Thermal Barrier Coatings : the Thermal Conductivity challenge

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ABSTRACT. In this paper, the importance of the challenge associated with the control of the thermal conductivity of thermal barrier coatings for turbine engines hot stages is being reviewed (yttria stabilised zirconia mostly). It is firstly illustrated by the description of a practical aeronautic coated and uncoated turbine blade design exercise. The various contributions to TBC thermal conductivity are then reviewed. Their low conductivity finds its source not only in the nature of the ceramic layer (highly disordered material), but also in the morphology of the insulating layer, closely linked to its fabrication process parameters. The influence of various factors (such as yttria content, temperature, porosity content and distribution, etc.) on the thermal conductivity is examined, largely based on a literature review. In this field of investigation, the modelling tool should allow to predict, to a certain extent, which morphology would lead to the lowest values of thermal conductivity. Eventually attempts are made to identify research domains where further understanding is needed, and to formulate several suggestions concerning possible ways to lower the thermal conductivity.

1. INTRODUCTION

Yttria stabilised zirconia based thermal barrier coatings are viewed today as the new generation of protective coatings that will allow to take the next quantum step forward to increase turbine engine efficiency, without having to pay the price of replacing nickel-base superalloys by some other more refractory material [1]. They are also considered by diesel engine manufacturers to increase the efficiency of their engines. These coatings have been studied and developed for more than 20 years in the western countries and even longer in former USSR.

It can be said that one of the first concern of materials scientists in the TBC field was to optimise the coatings from a materials science standpoint. In the early days, important studies have been carried out to determine for instance which was the most adequate stabilising agent of zirconia for a given application, and in what amount [1-3]. As far as very high temperatures applications are concerned (mostly driven by the aero industry), there was a rapid and general move towards 6-8 wt. % yttria partially stabilised zirconia (Y-PSZ) because these coatings showed the highest degree of resistance to spallation in thermal fatigue solicitations [3] and an excellent thermal stability. Later, explanations of the phenomenon appeared through the identification of

the well-known t' phase [5] and its toughening mechanisms [6]. Important materials studies have also been devoted to finding an optimal metallic bond coating to support the ceramic topcoat [7,8]. The development of TBC has also been closely linked to that of the corresponding deposition processes: plasma spraying and electron beam physical vapour deposition (EBPVD). A number of studies [4, 9, 10] have thus been devoted to optimise the deposition process parameters to obtain favourable structures in order to achieve longer life cycles. The general idea there, was to try to relate coatings microstructure to their thermomechanical resistance.

This necessity to address in the very first place the feasibility and reliability problems for such coatings has somewhat hindered, until recently, the extent of research activities directly dealing with their thermal conductivity (K). The implicit notion there, was that by using stabilised zirconia as TBC would lead to a value of K for the coating not significantly different from one coating to the other, lower in any case than that of the dense material having the same composition. The scope of this paper is to emphasise the importance of the challenge associated with the control of coating thermal conductivity. It is first illustrated through a practical aeronautic turbine blade design. The various contributions to thermal barrier coating thermal conductivity are then reviewed. The low conductivity of thermal barriers comes on the one hand from the nature of the yttria stabilised zirconia ceramic layer, a highly disordered material indeed, and on the other, from the morphology of this layer, closely linked to coating processes: pores, cracks, etc. The influence of various factors (such as yttria content, temperature, porosity distribution, etc.) on the thermal conductivity is examined, largely based upon a literature review. In this field of investigation, the modelling tool should allow to predict, to a certain extent, which type of morphology would lead to the lowest values of conductivity. Eventually, attempts are made to identify research domains where further understanding is needed and to formulate several suggestions concerning possible ways to lower the thermal conductivity.

2. A REAL CASE DESIGN STUDY

In this case we consider a high pressure turbine vane airfoil of an aero-engine. The component is meshed for 2D finite element calculation ; for one airfoil, about 350 elements and 1200 nodes are being generated. The thermal barrier coating is represented as a single element in the foil thickness.

