Thermal barrier coating by electron beam-physical vapor deposition of zirconia co-doped with yttria and niobia

Abstract: The most usual ceramic material for coating turbine blades is yttria doped zirconia. Addition of niobia, as a co-dopant in the $\text{Y}_2\text{O}_3$-$\text{ZrO}_2$ system, can reduce the thermal conductivity and improve mechanical properties of the coating. The purpose of this work was to evaluate the influence of the addition of niobia on the microstructure and thermal properties of the ceramic coatings. SEM on coatings fractured cross-section shows a columnar structure and the results of XRD show only zirconia tetragonal phase in the ceramic coating for the chemical composition range studied. As the difference $\text{NbO}_{2.5}$-$\text{YO}_{1.5}$ mol percent increases, the tetragonality increases. A significant reduction of the thermal conductivity, measured by laser flash technique in the zirconia coating co-doped with yttria and niobia when compared with zirconia-yttria coating was observed.

Keywords: TBC, EB-PVD, Zirconia, Niobia, Thermal conductivity.

INTRODUCTION

The great advantage of coatings is that it is possible to modify its response to the environment by changing only the superficial part of the component, thus providing completely different properties. Some of the obtained benefits are: reduction of maintenance costs, increase of the working temperature, reduction of thermal loads, resistance increase to erosion and corrosion and reduction of the high temperature oxidation (Funatani, 2000).

The electron beam-physical vapor deposition (EB-PVD) process enables to attain coatings with unique properties. The process parameters are adjusted so that the deposit has a columnar grain structure perpendicular to the interface. This morphology maximizes the resistance to strains that arise from differences in thermal expansion coefficients. Other advantages are: aerodynamically favorable smooth surface, better interaction with the substrate, greater thermal cycle tolerance and, hence, greater lifetime comparativeness with the plasma spray process (Xu, Goug and Deng, 1998; Schulz et al., 2000; Evans et al., 2001; Zhu et al., 2000; Goward, 1998; Nicholls, Deakin, Rickerby, 1999; Czek et al., 1999; Hass, 2001; Almeida et al., 2007 and 2006; Nicholls et al., 2002; Guo and Wang, 1998).

There are four primary constituents in a thermal protection system. They comprise: (1) the thermal barrier coating (TBC) itself based usually on ~8 wt. % (8.7 mol % $\text{YO}_{1.5}$) yttria stabilized zirconia; (2) the metallic component, treated here as the substrate; (3) an aluminium containing bond coat (BC) located between the substrate and the TBC; and (4) a thermally grown oxide (TGO), predominantly $\alpha$-alumina, that forms between the TBC and the bond coat. The TBC is the thermal insulator, the bond coat provides oxidation protection, since the zirconia is essentially transparent for the oxygen at high temperatures, and the metallic component, usually a nickel base super-alloy, sustains the structural loads. The TGO is an oxidation reaction product of the bond layer, and plays a role in the metal/oxide adhesion. Each of these elements is dynamic and all interact to control the performance and durability (Mumm and Evans, 2001; Stöver and Funke, 1999).

When $\text{ZrO}_2$ is utilized for technical applications, the high-temperature polymorphs cubic (c) and tetragonal (t) phases should be stabilized at room temperature by the formation of solid solutions, which prevent deleterious tetragonal-to-monoclinic (m) phase transformation. The alloying oxides, which lead to the stabilization, are alkaline-earth, rare-earth, and actinide oxides. It has been suggested that the factors that may influence the stabilization are size, valency, and concentration of solute cations and crystal structure of the solute oxides, where the valency and concentration determine the number of oxygen vacancies created by the formation of substitutional solid solutions (Kim, 1990; Lehmann et al. 2003).

Dense zirconia-based materials already exhibit low thermal conductivity. The introduction of a stabilizer,
required to avoid the detrimental effect of tetragonal to monoclinic phase transformation, is accompanied by the incorporation of a substantial amount of vacancies providing an efficient source of phonons scattering (Schulz et al. 2000). When a trivalent oxide, e.g., Y₂O₃, is added to ZrO₂ as a stabilizer, a certain amount of lattice defects, e.g., oxygen vacancies and negatively charged solutes, are produced in the ZrO₂ lattice (Kim, Tien, 1991).

