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OPPORTUNITIES FOR MINIMIZING RADIATIVE HEAT TRANSFER IN FUTURE THERMAL AND ENVIRONMENTAL BARRIER COATINGS

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ABSTRACT

The possibility of identifying new classes of oxides having lower thermal conductivity at high temperatures is unlikely as the values are approaching the theoretical minimum. At the same time, the drive for higher engine efficiency requires higher gas temperatures, increasing the radiative heat flux. The significance of radiative heat transfer in the selection of coating materials is examined. It is concluded that optically opaque materials will perform better as coatings under high convective flow conditions, such as on blades, by minimizing radiative heating through the coating. This can be achieved by a combination of atomic level doping and scattering.

One of the great successes of advanced structural materials has been the continuing development of ever more efficient and powerful high-temperature gas turbines. In large part this has been achieved by increasing the gas temperature and implementing more effective blade cooling design approaches [1, 2]. Indeed, for some years now, the temperature of the combusted gas entering the high-pressure turbine (the T4 temperature) has exceeded the use temperature of the blade metal and, by some accounts, its melting temperature. To keep the temperature of the outer surface of the blades below some maximum temperature, for instance below which degradation mechanisms, such as oxidation or, alternatively, creep are unacceptably large, the turbine blades have been internally cooled using air from the engine by-pass [1, 2]. Consequently, while the outer surface is exposed to thermal radiation and convection from the high-temperature gas that flows over the blade surface, heat is removed from the inside of the blade by convection to a cooling gas. Figure 1. In addition to satisfying the overall aerodynamic constraints, the engine designer is constrained to ensure that the metal surface does not exceed a maximum allowable, material imposed temperature, and also to minimize the heat extracted from the hot working gas by the internal gas cooling. The advent of thermal barrier coatings, now widely used on the first row of blades and vanes of the high performance, high-pressure turbines, has enabled the gas temperature to be increased by providing an additional thermal resistance while not lifting the metal surface temperature limitation. In essence, the use of thermal barrier coatings has provided an additional degree of freedom to the designer to accommodate increases in gas temperature, principally by altering the cooling gas flow and the TBC surface temperature.

In principle, higher gas temperatures can be accommodated by increasing the thermal resistance of coatings, for instance selecting a material that has lower thermal conductivity than 8 m/o yttria-stabilized zirconia (8YSZ), the current material of choice [3, 4], and/or increasing its thickness. Increasing thickness is possible but increases the centrifugal forces on the rotary components. Also, the thicker the coating, the greater the propensity for failure under oxidative thermal cycling [5]. In the last decade several oxides have been identified [6, 7] having lower thermal conductivity than 8YSZ but the values are approaching the so-called minimum thermal conductivity [8, 9] values meaning that there is little prospect for identifying oxides with lower thermal conductivity than this theoretical value.

In this work we illustrate the effect of various materials design parameters on the heat transfer by a combination of conduction and radiation through a coated metallic blade for a range of hot gas temperatures and internal metal cooling conditions. Calculation of the heat fluxes and temperatures is highly complex and so they are computed using the Siegel-Spuckler two-flux model [10] [11] [12] for heat transfer based on solving, in one-dimension, the heat flow equations for a coated metal exposed to a gas at temperature, T_{gas}, on one side with internal cooling on the other side. The model uses, as input materials properties, optical and thermal conduction properties, convection coefficients as well as coating and metal thicknesses. In the past, the model has been used to compute the temperatures through the thickness of electron beam deposited and plasma-sprayed TBCs under a variety of representative engine operating conditions [10]. In this work it is used to illustrate the effect of various parameters, including the hot gas temperature, on the heat flux through coatings. The total heat flux, q_{total}, through a coating can be written [10, 12] as the sum of the conductive, q_c, and radiative, q_r, fluxes:

$$q_{total} = q_c + q_r = -k_c \frac{dT(x)}{dx} + \int_{\nu_1}^{\nu_2} q_{r\nu}(x) d\nu$$

$$= -k_c \frac{dT(x)}{dx} - \frac{1}{3(a_\nu + \sigma_{s\nu})} \int_{\nu_1}^{\nu_2} \frac{dG_\nu(x)}{dx} d\nu \tag{1}$$

where k_c is the thermal conductivity of the oxide coating, the net spectral flux $q_{r\nu}(x)$ is integrated over the spectral range, ν, and the parameters a_ν and $\sigma_{s\nu}$ are the optical absorption and optical scattering coefficients. Equation 1 is based on the two-flux model of the radiative flux consisting of a forward, $q_{r\nu}^{+}$, and backward, $q_{r\nu}^{-}$, propagating, hemi-spherically isotropic fluxes, $q_{\nu r} = q_{\nu r}^{+} - q_{\nu r}^{-}$. The parameter G_ν is twice the two directional fluxes, $G_\nu = 2\left(q_{\nu r}^{+} + q_{\nu r}^{-}\right)$. (The development of the equations leading up to equation 1 is detailed in [12]. As a verification check, our computations successfully reproduced all the results shown in [10, 13]). The temperatures of the coating surface and the metal surface are not boundary conditions but have to be calculated from the overall thermal boundary conditions.

To place the results of the calculations for the heat fluxes and temperature distributions in perspective, they are compared with those for a 1 mm thick EB-PVD deposited TBC made from 8YSZ on a 0.79 mm metal blade with internal cooling by air at 800 ^{o}C. [Table S1. Supplementary Materials]. Unless otherwise stated, the thermal conductivity is taken to be 0.8 W/mK, the convective heat coefficient on the inner surface of the metal was taken to be 3,768 W/m^{2}K, a value used by Siegel and Spuckler [10], and an optical absorption coefficient of 100 m^{-1} up to a cut-off wavelength of 5 micron.