A mission profile is defined for the component, as the variation with time of relevant engine parameters such as altitude and thrust. Aerothermal Navier-Stokes codes are used to calculate thermal exchanges in the internal cooling passages ; thermal exchanges with hot gases are also computed, taking into account film cooling (cold gas from the cooling circuit reemitted in flow path). The result of these computations is an array of boundary conditions at the external and internal walls of the airfoil : hot and cold gas temperatures within the boundary layer, values of the wall exchange coefficients. The next step of the calculation consists in solving the Fourier equation across the airfoil walls using the above given limit conditions. The calculation ends up with a mesh of computed temperatures for each node, for every point of the mission profile : T = f(node #, t).
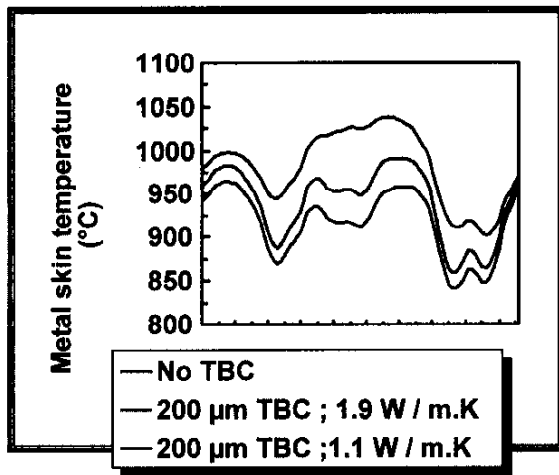

Figure 1 : *Metal skin temperature distribution experienced by a vane during typical flight mission (leading edge profile).*

In order to visualise the effect of thermal barrier conductivity, such calculations have been made for an airfoil without thermal barrier and with a coating of thickness 200µm. In the latter case two values of the thermal conductivity of the ceramic have been taken into consideration : 1.1 and 1.9 W/m.K, typical of existing plasma sprayed and EBPVD coatings respectively.

Examination of the leading edge metal temperature profile (figure 1) shows that the application of a TBC (1.9W/m.K) reduces the maximum temperature (1090°C) of the metal by 50°C. Decreasing the thermal conductivity down to 1.1 W/m.K permits to gain a further 32°C. Considering the whole leading edge profile, the maximum gain even reaches 113°C.
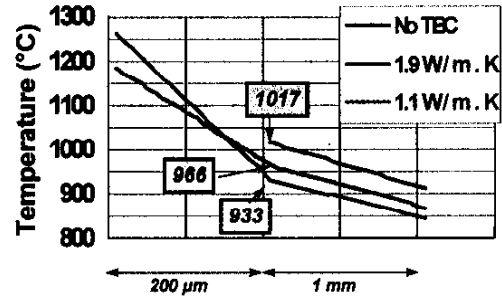

Figure 2 : *Temperature profile across the vane wall (leading edge).*

The temperature distribution across the airfoil leading edge is represented on figure 2. At the point considered, the metal temperature decreases from 1017°C for an uncoated airfoil down to 966°C with a TBC having a thermal conductivity of 1.9 W/m.K and 933°C with a low thermal conductivity coating. It is interesting to note that the ceramic coating external surface temperature increases correlatively (from 1190°C to 1260°C), this being explained in part by the fact that the heat flux is kept constant. Excessive temperatures may provoke an evolution of the ceramic microstructure : transformation t' ---> c + transformable t, sintering of the external layer associated with an increase of the thermal conductivity.

In terms of component life duration (taking into account creep and fatigue phenomena), and considering the leading edge, the application of a TBC with K = 1.1 W/m.K permits to gain more than an order of magnitude on the number of cycles. For less stressed regions (pressure side, trailing edge), the benefit is of course less.
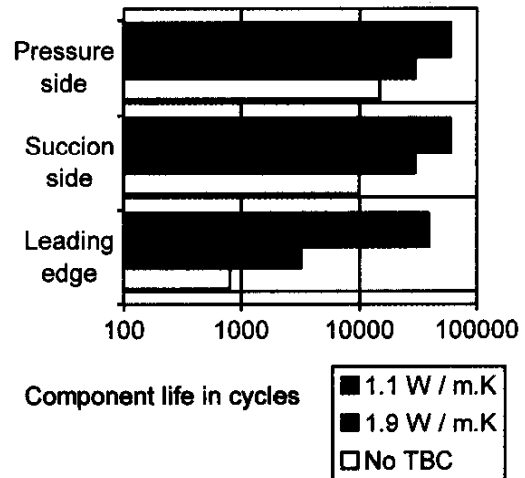

Figure 3 : *Component life duration (creep and fatigue)*
If we consider now that the engine is run so that the components keep the same life duration, but the gain is concentrated entirely on reducing the cooling rate and by way of consequence decreasing the fuel

consumption, table 1 shows that up to 0.7% specific consumption can be saved in the cases envisaged.

