



Effect of the microstructure of EB-PVD thermal barrier coatings on the thermal conductivity and the methods to reduce the thermal conductivity

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ABSTRACT

Purpose: The goal of the paper is to evaluate the effect of the microstructure of EB-PVD thermal barrier coatings on the thermal conductivity and the methods to reduce the thermal conductivity.

Design/methodology/approach: In this study, the effect of microstructure of the coating to the thermal conductivity of EB-PVD TBCs and the methods to reduce the thermal conductivity of these coatings have been investigated.

Findings: Microstructure of the EB-PVD coating - it is found that they are formed in two different structure and microstructural characteristics and they are different from each other.

Practical implications: Nowadays, selection of materials for usage purpose is getting important because of new high technologic developments. Especially for the parts operating at high temperatures, materials which have low thermal conductivity and high mechanical resistance are preferred. Thermal Barrier Coatings (TBCs) are used in aerospace, diesel engine and power plant technologies due to porous structures and low thermal conductivity. Generally these coatings are applied by two methods, Electron Beam-Plasma Vapour Deposition (EB-PVD) and Atmospheric Plasma Spray (APS).

Originality/value: This paper reviews the current status of EB-PVD thermal barrier coatings technology and investigation to reduce the thermal conductivity in future generations of EB-PVD thermal barrier coatings.

Keywords: Thermal barrier coatings (TBCs); Electron beam-physical vapour deposition (EB-PVD); Thermal conductivity; Zirconia

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Thermal Barrier Coatings (TBCs) were first successfully tested in the turbine section of a research gas turbine engine in the mid-1970s. By the early 1980s they had entered revenue service on the vane platforms of aircraft gas turbine engines, and today they are flying in revenue service on vane and blade surfaces. Advanced engines, for the foreseeable future, may be expected to rely even more heavily on these coatings [22, 32].

Two processes are used to apply today's TBCs. Plasma-sprayed coatings were brought into service first and currently remain in service. By the 1990s, a second type of TBC deposition process—physical vapour deposition (PVD) – had been successfully brought into commercial service. The success of both types of coatings in commercial aircraft gas turbine applications, especially the PVD coatings, played a pivotal role in the acceptance of this technology. However, with this acceptance come ever-increasing demands on these coatings to perform for longer hot times under increasingly severe conditions [22].

In comparing the typical microstructures and properties of thermally sprayed and EB-PVD, the differences in performances are attributed to the microstructures of the deposited coatings. In thermally sprayed TBC, typical grain size is approximately 1-2 μm and the coating microstructure is associated with intersplat boundary porosity, unmelted, partially melted particles and microcracks [4, 15].

This paper reviews the current status of EB-PVD thermal barrier coatings technology and investigation to reduce the thermal conductivity in future generations of EB-PVD thermal barrier coatings.

2. EB-PVD thermal barrier coatings technology

Plasma sprayed thermal barrier coatings have been used since the early 1950s 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 was drawn towards the use of thermal barriers on blades and vanes [1,6,9,11,19,33] but only within the last decade have they been used on highly stressed turbine components within commercial gas turbine engines [11,19].

Electron Beam Physical Vapour Deposited (EB-PVD) zirconia–yttria coatings were first developed at Pratt & Whitney in the late 1970s [8, 20, 33, 34].

By the early 1980s, lives of the best PVD zirconia-yttria coatings were exceeding the lives of the modern partially stabilized zirconia-yttria coatings [3, 8]. However, early PVD coatings suffered from poor reproducibility, which was attributed to small differences in the coating microstructure caused by subtle differences in the processing parameters [8]. By mid-decade the reproducibility problems had been solved [14, 20, 33].

The state-of-the-art TBCs are two layer systems comprised of a 50-150 μm thick metallic bond coat and a 100-125 μm top coat layer of 7-8 wt% Y_2O_3 -stabilized ZrO_2 (YSZ) [37]. The EB-PVD top coat consists of a thin region adjacent to the bond coat of

polycrystalline YSZ with equiaxed grains followed by columnar grains [18, 21, 25, 27]. The columnar grains are separated by channels normal to the ceramic/metal interface [21]. In addition to the micron-sized inter-columnar channels, the YSZ grains contain nanometre-scale intra-columnar pores which are revealed by transmission electron microscopy (see Figure 1) [17, 25, 35, 38].

