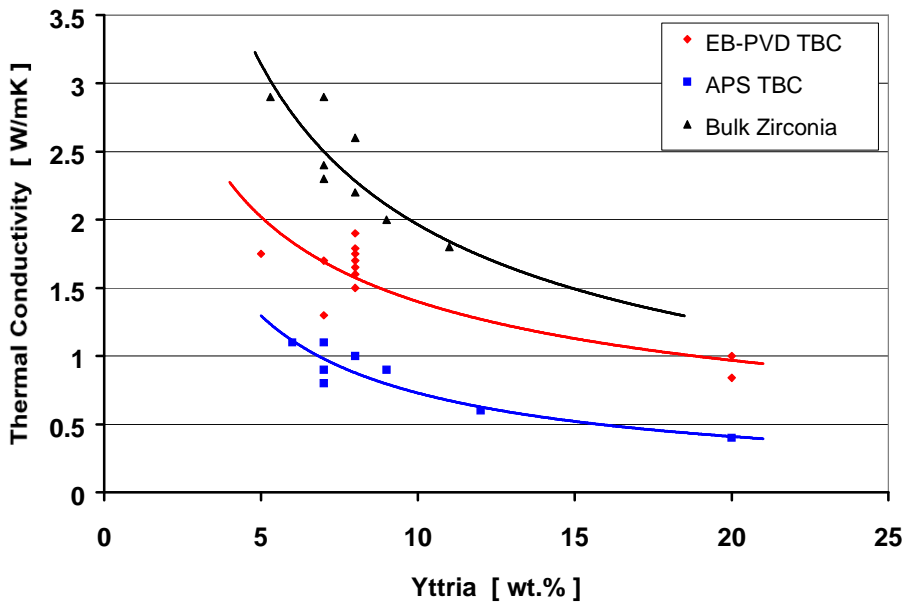


Figure 4 Thermal conductivities of zirconia ceramic and zirconia thermal barrier coatings as a function of the yttria content