This viewpoint article is organized as follows. The thermal environment of a high-temperature turbine and the incident radiative heat fluxes are first described. Then, the fluxes through a coating by conduction alone and by a combination of conduction and radiation are calculated and presented. These results are then used for the discussion of the effect of materials parameters. It is emphasized that although this article is illustrated with examples of thermal barrier coatings, the same issues are of concern in the development of environmental barrier coatings for CMC's for use at higher temperatures than currently projected TBCs as well as other higher-temperature applications of refractory oxides.

THE TURBINE BLADE THERMAL ENVIRONMENT AND RADIATIVE HEAT FLUXES

Key to addressing materials design issues is determining how large the contribution of thermal radiation through a coating is, and how this affects the temperature at the metal surface as well as the total heat flux extracted by the cooling air. The radiative power of the combusted gas is, of course, dependent on the fourth power of its temperature, its spectral emittance and its density but that does not mean the heat flux through the coating also increases with the fourth power of the temperature.

In considering radiative heat transfer from a hot combusted gas it is useful to consider it in two stages. The first stage is the flux radiated by the hot gas. The second is estimating the flux incident on the surface of the coating which can, depending on the radiative properties of the coating and the convective heat coefficient, enter into the coating. The former is simply the incident radiative power given by the Stefan-Boltzmann equation taking into account its volumetric density. (This depends on the gas pressure and its composition). The flux incident on the coating surface depends on both the local geometry and the boundary conditions, thermal and radiative, at the outer surface of the coating. The geometrical factor is the view factor between the blade and the hot gas. The most exposed portions of the blades are in the vicinity of the leading edge since they have line-of-sight of the combusting gas. For ease of calculation, we assume that the local surface is normal to the radiation from the hot gas. Figure 1. The second stage is the radiative heat transfer into and through the coating. This depends on a variety of materials parameters as well as the conditions at the three coating interfaces, that between the gas and the coating, between the coating and the alloy and between the alloy and the internal cooling.

Away from the leading edge, heat flows into the coating by convection. As the gas flows over the blade surface the gas velocity and gas temperature decrease as its' kinetic and thermal energy are converted into motion of the blades driving the turbine. Although the gas temperature is lower than where it enters the high-pressure turbine, it still hot and radiates thermally. The surfaces of the blades also radiate to each other. The actual radiative flux from the hot gas flowing over the surfaces depends in detail on the density of the gas, the spacing between the adjacent surfaces and location along the blade. But the minimum temperature radiating surface is the coating surface temperature. As facing surfaces are at similar temperatures, the net radiative heat transfer will be relatively small compared to at the leading edge. So, in the following, we consider thermal transport at the leading edge as it represents the most exacting condition.

While the radiant thermal energy incident on the coating surface depends on the radiative environment, the proportion that can propagate into the coating depends on the refractive index, absorptance and emittance of the coating material, as will be described in the following section. These materials parameters are only weakly dependent on temperature. In contrast, the non-radiative thermal energy that can enter into the coating depends on convection which, depends on the convection coefficient, *h*, and the surface temperature, $q_c = h\left(T_{gas} - T_{surface}\right)$.

To illustrate the radiative and convective heat fluxes entering the surface of the TBC, they have been calculated for a gas temperature of 3000 K as a function of the convective heat coefficient, h_1, in Figure 2 (top). In the limit $h_1 \rightarrow 0$, no heat convects into the coating and the radiative flux accounts for the total heat flux. As the convective heat coefficient is increased, the convective flux into the coating increases and the radiative heat flux decreases. The calculations also show that the surface temperature increases with the convective heat coefficient into the range more typical of high velocity gas streams, such as around blades.

CONDUCTIVE HEAT TRANSFER THROUGH A COATING

The simplest scenario is a fully opaque coating meaning that no radiative heat transfers through it. All the thermal energy propagates by phonon conduction and consequently in steady state the temperature decreases linearly through the thickness of the coating. The actual temperatures depend on the thermal resistance provided by the coating, the surface temperature and the internal cooling of the metal side. Figure 2 (bottom). Decreasing the value of the thermal conductivity significantly decreases the temperature at the alloy/coating interface but at the cost of increasing the TBC surface temperature by about the same amount. For the conditions shown, halving the thermal conductivity almost halves (to 65%) the heat flux through the coating. However, as indicated earlier, advances in identifying lower thermal conductivity oxides are approaching a physical limit and so major advances in lowering heat flux by conduction using new oxides cannot be expected.

In the absence of any radiative heat flux through a coating, the temperature is not only a linear function of position through the coating but also increases almost linearly with the hot gas temperature. Of equal significance, the total heat fluxes through an opaque coating, as well as the TBC surface and bond-coat temperature, increase almost linearly with gas temperature, but notably not to the fourth power. These findings are shown in figure 3 for gas temperatures in the range of 1000 to 3000 K (2727 ^{o}C). The wide temperature range allows the role of temperature to be investigated systematically even though it is recognized that current TBCs oxides will not be used at these temperatures. Nevertheless, the use temperatures of future coatings, such as environmental coatings, may approach the upper range of these temperatures. It is noted that the highest melting oxide, hafnia, melts at 3033 K, above the maximum of this range.