Thermal conductivity (W/m.K)	Cooling rate	Specific consumption
1.9	- 15%	- 0.4%
1.1	- 25%	- 0.7%

Table 1 : *Reduction in cooling rate and specific consumption owing to the application of a TBC of thermal conductivity K on a vane airfoil (for a given lifetime).*

These few results clearly demonstrate the importance of lowering the thermal conductivity in terms of economy and performance. Moreover, a decrease in the thermal conductivity permits to lower the thickness of the coating. Given the fact that a TBC represents an added stress on a rotating blade of 10% (for a 125 μm thick ceramic layer), lowering its thickness (provided the density is kept constant) will result in a significant gain on the stress applied on the rotating parts, blades and disks.

Of course, a rigorous computation would have to take into account the radiation contribution to the conductivity within the coating. This is an effect which depends on the actual environment seen by the airfoils within the turbine stage [11] and difficult to assess at present as the optical properties of zirconia-based plasma-sprayed and EBPVD coatings are poorly known.

3. THERMAL CONDUCTIVITY OF ZIRCONIA-BASED COATINGS

Although the thermal conductivity of thermal barrier coatings has not been a major research and development topic compared to work on thermomechanical behaviour for instance, a number of characterisations have been published, in particular to provide designers with data for lifetime prediction models. Looking through some of the data available and reported in table 2, several points are worth noticing :

- Thermal conductivity values for zirconia based coatings are relatively low (within the range 0.5 to 2 W/m.K). This is significantly lower than values determined on bulk zirconia [18, 19], typically in the 2 to 4 W/m.K range, depending on the composition and crystallographic structure. These values lie in the lower range of thermal conductivity for oxides.

- Thermal conductivities of EBPVD coatings are significantly higher than values measured for plasma sprayed coatings having the same composition. This can be explained by the structure of the coatings. Plasma sprayed coatings exhibit a microcrack network, with basically two crack populations : one oriented perpendicular to the coating surface and originating from cracking of individual splats during

cooling, as a result of the limited elastoplastic deformation capability of the ceramic. The other is mainly oriented parallel to the surface and corresponds to poor contacts between different splats. The latter, being perpendicular to the heat flux are particularly effective in reducing the thermal conductivity of the coating. In addition, a dispersed, spheroidal porosity contributes to lowering the conductivity.

In the case of EBPVD coatings, the reduction in thermal conductivity comes mainly from the intracolumnar fine porosity, the intercolumnar porosity being much less effective as it is arranged perpendicular to the surface. Schematically, the columnar coating can be considered, in an electrical analogy, more as a set of parallel resistances than a series set which gives a closer image of the (microcracked) sprayed coating.

System	Thermal conductivity		Comment Reference
	300K	1300 K	
ZrO₂-7%Y₂O₃ EBPVD	1.7	2	[4]
ZrO₂-7%Y₂O₃ APS	0.9		[12]
ZrO₂-7-9%Y₂O₃ APS	0.9 to 1.1		[13] Various porosity levels
ZrO₂-20%Y₂O₃ APS	0.4	0.55	As sprayed, 7% porosity [14]
ZrO₂-20%Y₂O₃ APS	1.5	1.7	100h, 1480°C, 7% porosity [14]
ZrO₂-6%Y₂O₃ APS	1.1		[15]
ZrO₂-8%Y₂O₃ APS	1.		[15]
ZrO₂-12%Y₂O₃ APS	0.6		[15]
ZrO₂-7%Y₂O₃ EBPVD	1.3	1.3	[16]
ZrO₂-7%Y₂O₃ APS	0.8	0.8	[16]
ZrO₂-7%Y₂O₃ APS	0.8	0.8	[16]
ZrO₂-8%Y₂O₃ EBPVD as coated	1.5	1.3	[17]
ZrO₂-8%Y₂O₃ EBPVD	1.9	1.5	[17]
ZrO₂-7%Y₂O₃ bulk	2.9	2.7	[16]

Table 2 : *Typical values of the thermal conductivity of zirconia-based coatings (EBPVD : electron beam physical vapour deposition, APS : air plasma spray) Composition percentages in wt%.*

System	ZrO$_2$-Y$_2$O$_3$	ZrO$_2$-MgO
Phase	K, W/m.K	K, W/m.K
Cubic	2.3	1.8
Tetragonal	3.5	4.8
Monoclinic	4.2	5.2

Table 3 : *Thermal conductivity for zirconia polymorphs calculated from experimental data on partially or fully stabilised zirconia bulk materials [18]. The different phases correspond to various stabiliser contents.*