3. Heat transfer in zirconia based ceramics

A schematic representation is shown in Figure 1 of the mechanisms by which heat transfer can occur in porous materials. Characteristics of conduction in solids, with electrons and/or phonons (lattice vibrations) as carriers, and of radiative transmission, are described in standard sources [5, 13, 26, 31]. Conduction in gases is also well characterized, with conductivity being dependent on the mean free path, λ , which in turn is a function of temperature and pressure (see Figure 2) [7,16].

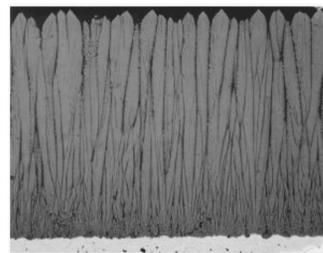


Fig. 1. SEM micrographs an EB-PVD TBC [23]

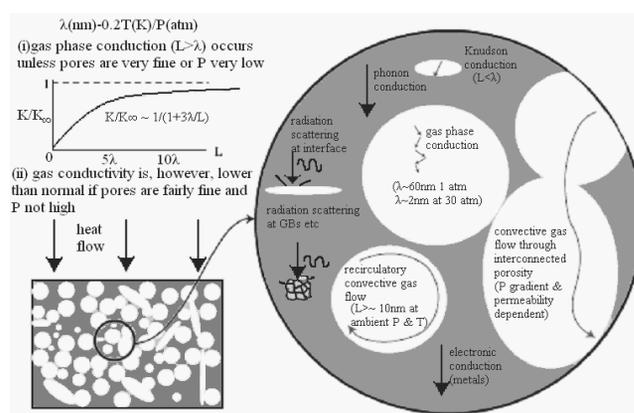


Fig. 2. Mechanism of heat transfer in porous materials [7]

The gas in the pores can also conduct heat. Because the pore thickness, L , is comparable to the mean free path of molecules in a typical gas at atmospheric pressure ($\lambda \sim 100\text{nm}$), convection can be neglected, and the thermal conductivity of the gas, k_{gas} , can be estimated using a simple analytical expression [17].

$$k_{gas} = \frac{k_{gas}^0}{1 + BT/(LP)} \quad (1)$$

where k_{gas}^0 is the normal conductivity of the gas at the temperature concerned, P is the pressure, T is the temperature (in degrees K), and B is a constant, with a value of 2.5 Pa m K⁻¹ for air [12].

At ambient temperature and pressure, λ has a value of about 60 nm, falling to 2 nm at 30 atm and rising to 0.4 μ m at 1727 °C. The gas conductivity within a pore is close to that in the free gas (e.g. $k_{air} \sim 0.025$ W m⁻¹ K⁻¹), provided the dimensions of the pore are much larger than the mean free path ($L > \sim 10\lambda$). However, it falls below the free gas value if the pore structure is finer than this and can approach that due solely to gas molecule-wall collisions (Knudsen conduction) if L is less than λ . This would require an exceptionally fine pore structure (unless the gas pressure is low and the temperature high), but even moderately fine structure ($L < \sim 1\mu$ m) can lead to conductivities significantly below that of the free gas [7].

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 [26]:

$$k_p = \frac{1}{3} \int C_v \rho \bar{v} l_p \quad (2)$$

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

As well as phonon conductivity, zirconia is susceptible to radiation conduction (photon transport) at high temperatures [18]. This contribution due to radiation can be written as [28]:

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

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

The total theoretical thermal conductivity of zirconia based systems is the sum of these two terms [23]:

$$k = k_p + k_r \quad (4)$$

4. Effect of microstructure to the thermal conductivity

As an application area, in this coating type in which the surface smoothness is very important, while providing the smoothness, an enforced strength structure can be obtained. As shown in the Figure 1, microstructure is composed of columnar channels and pores. The more these columnar channels and pores increase the lesser the thickness of coating is. Four different microstructures are shown in the Figure 3.