RADIATIVE HEAT TRANSFER THROUGH A COATING

The major effects of a coating's transparency as a function of gas temperature are illustrated by the comparison shown in figure 3. In marked contrast to an opaque coating, the heat flux through a translucent coating increases non-linearly with gas temperature. At $T_{gas} = 2000\ K$ the combined conductive-radiative flux is 30% higher than the conductive flux alone rising to 60% higher than the conductive flux alone at $T_{gas} = 2500\ K$. Therefore, even under what are believed to be the hottest operating temperatures today, the conductive heat flux only accounts for about 70% of the total heat flux through a 8YSZ coating deposited by EB-PVD. Reflecting the increased radiative flux propagating through a translucent coating, the temperature of the bond coat/TBC interface increases. On the scale used in figure 3, the increases in bond-coat temperatures do not appear large but are ~ 250 K and ~ 650 K higher at gas temperatures of 2500 K and 3000 K, respectively, than when the coating is opaque; significant differences. By contrast, the surface temperature of a translucent coating increases linearly with gas temperature but, at least for the parameters assumed, is almost the same as that for an opaque coating.

The calculations in figure 3 are based on the reported optical properties of 8YSZ deposited by EB-PVD. This oxide has a large band gap and, when fully dense, is almost transparent from about 350 nm to 5 microns. (Over this wavelength range the absorption coefficient is ~ 100 m^{-1} [14]) meaning that there is almost no absorption in a 1 mm coating). In its' single crystal form its refractive index is 2.1, also almost independent of wavelength. Its high-temperature optical properties have been evaluated up to 1360 °C [14] and in its tetragonal-prime form up to 1400 °C [15]. Turbine coatings made from this oxide are deliberately deposited to contain substantial levels of porosity to decrease both the effective thermal conductivity and the elastic modulus, the latter for enhancing strain compliance [5]. The pores scatter light as evidenced by the observation that coatings appear white and the optical scattering length decreases with increasing volumes of porosity [16]. It is assumed that the coatings have a thermal conductivity of 0.8 W/mK.

As mentioned, the foregoing calculations were for an almost transparent coating with optical properties similar to 8YSZ. To explore the effects of the optical properties in greater detail, a series of calculations were performed to investigate the effects of refractive index, bond-coat emittance and different values of the absorption coefficient and optical scattering coefficient. The calculated temperature distribution through the coatings together with the heat fluxes are shown in figure 4. These calculations are for the same values of convective heat coefficients as used in figure 3, representing convective flow over a blade. Because of the large value assumed for h_1, the calculated temperature differences are not large and the major differences are in the total heat fluxes through the coatings.

The refractive index, n_c, controls the proportion of the incident thermal radiation that enters into a coating, as well as the radiation that is scattered back out of the coating [11, 12]. (Supplementary Materials). The asymmetry in reflectance direction at the gas/coating surface results in higher temperatures at the bond-coat interface and higher heat fluxes with increasing values of the refractive index. Fig. 4(a). (For comparison, the total heat flux for an almost transparent coating (n=2.1) at 2500 K is 1.60 MW/m^2, from figure 3). The substantially higher total heat flux with larger refractive index is consistent with a larger trapping of radiative energy in the coating as is the higher bond-coat temperature.

There is also a strong effect of the bond-coat emittance on both the bond-coat metal temperature and the total heat flux through the coating. This is illustrated in figure 4 (b) for a wide range of emittances. The emittance of the bond-coat has a relatively large effect since the larger it is, the larger is the absorption at the interface and so the more the heat is radiated back into the coating. With the current state of materials knowledge, it is not known how to manipulate the bond-coat emittance but given its large effect it is a potentially important parameter to investigate.

The biggest effect in reducing the heat flux through a coating is by increasing the optical scattering, $\sigma_{s\lambda}$, as illustrated in Fig. 4 (c) and shown earlier by Siegel and Spuckler [10]. The physical basis for the reduction in the heat flux through the coatings is that scattering causes a proportion of the radiative flux to be scattered back out of the coating. Consequently, scattering also has the effect of decreasing the temperature at the TBC/alloy interface. (As will be described in section 6, scattering coefficients greater than about 1000 m^{-1} may not be achievable in practice with EB-PVD unless coatings much thicker than 1 mm are contemplated).

Absorption of the radiative heat flux within the coating also has a strong effect on the total heat flux and the temperature distribution. The most extreme case is where the coating absorbs so strongly that it acts as an opaque coating. In this limiting case, no radiative thermal transport can occur and the temperature distribution is linear through the thickness of the coating as shown in the simulations in figure 2. The other extreme is where the coating is almost transparent, such as is the case with YSZ up to about 4 microns. As indicated by figure 4 (d), the TBC surface temperature is the lowest for the transparent coating but increases with increasing absorption coefficient, a_{λ}. Interestingly, as the absorption coefficient is increased the TBC/alloy interface temperature increases and then decreases approaching the opaque coating limit.

In summary, the effect of varying the optical parameters is not simply to alter the effective optical extinction coefficient, as they would for optical transmission through a thin slab of the material. This is because the coating lies between a gas/coating interface and an interface with the underlying metal. Consequently, radiative energy transfer within the coating behaves as if it were in an incoherent optical cavity. Thus, the emittance and reflectance of both these interfaces, not just the coating/gas interface, also affects the heat flux through the coating. As these surfaces are not optically smooth, and the TGO grows with time at operational temperatures, it is reasonable to assume that they act as optically diffuse interfaces. This is in accord with the assumptions of the Siegel-Spuckler model.