- Thermal conductivity of EBPVD coatings remains approximately constant as a function of temperature up to about 1100°C, as illustrated in figure 4. This is in contradiction with a T^{-1} dependence predicted by the theory (cf. below) for ceramic materials. At higher temperature, though, an evolution of the structure involving sintering or phase transformation may result in an increase of the thermal conductivity. The same trend is observed for plasma sprayed coatings, in general with a transition at lower temperature.
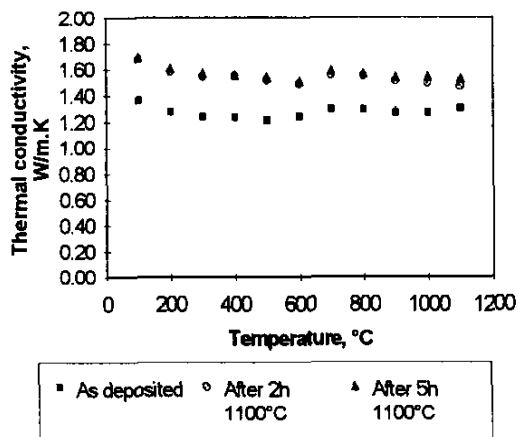

Figure 4 : *Thermal conductivity, as a function of temperature, of an EBPVD ZrO$_2$-7%Y$_2$O$_3$ thermal barrier coating in as-deposited and heat treated conditions [17].*

Given the fact that zirconia is translucent in the infrared, a radiation contribution to the thermal conductivity measured (which is actually an effective thermal conductivity) would result in a rise at high temperature. Such an effect has been reported by Youngblood et al. [19] in the case of single crystal ZrO$_2$-20wt.%Y$_2$O$_3$ (the thermal diffusivity increases rapidly as a function of T above 600°C). However, in the case of polycrystals, the same authors observe an opposite trend and it is likely that in the case of coatings (for which the dependence in temperature is much less important than the T^3 predicted by theory), as well as in the polycrystals mentioned, the numerous interfaces present (gas/solid interfaces, grain boundaries) scatter the penetrating photons and thereby lower this radiation contribution to the heat flow. Yet, a thorough study would certainly be of

interest to correctly evaluate this effect with coatings, especially at very high temperature.

- A heat treatment affect the thermal conductivity of the coatings (increase). After a heat treatment, the thermal conductivity of TBCs increases, both for EBPVD [14] and plasma sprayed coatings [14, 20]. This effect is attributed to the evolution, through a sintering effect, of the porosity (cracks included) during heat treatment. For example, in plasma sprayed coatings, the poor contacts between lamellas in the as-sprayed coatings, with possible nanocrystalline (amorphous) zones corresponding to rapidly solidified regions, are likely to evolve towards equilibrium structures, assisted by atom diffusion processes at high temperature. One consequence is that thermal conductivity should be determined after a heat treatment conducting to a structure corresponding to the one that will be in service if representative values are to be used, in particular for the coated blade design. Another consequence, is that as surface temperatures are likely to increase (see preceding part) as a result of lowering the thermal conductivity, this effect has to be taken into account if the benefit of a low K thermal conductivity is to be retained in service.

- Values reported cover a surprisingly wide range and it is important to keep in mind that they may be difficult to compare, even for coatings having the same nominal composition and porosity, as experimental set ups can be different, as well as interpretation procedures from diffusivity determinations. Scattering inherent to the fact that thermal conductivity is indirectly measured (via thermal diffusivity, density, specific heat) and that diffusivity itself is a somewhat difficult property to determine. Even with high thermal conductivity material such as tungsten, data reported in the literature are spectacularly scattered, as illustrated by Taylor [21]. Moreover, thermal conductivity values most often are derived from thermal diffusivity measurements (laser flash in general) and this implies that the porosity is accurately known. It would be interesting for several laboratories to gather their efforts and, on identical specimens conduct a Round Robin test on TBCs, and compare with absolute, but more lengthy and costly methods.