Both the inter-columnar channels and intra-columnar pores help reducing the conductivity of the EB-PVD YSZ coatings [25, 35, 30]. Since the pore distribution varies with thickness in the YSZ coating, the thermal conductivity may also vary with thickness [37]. The columnar pores lying in parallel to heat flux forms a little resistance to heat transfer. That does not create an important effect when compared with perpendicular pore to the heat transfer direction [2].

Related to microstructure, another important parameter which affects the thermal conductivity is yttria addition. The principal TBC material is zirconia (ZrO₂) partially stabilized with about 6 to 8 YSZ owing to its reasonable toughness (due to transformation toughening), low density, low thermal conductivity, high melting point, and good thermal shock resistance. Although YSZ has low thermal conductivity, yet further reductions in thermal conductivity are caused by porosity and thermal resistance at imperfect interfaces in the coating. However, there has been limited work [1,6,9,19,33] performed to generate an understanding of the coating aspects that influence the heat transfer characteristics. Additionally, the conductivity data reported in the literature exhibit significant variations due to differences in processing parameters and microstructural characteristics. Among the microstructural variables that are known to have an effect on thermal conductivity, only the effects of the type and the amount of stabilizer in ZrO₂ were studied in a systematic fashion [1, 9, 19]. Further, microstructural differences between bulk YSZ and the coatings often exacerbate the difficulty in the assessment of coating thermal conductivity.

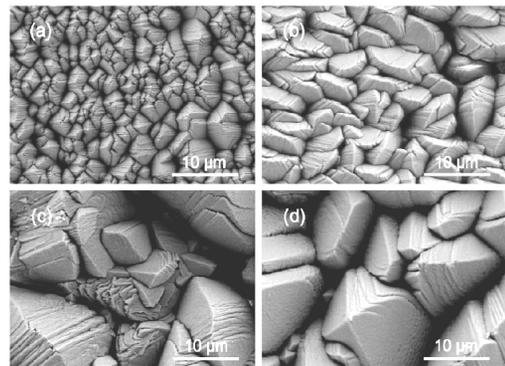


Fig. 3. SEM micrographs showing the surface of EB-PVD PYSZ coatings of different thickness: (a) 50 μ m, (b) 130 μ m, (c) 280 μ m, and (d) 350 μ m [29]

5. The methods to reduce the thermal conductivity values

Different methods were developed to reduce the thermal conductivity of EB-PVD coating. Earley [10] analyzed the variation in thermal conductivity with the thickness of the EB-PVD PYSZ coatings for the first time quantitatively. He thinned a TBC sample 50 μ m and measured a thermal conductivity of about 0.5 W/mK between 200 and 1000 °C. This conductivity value is extremely low, when compared to the PYSZ bulk material of

2.2 – 2.6 W/mK at RT. This result suggests that the structure of the EB-PVD coating near the interface to the metallic substrate has a markedly different thermal conductivity. To explain the effect of the coating thickness on the conductivity, Earley treated the EB-PVD PYSZ coating as a two-layer system composed of an outer layer with bulk conductivity (≈ 2.5 W/mK) and an inner 50 μm layer with a significantly lower conductivity (0.5 W/mK).

Nicholls et al. [24] developed a two-zone model. This model is based on the fact that ceramic coatings formed by the EB-PVD technique are characterized by a columnar microstructure with different grain densities and different slopes of the grain boundaries across thickness of the coating. Because of these structural differences an EB-PVD ceramic coating can be divided in two zones as the fine grained inner zone and the coarse columnar outer zone (Figure 4). The thermal conductivity of the finer grained inner zone (k_{iz}) is much lower than the thermal conductivity of the outer zone (k_{oz}). This effect is attributed to the higher grain boundary density as well as numerous oblique columnar boundaries in the inner zone.

Thus, the thermal conductivity is dominated by phonon scattering at defect/grain boundaries in this part of coating and this results in a lower conductivity of around 1.0 W/mK at room temperature. By increasing thickness, the structure is characterized by thicker columns predominantly aligned perpendicular to the plane of the substrate and by a decrease in the number of oblique columnar boundaries. The elongated intercolumnar pores are not effective in reducing heat transfer though the thickness of the coating.