MANIPULATION OF THE HEAT FLUXES BY DOPING

Between the limits of complete transparency and opacity, there is the possibility of exploiting doping in an otherwise transparent oxide to modify the heat fluxes and temperature distributions. One approach to increasing the absorption in an almost transparent oxide, such as 8YSZ and $Y_2Si_2O_7$, a candidate EBC, is to dissolve a concentration of transition metal or rare-earth cations into solid solution [17, 18]. Provided that the solute cations satisfy the Pauling rules associated with coordination number and ionic size [19], they can dissolve in the oxide and modify the optical properties of the host oxide through electronic transitions. In previous work, a substitution of a variety of rare-earth ions into the crystal structure of 8YSZ has been demonstrated for use as non-contact temperature sensors [20] [21] [17]. The rare-earth ions, commonly used in phosphors [18], are especially promising as several of them exhibit strong optical absorption in the spectral range over which a hot gas radiates [22]. An example of such overlap is illustrated in figure 5 with the super-position of black-body radiation curves for a range of temperature with the spectral absorption bands for Eu^{3+} and Dy^{3+} ions. For illustration of the doping effectiveness, our measurements of the optical absorption due to 1 m/o Eu_2O_3 are shown in Figure S3.

IMPLICATIONS FOR COATING DESIGN

As the gas turbine industry strives to increase engine efficiency and higher propulsion powers, the T4 temperature increases and consequently the proportion of radiative to conductive transport through a translucent coating is expected to increase as illustrated in figure 3. Interestingly, except for small values of convective heat coefficients more typical of combustor coatings, the surface temperatures of translucent and opaque coatings are very similar and close to the hot gas temperature. The major difference between opaque and almost transparent coatings, though, lies in the values of the heat fluxes that pass through the coating and the temperature at the interface between the bond-coat and the coating. Both depend on the optical properties of the coating material in the visible and near infra-red. The most important finding, from a materials design and selection perspective, is that the total heat flux and bond-coat temperature can only be minimized when the coating is opaque. Current, state of the art coatings, such as 8YSZ and Gadolinium Zirconate (GZO), are wide band gap materials, as indeed are all refractory oxides, and thus are not opaque, although they have very low thermal conductivities. Consequently, there are opportunities to manipulate their properties to decrease the radiative heat flux exposed to high-velocity gas flow despite being little prospect of decreasing the surface temperatures.

Although both absorption and scattering have the potential of making a wide band gap material opaque in order to decrease radiative heating through a coating, it should be emphasized that the calculations presented are based on continuum descriptions. Introducing optical absorption by the atomic substitution doping can be well represented by a continuum description and can also produce a wide range of optical absorption coefficient, from 100 m^{-1} typical of pure zirconia, to greater than 10,000,000 m^{-1}, corresponding to an absorption length smaller than 0.1 micron. To be effective, multiple dopants must be used so as to span the wavelength range over which large values of absorption can be achieved. However, the dopants must not introduce free electrons at high temperatures otherwise the thermal conductivity will increase due to electronic contributions, thwarting the objective of achieving the lowest possible thermal conductivity. As yet, despite extensive studies of rare-earth doping of oxides for phosphors, little is known about their concentration effects on electron conductivity at high temperatures.

In contrast to atomic doping, there are distinct microstructural size effects, such as pore sizes and size distributions, which determine the magnitude of optical scattering. Consequently, there are physical limits to how significant optical scattering can be in a finite thickness coating. In the absence of Monte Carlo simulations to trace the propagation of light rays through a representative microstructure, considerable insight can be gained from the physics of optical scattering [23] from particles, including pores the commonest form of optical scattering centers in coatings. [Supplementary Materials, S2]. Maximum scattering occurs when the diameter of a particle is approximately equal to the incident wavelength divided by its refractive index. (Pores with diameters much smaller than this value exhibit only weak (Rayleigh) scattering). The maximum scattering condition sets the scale for optical scattering since it limits the number of scattering centers through the thickness of a coating. This, in turn, constrains the maximum value of scattering coefficient that can be attained in a coating. An extreme case of optical scattering occurs when the pores are not spherical, or approximately spherical, and are instead flat discs oriented perpendicular to the propagation of the incident radiation. (In this respect, the shape of the porosity on scattering is akin to the shape effect on thermal conductivity.) It is likely that a combination of porosity and doping will be most effective in modifying the optical properties of oxides to approach the ideal opaque properties.

In presenting these findings, it is recognized that they may represent upper bounds on the heat fluxes and surface temperatures for actual blades. It has been assumed that the spectral emissivity of the hot gas is unity, consistent with a high luminosity carbon fuel, whereas fuels that do not create carbonaceous nanoparticles will have a lower emissivity. Similarly, the high surface temperatures, consistent with the high convective heat transfer coefficient used, may not be reached because of possible future advances in film or transpiration cooling, for instance. It is also unknown whether doping will lead to significant internal radiative emission. Lastly, although it can be confidently concluded that radiative heat fluxes will increase with increasing gas temperatures and become of greater importance, the pace at which this occurs over the next decade or so will depend on other considerations, such as minimizing CMAS formation, the acceptable thermal management cooling budget for an engine, and the introduction of regulations on NOx emissions, all of which will depend on gas temperature. Nevertheless, it will be necessary to transition from current low absorption, high scattering coatings, such as 8YSZ, to opaque coatings as described in this work. It is not yet known when this will be necessary but as materials developments can take many years it is timely to consider the effects of radiative heating in engine operation.

Finally, there is an additional consequence of radiative heat transfer not considered in this work, namely radiative thermal shock. As thermal radiation propagates at the speed of light, radiative shocks due to sudden changes in combustion conditions do not decay in passing through a coating. This is in marked contrast to they are buffered by the thermal diffusion time constant of opaque coatings, typically the coating thickness squared divided by its thermal diffusivity. This new form of thermal shock is likely to affect the prime reliance of coatings.