4. LOWERING THERMAL CONDUCTIVITY

4.1. Intrinsic conductivity and chemistry:

It has been noticed in the preceding part that zirconia is already a low thermal conductivity material. One can wonder whether other materials would not present a lower thermal conductivity and could be envisaged as TBC. In fact, experimental thermal conductivity of pure zirconia, i.e. with no stabiliser, does not seem to have been reported. This is most certainly due to the difficulty of obtaining bulky specimens of pure zirconia, zirconia presenting three allotropic forms : monoclinic up to 1170°C, tetragonal in the range 1170°C- 2370°C and cubic up to the melting point

(2680°C), and the tetragonal to monoclinic transformation being accompanied by a large volume variation. The only available data seem to have been derived by Hasselman et al. [18] from experimental determination on various bulk zirconia-based system, knowing the relative proportion of the different crystallographic forms and assuming that the thermal conductivity of a mixture can be expressed simply as a function of the individual thermal conductivity. As reported in table 3, the monoclinic form would present a conductivity in the range 4 to 5 W/m.K.

Another approach, based on purely theoretical considerations, has been proposed by Klemens [22] for calculating an « intrinsic thermal conductivity » of cubic zirconia, supposed to contain no stabiliser (and therefore no associated vacancies). In a most general way, the thermal conductivity K can be expressed as :

$$K = (1/3) \int C'(\omega) \cdot v \cdot l(\omega) \, d\omega$$

where $C'(\omega) \, d\omega$ is the contribution of the specific heat in the frequency range ω, $\omega+d\omega$, v is the transverse phonon velocity and $l(\omega)$ is the phonon mean free path.

In the high temperature limit and in the case of no defect present, the mean free path of phonons is limited by three phonon interactions, owing to the cubic anharmonicities of the lattice forces, and this expression leads to the following expression of the intrinsic thermal conductivity [23] :

$$K = (3/2)\gamma^{-2} \cdot (\mu \, v^2/\omega_D)T^{-1} \cdot N^{-2/3}$$

where γ is the Grüneisen constant, μ is the shear modulus, v is the transverse sound velocity, ω_D the Debye frequency, T the temperature and N the number of atoms per primitive unit cell. Recently, Klemens [22] applied such an approach to zirconia and derived for the intrinsic thermal conductivity of zirconia (i.e. that of an hypothetical « pure cubic zirconia ») :

$$K \, (W/m.K) = 1700 \, / \, T(K)$$

According to this expression, the intrinsic thermal conductivity of zirconia :
- would amount to 5.7 W/m.K at room temperature, a value surprisingly close to the values derived by [18] for pure monoclinic zirconia,
- decreases with a classical T^{-1} variation, classical for non-metallic materials [24], down to 1.3 W/m.K at 1300K. This last value appears excessively low, considering that dense PSZ polycrystals have a thermal conductivity higher than 2 W/m.K [18] and this represents a strict lower limit of pure zirconia.

Even if absolute values cannot be derived from such simplified theoretical approaches, it is possible to infer trends concerning the effect of different parameters on the thermal conductivity. This is actually easier starting from an expression proposed by Slack [25] for non-metallic crystals and for temperatures higher than the Debye temperature θ_D and derived form the same principles as the one followed by [22] :

$$K = B \cdot <M> \cdot \delta \cdot \theta_D^3 / T \cdot N^{2/3} \cdot \gamma^2$$

where B is a constant, <M> is the average atomic mass in the crystal, δ^3 is the average volume occupied by an atom and γ is the Grüneisen's constant ($\gamma = \alpha/C_v.\chi$ with α the thermal expansion coefficient, χ the compressibility and C_v the specific heat). Bearing in mind that θ_D is inversely proportional to $<M>^{1/2}$, it is clear that low conductivity crystals correspond to :

- high atomic mass and weak interatomic bonding (low θ_D, which is a dominant term),
- complex crystal structure (large N),
- high anharmonicity (large γ).

According to these considerations, other ceramic materials could then be envisaged as a basis for thermal barrier coatings, keeping in mind that other criterias have to be fulfilled (thermal expansion coefficient, thermal stability, etc.). Among the parameters which can have a large influence on K, <M> is certainly a privileged one, and to a lesser extent N. The Grüneisen's constant (γ) does not vary much from one material to another. An interesting candidate, for example, is CeO_2 (the atomic mass of CeO_2 is 40% higher than that of zirconia) a material which has been tested recently by Schulz et al. [26] and Maloney et al.[27]. However, if EBPVD CeO_2-9wt.%Y_2O_3 coatings present a low thermal conductivity (around half that of standard EBPVD ZrO_2-8wt.%Y_2O_3 coating [27]), they seem to exhibit a poor erosion resistance, a shortcoming which might be alleviated though, if a multilayer architecture is adopted, with a more erosion resistant external layer added on top of the coating.