The addition of Ta₂O₅, Nb₂O₅ and HfO₂ to bulk Y₂O₃–stabilized tetragonal ZrO₂ increases transformation, as for example the tetragonal (t) to monoclinic (m) transformation temperature, of the resulting zirconia ceramics. The enhanced transformability is related to the alloying effect on the tetragonality (c/a – cell parameters ratio) of stabilized tetragonal ZrO₂ (Fig.1), subsequently, by adding these oxides the tetragonal distortion of the cubic lattice is increased. The increase in the tetragonality, due to alloying, is consistent with the increase in the fracture hardness and the increase in the t to m transformation temperature (Guo and Wang, 1998; Raghavan et al., 2001; Guo et al., 2001; Raghavan et al., 1998; Kim, 1990). Evidently, t-ZrO₂ become unstable as their tetragonality increases toward 1.020, which corresponds to the c/b axial ratio of m-ZrO₂ at room temperature. On the other hand, they become stable as the tetragonality decreases toward unity, which corresponds to c-ZrO₂. This relationship allows the classification of oxides into either a stabilizer (decreasing tetragonality) or a destabilizer (increasing tetragonality) for the t-ZrO₂ phase (Kim, 1990; Kim and Tien, 1991; Lee et al., 1998).

Thermal conductivity is one of the physical key properties of the TBCs and increasing its insulation capability emerges as a technical and economical challenge for engine manufacturers. Lowering TBCs thermal conductivity would increase the engine performance by improving the combustion efficiency (higher turbine entry temperature), reduce the specific fuel consumption, allow the reduction of internal cooling, reduce the metallic component temperature and extend their lifetime (Hass, 2001; Kim, 1990; Kim and Tien, 1991; Raghavan et al., 1998; Lee et al., 1998).

The thermal conductivity, \( k \), of ceramic coatings can be measured using either a direct (steady state) or a transient approach. In the latter, the thermal diffusivity, \( \alpha \), of a material is measured and subsequently related to thermal conductivity using the relationship, as shown in Eq. (1):

\[
k = \alpha cp
\]

Where \( cp \) is the heat capacity at constant pressure and \( \rho \) is the specific mass of the material.

There are several classical techniques to measure the thermal properties of a material. Such classical methods, which involved the fitting of steady state and non-steady state experimental temperature data to theoretical models, were usually time expendable. Furthermore, the large sized samples imposed intolerable limitations, usually tied to heat losses and contact resistance between the specimen and its associated heat source, heat sinks and measurement devices. The flash method, used in the present work, eliminated the problem of contact resistance and minimized heat losses by establishing the measuring time to be sufficiently brief so that very little cooling could take place (Couto et al., 2003; Degiovaninini and Lament, 1986).
The study of the considered ceramic coating is motivated by the potential of the niobia to overcome the deficiencies presented in conventional yttria stabilized zirconia coatings, i.e. high thermal conductivity when compared with plasma spray coatings and relatively low mechanical properties.

EXPERIMENTAL

SAE 304 stainless steel plates were used as metallic substrates. Both bond layer and ceramic top coating were EB-PVD deposited using one source 30kW electron beam equipment. This consists of an electron gun with accelerating voltage of 25 kV and beam current variation from 0 to 1.2 A. The vacuum system has an ultimate pressure of 10^-4 torr (≈10^-4 Pa). A substrate holder assembly is situated above the vapor source at a vertical distance of 150 mm. A tungsten filament is used to heat the substrate by Joule effect to the desired temperature (~500°C) during bond coating deposition and ~900°C during ceramic layer deposition, which is measured and maintained by a thermocouple and programmable temperature controller. A water-cooled copper crucible is used for evaporation of sintered targets. The ceramic targets (cylinders of 20 mm diameter and mass of 20 g) were prepared from cold compacted powder mixtures of zirconia, yttria and niobia sintered at 1700°C under vacuum (10^-4 Pa). The MCrAlY targets were prepared from a Ni–31Cr–11Al–0.65Y (wt %) powder alloy sintered at 1340°C under vacuum (10^-4 Pa). The bond layer has a 25 μm thickness.

The crystalline phases of ceramic coatings, with an average thickness of 50 μm, are identified by X-ray diffraction using a X’Pert Philips PW 1380/80 diffractometer and a X’Pert – MRD Philips diffractometer with a PW 3050 goniometer. The ceramic coating microstructure and grain morphology were observed by SEM and the chemical composition was estimated by EDS using a LEO 435 VPI scanning electron microscope.

The specific mass (ρ), disregarding pores and other defects, was calculated from the cell parameters (from XRD data) and molar concentrations of zirconia, yttria and niobia (from EDS analysis), using the Eq. (2):

\[ \rho = \frac{n \cdot [x \cdot A_{\text{YcY}} + y \cdot A_{\text{NbC}} + (1-x-y) \cdot A_{\text{ZcZ}}]}{6.02 \cdot 10^{23} \cdot a^3 \cdot c} \]  (2)

Where:

n: cations in unit cell (n=4 for fcc); A_{YcY}: yttria atomic mass (112.905); A_{NbC}: niobia atomic mass (132.905); A_{ZcZ}: zirconia atomic mass (123.22); x and y: molar fraction of yttria and niobia, respectively; a and c: cell parameters of t-ZrO₂ calculated from XRD data.