SUMMARY

As engine temperatures increase, the radiative heat load on the hot-section turbine components increase non-linearly with gas temperature. For coatings opaque in the visible and near infra-red, no radiative heat flux through the coating can occur and the coating's thermal conductivity determines the heat fluxes and temperatures through the coating. However, when the coating material is not opaque, calculations show that the radiative heat transport increases the total heat flux through the coating as well as the metal/coating interface temperature. The very high heat fluxes resulting from radiative heat transport through the coating impose additional demands on the internal cooling lowering the overall engine efficiency. Currently used low thermal conductivity oxides are not effective in blocking radiative heat transport providing an opportunity to design oxides that can reduce the overall heat flow through coatings. However, the ability to manipulate the radiative properties of a coating, such as 8YSZ, by doping and scattering offers the possibility of reducing the radiative heat flux. Although the simulations are based on 8YSZ, similar findings are expected for other oxides at higher temperature, such as EBCs being considered for the protection of CMCs.

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FIGURES

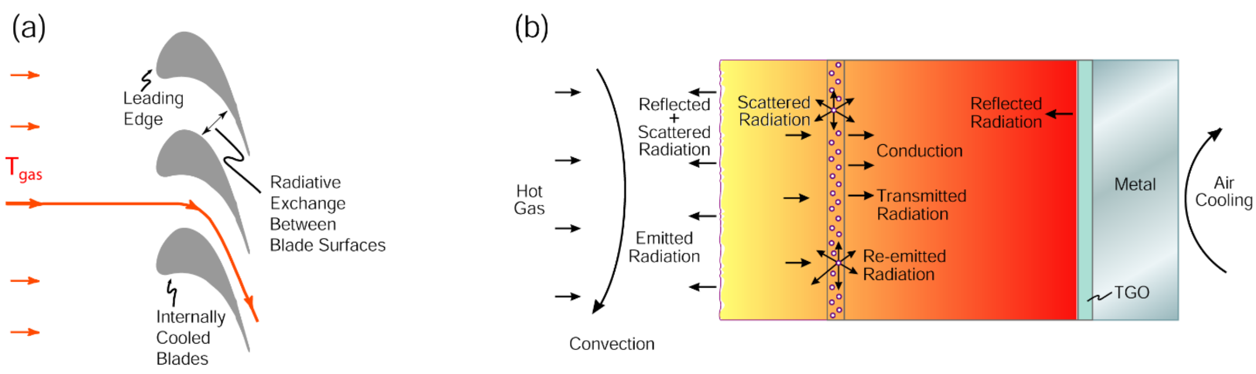

Figure 1. (a). Schematic diagram of the blade geometry relative to the hot gas coming from the combustor. (b). The radiative heat fluxes through the thickness of a coated metal blade with internal cooling.

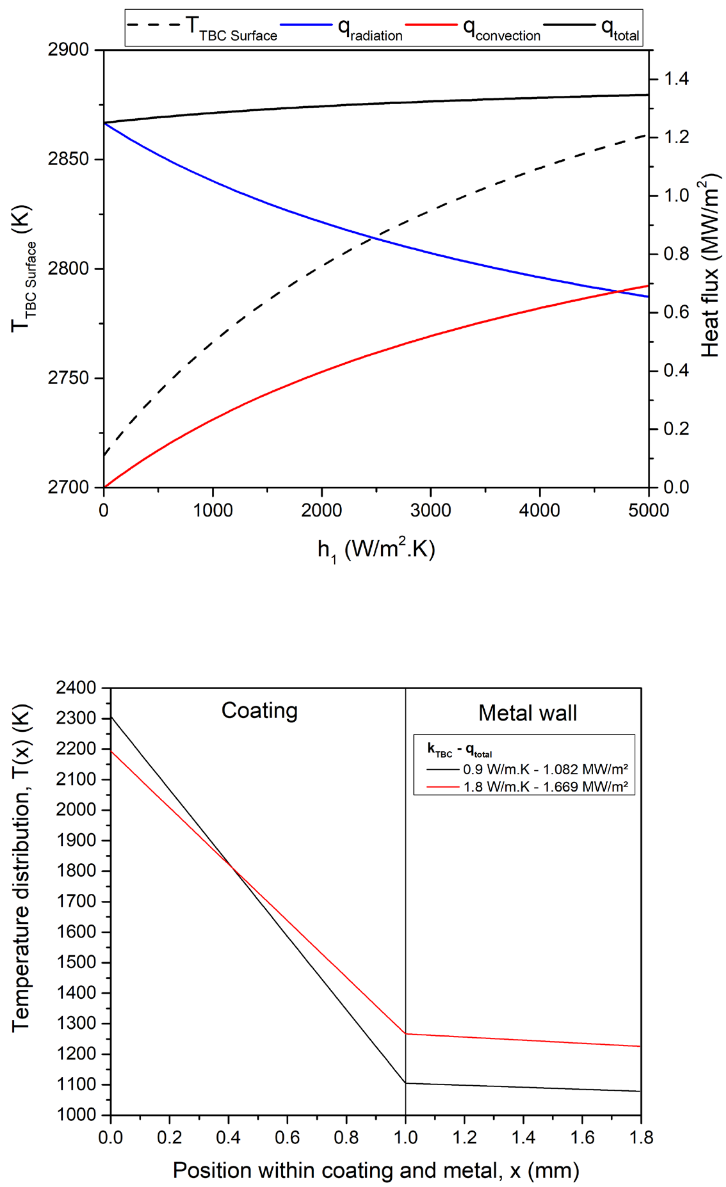

Figure 2. (top). The variation in the radiative and convective contributions to the total heat flux at the surface of an opaque coating as a function of the convective heat coefficient. $(T_{gas} = 3000\,K)$ *. (Bottom). Temperature distribution as a function of position through an opaque 1 mm thick TBC for the indicated values of thermal conductivity.* T_{gas} *= 2500 K. The heat fluxes are 1.67 MW/m*^{2} *and 1.08 MW/m*^{2} *for the 1.8 and 0.9 W/mK thermal conductivity coatings, respectively.*