As far as compositions for the basis are concerned, other ways are explored. Observing that only the thermal conductivity at high temperature is relevant, and that for most ceramics, the thermal conductivity is a decreasing function of temperature (in principle T^{-1} law above), Padture and Klemens [28] are considering ceramic materials with complex lattice cells. An additional idea in this case is to try to develop an oxygen-impermeable dense ceramic layer to avoid or to minimise the oxidation of the bondcoat with formation of a thermally grown alumina at the ceramic/bondcoat interface (locus of the final failure in the most advanced systems). It is far from certain however, that such a ceramic material can be deposited as a reliable and dense coating and stay there in service (thermomechanical cycles). Moreover, the garnet compositions these authors propose still have a relatively high thermal conductivity, even at 1000°C (typically above 2.5 W/m.K).

In conclusion, possibilities exist to change the chemistry of the basis material to decrease thermal conductivity. A balance has, of course, to be carefully evaluated between the expected gains and the consequences on other properties (density, thermal stability, thermomechanical resistance, erosion resistance, etc.) to evaluate the final interest of these potential new candidates.

4.2. Defects :

An efficient way to decrease the thermal conductivity of an insulator is to introduce structural defects which constitute obstacles to the propagation of phonons. Several types of defect may be envisaged : vacancies, substitution ions, dislocations, interfaces (grain boundaries), etc.

The role of vacancies is particularly important in this respect for zirconia-based materials. In fact, as pure zirconia cannot be of practical use, due to its undesirable transformation at around 1100°C, it is stabilised (partially or completely) by adding heteroelements (most often Y, Mg, Ca) which stabilise the cubic (or the tetragonal phase). Thus the addition of 20wt% Y_2O_3 fully stabilises the cubic form. Addition of 6 to 8wt. % Y_2O_3 permits to obtain the so-called metastable t' phase (nontransformable up to around 1200°C). The incorporation of heteroelements is accompanied by the introduction of vacancies to maintain the electrical neutrality of the ionic lattice. Thus, introducing two yttrium ions is accompanied by the introduction of one vacancy according to the following reaction, using the nomenclature by Kröger and Vink :

$$Y_2O_3 \rightarrow 2\ Y_{zr}' + V_O^{\infty} + 3\ O_o^x$$
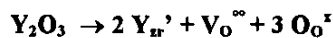
where Y_{zr}' is an yttrium ion on a zirconium site (single negative charge), V_O^{∞} is an oxygen vacancy twice positively charged and O_o^x is an oxygen ion on an oxygen site (no charge).

Effectively, incorporating heteroelements such as Ca, Mg or Y in zirconia lowers its thermal conductivity and a comparison of diffusivity measurements on zirconias with different stabilisers indicates that similar defect populations result in comparable thermal diffusivity [19]. It is to be noted though that this effect is observed only for stabiliser contents less than a critical value [29]. For high vacancy contents, they cannot be considered as independent defects and ordering may appear (as demonstrated by [30] in the case of cubic zirconia stabilised with yttria and magnesia). It is therefore likely that phonons interact less strongly with a population of ordered vacancies than with a population of randomly distributed defects.

Another source of efficient point defects acting as phonon scatter centres is substitution ions. This acts essentially through two factors : $\Delta M/<M>$, the ratio of the mass difference between solute and solvent to the

average atomic mass, and relative difference in ionic size between solute and solvent. Diverse expressions have been proposed to describe their influence on the thermal conductivity [see for example 31, 32] and a critical study would be necessary to clarify the case of zirconia-based materials.

In the case of ZrO_2-Y_2O_3, the replacement of zirconium ions (M = 91.22, r = 0.080 nm) by yttrium ions (M = 88.90, r = 0.093 nm) should have a minor effect, their atomic mass in particular being relatively close. However, a significant effect may be expected from other substituents, in particular heavy rare earth elements (at the expense though of the density, an important drawback for mobile components). Very few elements lighter than zirconium would satisfy these criteria, with the exception though of (expensive) scandium. As far as divalent ions are concerned, the choice is much more limited. Calcium or magnesium cannot be envisaged in high temperature applications due to structural stability problems.

Grain boundaries and interfaces can also scatter phonons and reduce the thermal conductivity. These processes are most effective at low temperature for ceramics in general [33], and only slightly at high temperature. It is to be noted that in TBCs, the grain size is much larger (typically 0.1 to 1 µm) than the mean free path calculated according to :

$$K \sim (1/3)\ C\ .\ v\ .\ 1 \sim 0.5\ nm$$

and it is doubtful that, in these conditions, conventional grain boundaries may have a significant effect.