For thermal properties determinations of coatings, the Thermal Flash 2000/Holometrix equipment was used. This method, laser technique, consists of heating the front surface of a thermally insulated specimen with a high-intensity short-duration radioactive heat pulse and measuring the temperature evolution on the back surface by means of an infrared detector. The non-intrusive backside measurement method eliminates the concern and issues with sensor attachment to the sample, and removes all uncertainties associated with contact resistance and sensor measurement accuracy (Couto et al., 2003). After stabilizing the sample at a desired uniform temperature (T₀), a nearly instantaneous pulse of energy (usually laser, Xenon lamp or other discharge source) is imposed on its front surface, as well as on the temperature increase on the rear surface of the sample and is then recorded as a function of time. The thermal diffusivity is then determined by comparing this thermogram with theoretical models that describe this transient heat conduction phenomenon. Several theoretical models are available for the flash method, which includes adiabatic boundary conditions, heat losses, surface coating effects, among many other aspects. The values of thermal diffusivity (average of three measurements, for each sample at each temperature) were calculated in accordance with the Degiovaninno model (Degiovaninni and Lament, 1986). Considering that the energy of the laser is used only for heating the sample, disregarding the interfaces (contact resistance) and using Eq. (3) it is possible to calculate the coating thermal conductivity from Holometrix equipment measurements.

\[ \frac{e_x^2}{a_x} = \left( \frac{e_m^2}{a_m} \right)^{-1} \left[ 1 + \frac{\rho_x c_x e_x}{\rho_m c_m e_m} \left( 1 + \frac{3 e_m}{k_m} \right) \right]^2 \]  (3)

Where c is the heat capacity (J/KgK), r is the specific mass (g/cm³), a is the thermal diffusivity (cm²/s), k is the thermal conductivity (W/mK), e is the thickness (m) and the index a, m and c is relative to the sample, metallic substrate and ceramic layer, respectively.

RESULTS AND DISCUSSION

Typical microstructure of EB–PVD coating, as seen by scanning electron microscopy on fractured cross-section, is shown in Fig. 2. It is possible to see the ceramic layers where the columnar structure is evident. Measurements on ceramic coatings fractured cross-section show almost the same size of columns diameter for samples 1 and 6,
without significant differences in the columns morphology. However, for the sample 11, where the amount of niobia is higher, the columns diameter was increased.

X-ray diffractions with high angular resolution (0.0001° for 2θ) performed on the ceramic coating samples surface with different niobia contents show only the zirconia tetragonal phase. XRD techniques do not allow the identification of special textures related to XRD peak intensity because the PVD coatings show a strong crystallographic texture and the diffraction patterns are taken normal to the substrate surface, not in the coating primary growth direction (Bernier et al., 2003). However, the X-ray diffraction technique allows determining, with sufficient precision, the position of the peaks. The position of the peaks is correlated with crystalline cell lattice parameters and they vary strongly with the chemical composition of the films.

The chemical composition, the cell parameters deduced from diffraction patterns and the values of specific mass of the coatings are reproduced in Table 1.

Table 1: Chemical composition and lattice parameters of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>YO₁.₅ mol%*</th>
<th>NbO₂.₅ mol%*</th>
<th>Cell parameters</th>
<th>ρ</th>
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<tr>
<td></td>
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<td>NbO₂.₅</td>
<td>a   c     c/a</td>
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<tr>
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<tr>
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<td>5.13</td>
<td>5.10</td>
<td>-       -       -       -</td>
<td></td>
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<td>5.6</td>
<td>5.100 5.212 1.0220 6.02</td>
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</table>

*From EDS analysis on ceramic coating cross-section.

Figure 3 shows the influence of the difference (NbO₂.₅ - YO₁.₅) mol% on the zirconia tetragonality. The tetragonality was calculated from the (111) and the (400) peaks position of the XRD diffractograms on the surface.
of the zirconia-based coatings. Chemical composition was determined by EDS analysis on the ceramic coating cross-section. As the difference (NbO$_{2.5}$–YO$_{1.5}$) mol% increases, the ratio c/a (tetragonality) increases. Despite the compositional gradients in the coatings and inaccuracy of oxide semiquantitative analyses by EDS techniques, the linear regression shows a high linear coefficient (R=0.920).

Research with sintered tablets (bulk material) of stabilized tetragonal ZrO$_2$ shows that they become unstable as their tetragonality increases toward 1.020, at room temperature (Hass, 2001; Kim and Tien, 1991). This research agrees with the present work’s experimental results, in which niobia–yttria–zirconia coatings with NbO$_{2.5}$ contenting higher than 7 mol% (c/a >1.020) had a tendency to spall after the deposition cycle. It is possible to evaluate the maximum content of niobia that can be added to the yttria-doped zirconia coating without losses in its mechanical properties. Thus, through the graph of Fig. 3, a coating with 8.7 mol% YO$_{1.5}$ (8 wt.% yttria) can be co-doped with up to 10 mol% NbO$_{2.5}$ (10.8 wt.% niobia).