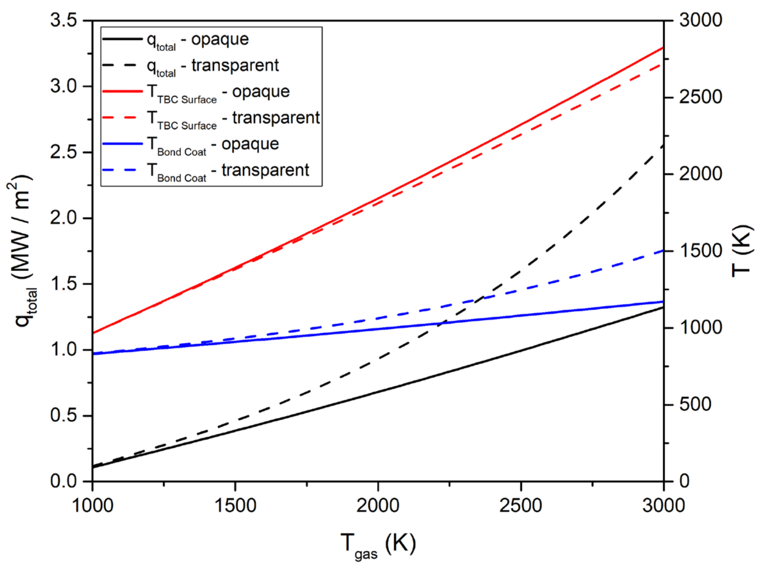

Figure 3. Comparison of the total heat fluxes through an opaque and a translucent 1 mm thick TBC as a function of the hot gas temperature using optical properties reported for 8YSZ. Also shown are the computed TBC surface temperatures and the temperatures at the interface with the bond-coat.

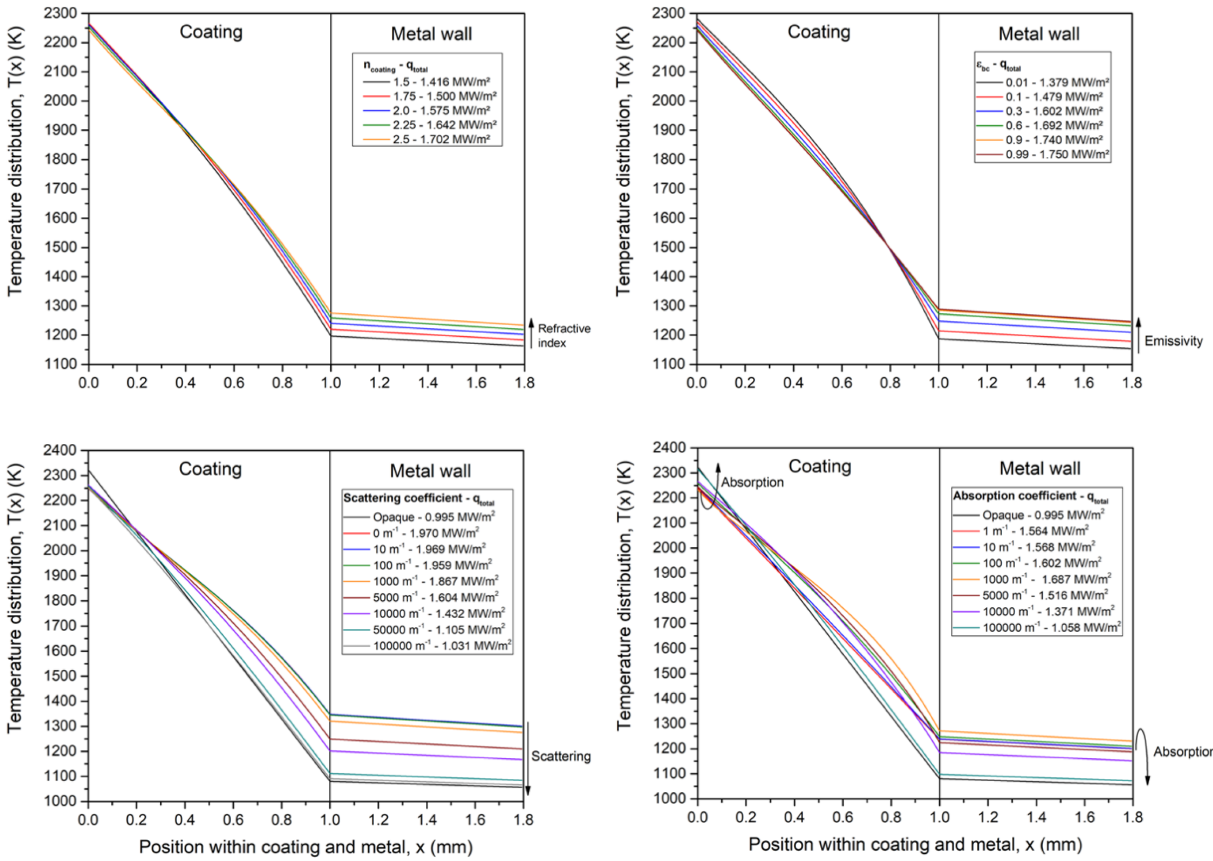

Figure 4. The temperature distribution through a 1 mm thick coating together with values of the corresponding total heat fluxes. Note, that except for the case of an opaque coating, the temperature distributions are non-linear. T_{gas} *= 2500 K.* $k_c = 0.8\ W/m.K$ *.*