As a conclusion, it can be said that the most efficient ways to decrease the thermal conductivity are to introduce point defects :
- vacancies associated with stabilising dopants. In zirconia-based coatings, up to 12 mol.% $RO_{1.5}$ for a trivalent dopant R, corresponding to the stabilised cubic form, seem possible. However a fully stabilised plasma sprayed material may not present a satisfactory thermomechanical behaviour.
- for a maximum effect, the dopant should have a very different atomic mass than zirconium, provided that elastic factor does not counterbalance the mass one.

Finally, one could wonder what the minimal thermal conductivity would be with completely disordered materials, in other words what the minimal thermal conductivity for a refractory material could be. Two attempts have been proposed to calculate this minimal thermal conductivity.

Slack [25] derives the theoretical minimum conductivity assuming that the minimum mean free path for a phonon cannot be less than one phonon wavelength. For pure zirconia, the value calculated is 2.1 W/m.K. In a more recent approach, based on an adaptation of the Einstein model for highly disordered

materials, Cahill et al. [34], calculate a minimum thermal conductivity of 1.3 for dense zirconia-yttria systems. These values show that a gain may be obtained by increasing the atomic disorder, but this gain will remain limited if the base material (in occurrence zirconia) remains the same.

4.3. Optimising coating architecture :

a. Pores, crack network.

The fact that the thermal conductivity of EBPVD, and in particular plasma sprayed coatings is much lower than for bulk materials of the same composition is explained by the presence of pores and microcracks originating from the coating deposition process, as described above. It is important to remark that up to now, only few studies have been devoted to optimise the porosity distribution and crack network with respect to thermal conductivity. In fact, most of the effort in this field has been devoted instead to the influence of these features on the thermomechanical resistance of the systems, with mainly empirical approaches.

As a first step, it is necessary to understand and describe the relationship between thermal conductivity and morphological features (pores, cracks,..). McPherson [35] was probably the first to propose a model for the microstructure of plasma sprayed coatings involving regions of good and poor contact between lamellae to explain the low thermal conductivity of coatings with respect to bulk materials. The regions of poor contact act as thermal resistances. Considering an electrical analogy, and assuming a very schematic geometry for the coating, the ratio of thermal conductivity of the coating (K_c) to that of solid material (K_0) can be expressed as :

$$K_c/K_0 = 2 \cdot f \cdot \delta / \pi \cdot a$$

where f is the fraction of « true contact », δ is the lamellae thickness and a is the radius of the individual contact areas. With a value of 0.2 for f and assimilating a with δ/2, this relation gives K_c/K_0 approximately 1/4, a right order of magnitude. It is to be noted however that the predictive capacity of such an approach is extremely limited due to the simplicity of the geometry assumed and the experimental difficulty to determine the parameters involved. This approach has been employed by Moreau et al. [36] to describe the thermal diffusivity of plasma-sprayed tungsten based coatings, the geometrical quantities being determined from image analysis.

As described in Dorvaux et al. [37], the most promising approach for developing a tool to describe the thermal conductivity in relation with microstructure seems to be via a finite difference calculation carried out on digitised images of real coatings. This type of approach presents the advantage of taking into account the complexity of the geometry involved (interconnected porosity for

example) while keeping the computations tractable on microcomputers.

This type of approach should offer guidelines for designers and coaters, provided the relationship between process parameters and coating morphology is known.

b. Thin films.

It has been reported by several authors [38-42] that ceramic thin films may exhibit a lower thermal conductivity than the corresponding bulk materials. Some examples are reported in table 4.

Material	Thermal conductivity of thin films (W/m.K)	Thermal conductivity of bulk material (W/m.K)	Ref.
PECVD SiO_2	0.05 (100 nm) 0.4 (1.4 µm)		[38]
Glassy SiO_2	0.12	1.3 (amorphous)	[39]
TiO_2	1.5-5 (depending on deposition method)	7	[40]
TiO_2	0.6 (evaporated) 0.5 (sputtered)	5.5 - 7.6 (rutile)	[41]
ZrO_2(evaporated, annealed 1h, 730°C)	0.8	2-5	[42]
AlN	16	70-220 (polycrystalline)	[42]

Table 4 : *Examples of thermal conductivity of thin films compared with bulk values.*

Although this effect is clear, the values reported have to be taken with care as measurements of thermal conductivity of submicronic films are very delicate and the error margins reported may be important.