This results in a higher thermal conductivity of the outer part of the coating which nearly approaches that of bulk zirconia at room temperature values of about 2.2 W/mK [29].

Modifying TBC microstructures should offer the best properties available for commercial EB-PVD coatings, namely, low thermal conductivity, high hemispherical reflectance, high strain tolerance, and good erosion resistance. By altering the macrostructure on the micron and submicron levels through periodically introducing strain fields (i.e., density changes by the incorporation of microporosity and surface restructuring), the thermal conductivity of TBC materials can be significantly reduced (Figure 5b). As previously discussed, layered periodicity in the coating will significantly reduce both the phonon scattering and photon transport resulting in lower thermal conductivity and higher hemispherical reflectance [36].

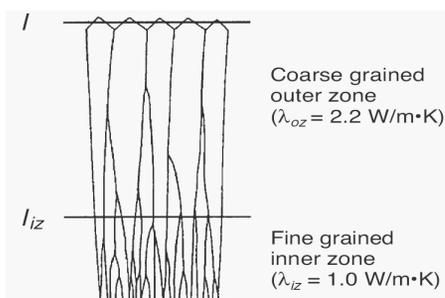


Fig. 4. Two-zone model for explaining the increase in thermal conductivity with coating thickness of EB-PVD PYSZ thermal barrier coatings [29]

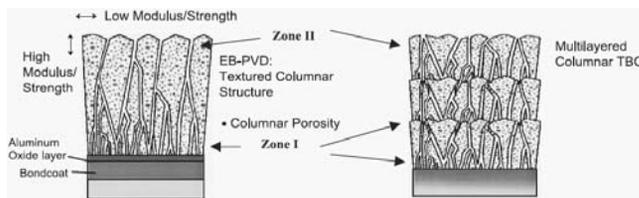


Fig. 5. Schematic diagram illustrating (a) typical standard vapour phase columnar microstructure and (b) modified columnar microstructure with multiple interfaces [36]

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 [23]. Thermal conductivity data for zirconia ceramics and coatings as a function of the yttria addition in the ceramic is shown in Figure 6.

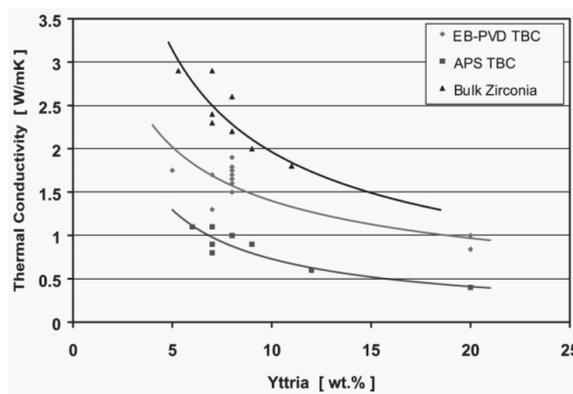


Fig. 6. Thermal conductivities of zirconia ceramic and zirconia thermal barrier coatings as a function of the yttria content [23]

Figure 6 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 6, 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 are operated 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 [23].

6. Conclusions

The following conclusions can be drawn from the brief review of thermal conductivity of EB-PVD coatings, and novel methods to reduce the thermal conductivity values are presented here.

When microstructure of the EB-PVD coating is investigated, it is found that they are formed in two different structure and microstructural characteristics and they are different from each other. Because in the first area where bond coat and coating are in contact, the porosity is high, the thermal conductivity of this area which is farther to bond coat and the second area closer to surface is lower. Using this property, a microstructure whose porosity is higher can be obtained with layered coating technique. Thanks to this structure, the effective thermal conductivity can be lowered dramatically. On the other hand, the yttria addition to the coating materials shortens the mean free path in zirconia. Thus, phonon dispersion increases and depending on this thermal conductivity decreases.

Among the investigated methods are restrictions in yttria addition (6-8 % Y_2O_3). However, there are no similar restrictions in layered structure, and there is no requirement for additional equipment and that, it is applicable easily and cheap, are the reasons why it is a current method which can lower the thermal conductivity

Additional information

The paper was published also in the Archives of Materials Science.

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