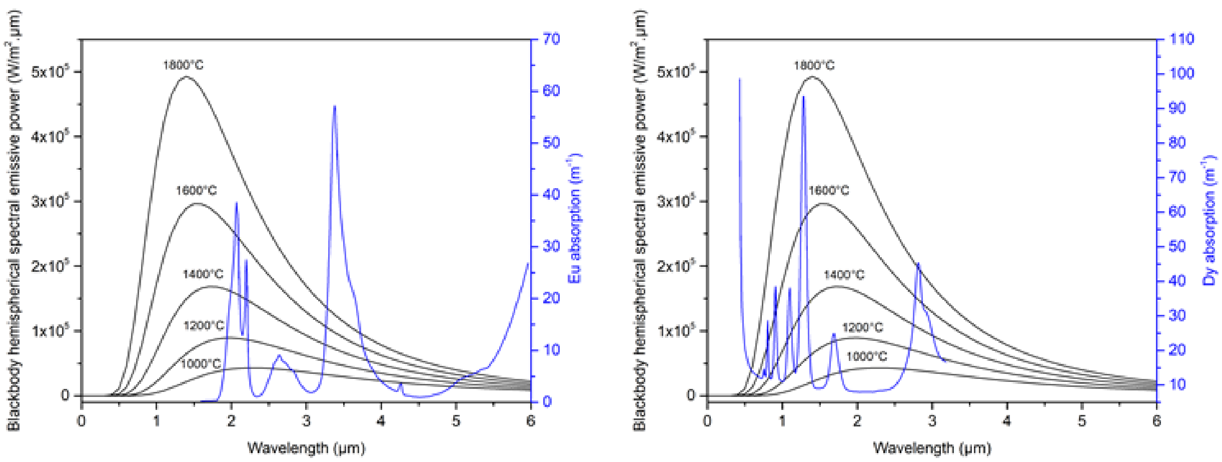

Figure 5. Spectral overlap of the Eu^{3+} (left) and Dy^{3+} (right) optical absorption bands with the black body spectral emissive power at the temperatures indicated.

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OPPORTUNITIES FOR MATERIALS DESIGN OF FUTURE

THERMAL AND ENVIRONMENTAL BARRIER COATINGS

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SUPPLEMENTARY MATERIALS

A. Parameters Used in Calculations

The results presented in the text were computed using the parameters listed in Table S1 unless specified otherwise.

Table S1

Parameter name	Description	Value
h_1	convective coefficient, coating side ($W/m^2.K$)	3014
h_2	convective coefficient, metal side ($W/m^2.K$)	3768
k_c	Thermal conductivity of the coating (W/m.K)	0.8
k_m	Thermal conductivity of the metal (W/m.K)	33
δ_c	thickness of the coating (m)	$1x10^{-3}$
δ_m	thickness of the metal (m)	$0.794x10^{-3}$
$n_{coating}$	refractive index of the coating	2.1
ε_{bc}	emittance of the bond coat	0.3
ε_m	emittance of the metal	0.6
T_{s1}	blackbody temperature of surroundings (coating)	$T_{s1} = T_{g1}$
T_{s2}	blackbody temperature of surroundings (metal)	$T_{s2} = T_{g2}$
T_{g1}	gas temperature on the coating side	Varied
T_{g2}	gas temperature on the metal side	800
ε_{gas}	Emittance of the hot gas	1.0

For the 8YSZ materials, an absorption coefficient of 100 m^{-1} independent of wavelength was used. Also, unless otherwise specified, the scattering coefficient shown in figure S1 below was used for the calculations for radiative heat transfer in 8YSZ coatings. The values are based on measurements of 8YSZ coatings deposited by EB-PVD [16].

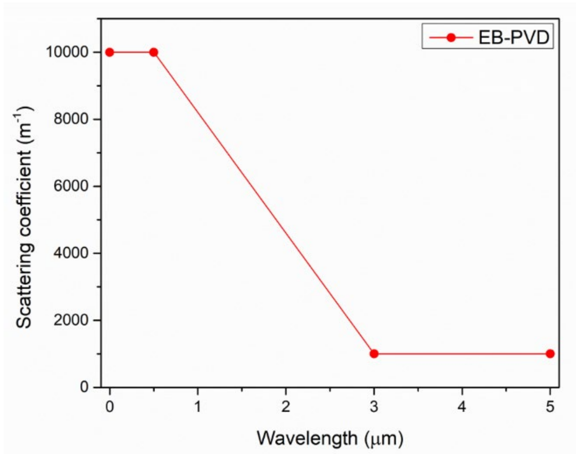

Figure S1. Spectral scattering coefficient assumed for 8YSZ.

B. Effect of Refractive Index on Radiative Trapping in a Coating

For the calculation of radiative heat transfer through a coating, both the radiative flux that enters the coating as well as the radiative flux that is directed back out of the coating from scattering events within the coating must be known. As coatings on curved surfaces, such as blades and vanes, in the hot sections of a turbine are bathed in thermal radiation from all directions, the hemispherical reflectance, ρ_i, as distinct from the specular reflectance for an incident beam of parallel radiation, is the appropriate reflectance parameter. For the radiative transfer from a hot gas into a coating, the hemispherical reflectance, ρ_i, [11, 12] can be expressed in terms of the refractive index of the coating by:

$$\rho_i = \frac{1}{2} + \frac{(3n+1)(n-1)}{6(n+1)^2} + \frac{n^2(n^2-1)^2}{(n^2+1)^3}\ln\left(\frac{n-1}{n+1}\right) - \frac{2n^3(n^2+2n-1)}{(n^2+1)(n^4-1)} + \frac{8n^4(n^4+1)}{(n^2+1)(n^4-1)^2}\ln(n) \tag{S1}$$

where n is the refractive index of the coating material. In the reverse direction, for radiative heat flow scattered back out of the coating into the gas, the angular distribution of scattering out of the coating is limited by total internal reflection at the coating/gas surface. The operative reflectance is then given by:

$$\rho_o = 1 - \frac{1}{n^2}[1-\rho_i] \tag{S2}$$

C. Scattering from porosity and particles within a coating

The calculations presented in the text are based on representing heat transfer through a coating in terms of its continuum properties. Consequently, they do not take into account microstructural variables, such as pores and particles within the coating that can affect both thermal conductivity (by phonon scattering) and radiative transport (by photon scattering).