Different explanations have been proposed for this effect. Most likely, this effect is due to a combination of grain-boundary scattering (the grains are particularly small) and of atomic disorder during growth of thin films. Non equilibrium structures may be obtained by PVD or PECVD, in particular for relatively low substrate temperatures (the diffusion of species on the surface of the growing coating, and bulk diffusion within the coating being too slow to reach an equilibrium state). In this respect, it is to be noted that the diffusion of cations within zirconia is quite slow. With the diffusion data ($D = D_0 \cdot \exp$-Q/RT with $D_0 = 0.031$ cm^2/s and Q = 391 kJ/mol) published by [43], one can estimate that it takes about 8 years for a cation to travel 1 µm at 1100°C by solid state diffusion .

To fully exploit this thin film effect, one could imagine thermal barrier coatings constituted of multiple nanolayers of different materials, such as zirconia and alumina as in [44], with the added advantage of incorporating boundary thermal resistances. The materials of each layer and the process parameters should have to be selected so that prolonged exposure at service temperature would not result in structural transformations towards equilibrium structures

(crystallisation of amorphous material for example), activated by solid state diffusion and accompanied by an undesirable increase in thermal conductivity. In this respect, it is interesting to note that, as reported by Lee et al. [40], annealing a HfO_2 thin film at 900°C enhances its thermal conductivity by only 20%. It is to be noted also that the fabrication of such coatings would certainly require serious modifications of techniques employed at present in production, or adapting new techniques to this application (sputtering with multiple targets for instance).

4.4. Concluding remarks

Several possibilities exist, in principle to lower the thermal conductivity of TBCs : incorporation of point defects (vacancies, substitution cations), optimising the microcrack network and, to a lesser extent, porosity distribution, and introducing structural disorder via the deposition process. It must be kept in mind though that, as exposed in the introduction, TBCs must fulfil a set of requirements, and thermal conductivity is only one of them. In particular, it would be highly questionable to develop TBCs that could not be deposited with processes such as plasma spraying or EBPVD (or alternative processes currently under development). And the design of low thermal conductivity coatings must take into account the requirements associated with the processes. For instance, depositing materials having complex compositions, in particular with elements having widely differing vapour pressures, may prove to be too difficult to control in production with EBPVD processes ; similarly, a stack of numerous very thin layers presenting a highly disordered structure may be possible to fabricate by a PVD (or a CVD) process, but not by plasma spraying. Additional work is needed however to study the thermal (meta)stability of these defective structures.

5. CONCLUSION

Lowering the thermal conductivity of the ceramic coating of a TBC applied on airfoils in the hot stages of a turbine represents an important challenge for designing improved performance systems. This paper has modestly indicated and listed a few paths to tackle this topic, some of which have already been explored :

■ changing the chemistry of the ceramic material in order to incorporate point defects (vacancies, substitution cations) by playing both on the base element (zirconia at the moment) and on the stabiliser, the main difficulty being to obtain sufficiently stable phase structures and staying within composition ranges such that the disorder is maximum as far as phonon scattering is concerned.

■ optimising the coating morphological features (porosity, crack network) so that the heat transfer perpendicular to the external surface is minimised. This requires the development of modelling tools such as in the approach described in [36] and a good knowledge of the relationship between processes parameters and coating structures.

■ designing new coating architectures (nanolayers).

It is felt that, up to now, several points have received little attention and would be worth exploring in more details :

■ characterising the optical properties of the real coatings, in order to evaluate the possible influence of radiation to the heat transfer through the ceramic coating, and develop ways to decrease this contribution.

■ assessing the thermal stability of the new systems ; with TBCs having low thermal conductivity, the surface temperatures of the ceramic coating are likely to rise, compared to the temperatures reached with present systems, and provoke a microstructural evolution of the outmost region of this ceramic layer, through sintering, or phase transformations, which in turn will increase the thermal conductivity.

Finally, it is important to insist on the fact that designing TBCs for engine airfoils requires a multidisciplinary approach taking into account various aspects : materials (ceramic behaviour, oxidation of bondcoat, thermal conductivity, etc.), processes (ceramic morphology), life prediction modelling, blade design, quality control, commercial (patents),.. Thermal conductivity is only one aspect of the design and changing the ceramic composition to lower the intrinsic conductivity, for example, is likely to have important repercussions on the other properties. The design of the final coating may have to fully exploit the flexibility and capabilities offered by present coating processes, by developing multilayer coatings, each layer (corresponding to a temperature range and a particular environment in service) having a specific function .

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