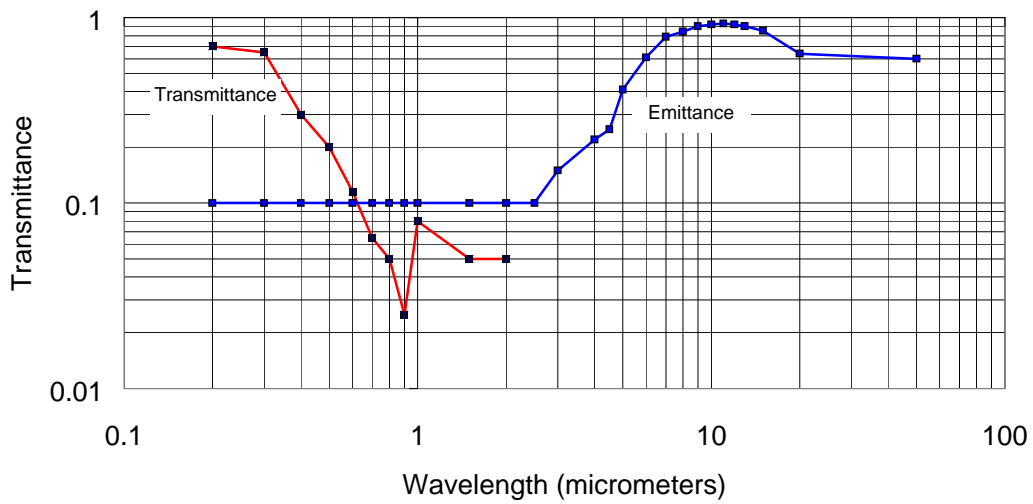


Figure 5 Emittance and transmittance of zirconia as a function of wavelength

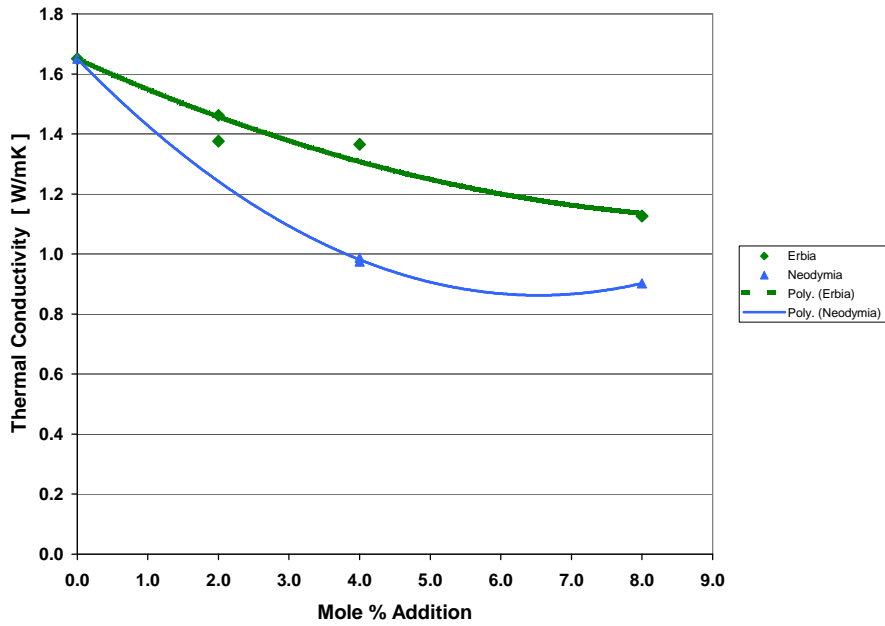


Figure 6 Thermal conductivity of dopant modified EB-PVD TBC systems, as a function of mole fraction of dopant addition [data corrected to a 250 $\mu$ m reference coatings thickness [18]; data measured at room temperature].

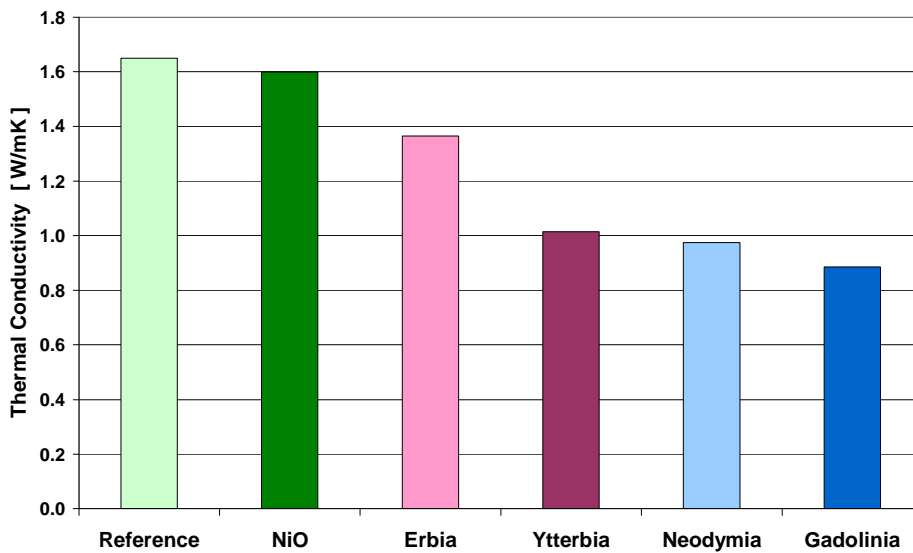


Figure 7 Thermal conductivities of dopant modified EB-PVD TBCs at 4 mole % addition and 250 $\mu$ m thickness; data measured at room temperature.