The optical scattering from non-absorbing particles, whether they are pores or particles of a different composition is very well established and can be computed in considerable detail based on Lorenz-Mie scattering due to differences in refractive index and shape. Nevertheless, it is helpful in the context of this perspective article where the spectral dependence of scattering affects radiative heat flow, to consider the parametric effects of particle size in an analytical form. According to Blevin and Brown [23], the effective scattering coefficient, σ_s , per unit volume by a small volume fraction, V_p , of uniform sized particles can be expressed as:

$$\sigma_{s,e} = \frac{3\pi n_p}{2\lambda_o} V_p \frac{(1-\overline{\mu})K(x,m)}{m\,x} \tag{S3}$$

where $m = n_p / n_m$, the ratio of the refractive index of the pores and the coating, $m\,x$ is a particle size parameter ($= 2\pi\, a\, n_p / \lambda_o$). The particle radius is a and the wavelength of the incident radiation (evaluated in free space) is λ_o. $K(x,m)$ is the Mie scattering coefficient [24, 25].

As indicated in the graph of figure S2 from Blevin and Brown, the scattering efficiency depends on the normalized particle size and increases with the ratio of refractive index of the coating material and the particles. For this reason, pores are more effective in radiation scattering in coatings than are particles of a second phase. Notably, the scattering efficiency also peaks when the particle diameter is commensurate with the incident wavelength, $2\,a \sim \lambda_o / n_p$. Based on this equation, in order to be effective in scattering the wide spectral range of thermal radiation typical of combustion gases at high temperatures, it is necessary that the coating contains a population of particles of different sizes. This finite size effect, in turn, limits the number of particles or pores that can exist within the thickness of a coating. Although this equation is for a dilute concentration of particles, each scattering independently of one another, the effects of particle size on scattering are not substantially modified at higher concentrations.

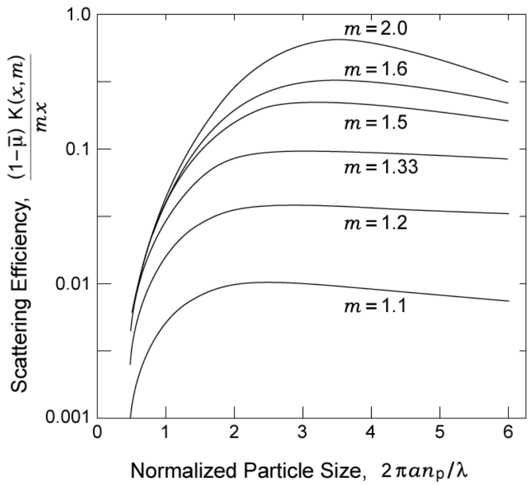

Figure S2. Dependence of the optical scattering strength as a function of particle (pore) size for different ratios of the refractive indices, m. (Reproduced and redrawn from reference [23]).

D. Optical Absorption by Europium Ions in Yttrium Zirconium Tantalate

Europium ions are one of the rare-earth dopants that have been identified in the text that could be used to decrease the radiative transport through an otherwise transparent, refractory oxide by absorption. To illustrate that europium in solid solution can lead to optical absorption not present in the oxide absent the dopant, the optical absorption spectrum up to 2.5 micron of yttrium zirconium tantalate (YZT) are compared in Figure S3 with and without 1 m/o Eu_2O_3. The optical absorption of Eu^{3+} ions in the wavelength range of 1.8 to 2.3 microns, due to characteristic ^7F electronic transitions [22], is evident in the oxide doped with 1 m/o Eu_2O_3.

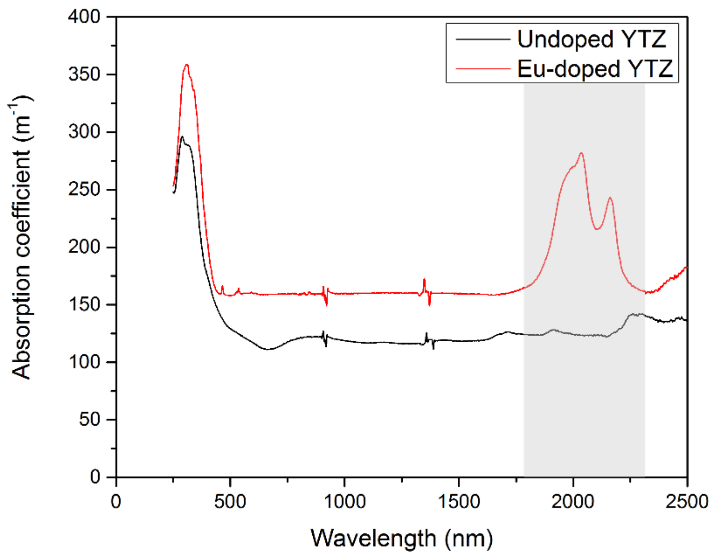

Figure S3. Comparison of the spectral optical absorption coefficient for a 1 m/o Eu_2O_3-doped YTZ material with that of an undoped material prepared in the same way. The enhanced absorption is shown in the shaded box.

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