Figure 4 shows the typical microstructure of EB–PVD ceramic coating, as seen by SEM on polished cross-section. The ceramic layer shows that color bands associated with chemical composition changes due to the differences in saturation vapor pressure of the individual components as function of the temperature and complex chemical interactions between them. For these reasons, the evaporation of alloys is a selective process, resulting in depletion and enrichment in the melt pool and, consequently, in the coating.

Figure 4: SEM (BS mode) of an EB-PVD ceramic coating polished cross-section (sample 3).

The results of EDS analysis performed on the ceramic coating cross-section are summarized in Fig. 5. The composition of the ceramic layer differs point-to-point, remarkably for the niobia concentration, due to the difference in melting point and vapor pressure between niobia, zirconia and yttria. It is clear that compositional gradients can reduce the thermal stability due to differences in layers thermal expansion coefficients. Nevertheless, because of the high melting point of the ceramic, the liquid pool during evaporation is shallow in comparison with target volume, there is not sufficient liquid volume for high level of segregation and as the process is predominantly random, the influence on the thermal stability and in the X-ray data is not high.

Another factor that reduces the influence of the multilayer nature of the coatings with differences in composition between the layers in the XRD data is the X-ray penetration (attenuation length) (Henke et al., 1993). ZrO$_2$ has an attenuation length of 17 mm (phonon energy of 8050 eV and incident angle of 90°), thus the XRD data is based on integration or average of a significant thickness of the coatings.

Two ceramic formulation coating samples (sample 12 and 13, Table 1) were used for determination of the coatings thermal conductivity. The measurements of thermal diffusivity samples are carried out on coatings with their substrates and bond coats attached to them. All samples were coated with colloidal graphite to optimize the laser energy absorption (black body) and to make the infrared sensor data acquisition uniform in the sample backside during thermal diffusivity measurements. On account of its high thermal conductivity value in comparison with zirconia ($k_{\text{graphite}} = 24$ W/m K, $k_{\text{zirconia}} = 1$ W/m K, at 25 °C), the graphite layer (thickness of ~30mm) was not considered in the calculations.

Figure 6 presents the coatings thermal conductivity variation with the temperature as calculate by using
Eq. (3). The zirconia heat capacity values were taken from literature (Raghavan et al., 1998), an approach which is possible due to the little influence of the oxides dopants in these physical properties of zirconia. Thermal conductivity of standard 6–8 wt.% yttria partially stabilized zirconia EB-PVD coatings is typically 1.5–1.9 W/m K. The thermal conductivity of a ceramic layer depends on the intrinsic thermal conductivity of the bulk ceramic, which is linked to its composition and structure, and to the framework of the porous structure, i.e. pore volume fraction, geometry and distribution (Schulz et al., 2000; Schulz et al., 2003).

The present work shows an yttria-doped zirconia coating, with mean thermal conductivity value of 1.17 W/m K significantly lower than those indicated by literature for EB-PVD coatings (1.5–1.9 W/m K). This reduction can be explained by the coating thickness. The thermal conductivity of EB-PVD PYSZ coatings strongly depends on the coating thickness with lower values for thin TBCs, this effect is caused by the different microstructure across the coating roughly characterized by a fine grained inner zone and a coarse grained outer zone (Rätzer-Scheibe et al., 2006). A 50% reduction in the yttria niobia co-doped zirconia coating thermal conductivity (average value: 0.54 W/m K) was observed when compared with yttria-doped zirconia coating.

Schulz et al. developed a model based on solid state physics considerations regarding heat conduction mechanisms in disordered oxide ceramics for the calculation of the thermal conductivity of zirconia based materials doped with trivalent ions and co-doped with pentavalent metallic ions, showing that significant decrease in thermal conductivity (up to 40%) can be achieved, when compared to the standard 8 wt.% yttria partially stabilized zirconia.

The reduction of almost 50% in the thermal conductivity coating promoted by niobia addition can be attributed to several factors: the increase in the level of porosity of the yttria niobia co-doped zirconia coating; the phonons scattering promoted by the ionic radii differences and chemical bonds between matrix (zirconia) and dopants (niobia and yttria) and, in lower degree, to the small reduction of the specific mass coating promoted by the niobia addition.

CONCLUSIONS

The niobia addition, up to 6 wt.%, as co-dopant in the yttria partially stabilized zirconia coatings is insufficient to change its microstructure.

The laser flash technique in conjunction with Degiovaninni model demonstrates efficiency to determine thermal conductivity of the TBC attached to the substrates.

The single-phase tetragonal niobia and yttria co-doped zirconia coatings show a lower thermal conductivity than conventional 6-8 mol% yttria stabilized zirconia coating, the material conventionally used for thermal barrier coating.

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