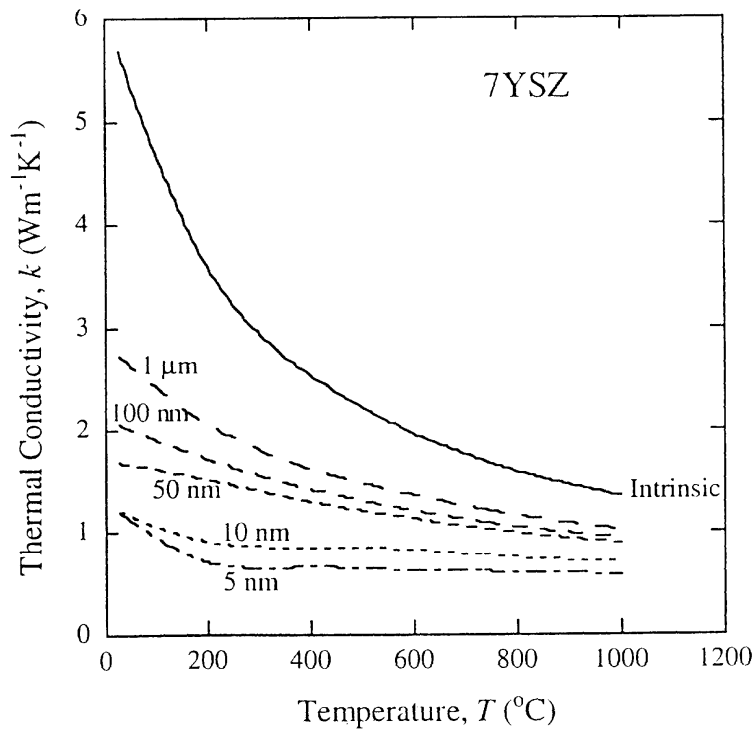


Figure 8 Thermal conductivity of zirconia-7wt% yttria versus grain size and temperature [39]

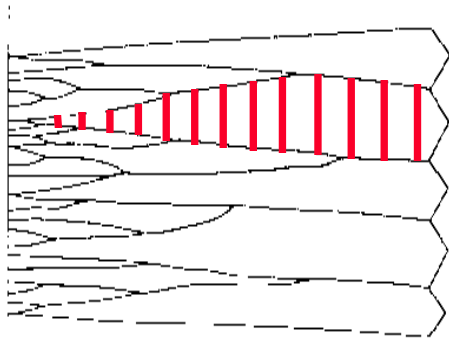


Figure 9 Schematic of layering within an EB-PVD column to reduce radiative heat transfers within the boundary region

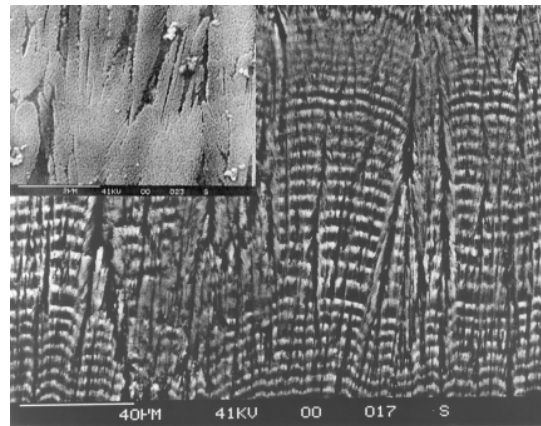


Figure 10 Layered structured EB-PVD TBC introduced by PAPVD processing of the ceramic. Insert is detail of a coatings boundary region.

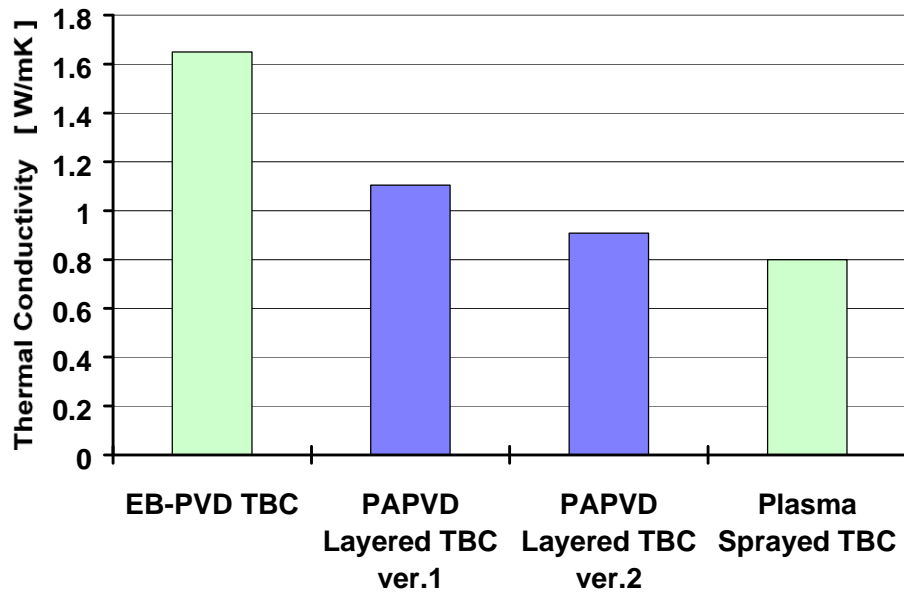


Figure 11 Thermal conductivities of layered EB-PVD TBC systems compared to the state-of-the-art and thermally sprayed TBCs [data corrected using a 250 $\mu$ m reference coating thickness [18]; data measured at room temperature]