

ELECTRON BEAM-PHYSICAL VAPOR DEPOSITION CERAMICS COATINGS STUDY

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ABSTRACT

One technique to improve the life and/or the working temperature of the turbine blades is the use of ceramic coatings over metallic material applied by Electron Beam – Physical Vapor Deposition (EB-PVD). The most usual material for this application is yttria doped zirconia. Addition of niobia, as a co-dopant in the Y_2O_3 - ZrO_2 system, can reduce the thermal conductivity. The purpose of this work is to show the influence of the addition of niobia on the some properties of the ceramic coatings. This new formulation will be able, in the future, to become an alternative to the composition currently used by the aerospace sector in EB-PVD Thermal Barrier Coatings (TBC). In a previous paper, EB-PVD TBCs of Zirconia Co-doped with Yttria and Niobia, a Microstructural Investigation, the influence of the addition of niobia on the ceramic coatings was analyzed by XRD, SEM and microhardness. In this paper, the coatings surface roughness and coatings thermal properties is investigated. A significant reduction of the thermal conductivity, using the laser flash technique, in the zirconia ceramic coatings co-doped with yttria and niobia when compared with zirconia-yttria coatings is observed.

1. Introduction

The great advantage of coatings is that, change only the superficial part of the component, it is possible to modify its response to the environment, conferring properties completely different. Some of the reached benefits are: reduction of the maintenance costs, increase the temperatures of operation, reduction of thermal loads, increase the resistance to erosion and corrosion and reduction of the oxidation at high temperatures [1].

The EB-PVD process allows attaining coatings with unique properties. The process parameters are adjusted so that the deposit has a columnar grains structure perpendicular to the interface. This morphology maximizes the resistance

to strains that arise from differences in thermal expansion coefficients. Others advantages are: aerodynamically favorable smooth surface, better interaction with the substrate, greater thermal cycle tolerance and, hence, greater lifetime comparatively with the plasma spray process [2-9].

There are four primary constituents in a thermal protection system. They comprise: the thermal barrier coating (TBC) itself based usually on ~ 8 wt. % (8.7 mol % $\text{YO}_{1.5}$) yttria stabilized zirconia; the metallic component, treated here as the substrate; an aluminium containing bond coat (BC) located between the substrate and the TBC; and a thermally grown oxide (TGO), predominantly α -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 [10-12].

In crystalline solids heat is transferred by three mechanisms: electrons, lattice vibrations, and radiation. As zirconia and its alloys are electronic insulators (electrical conductivity occurring at high temperatures by oxygen ion diffusion), electrons play no part in the total thermal conductivity of the system and thus conductivity of the system and thus conduction in zirconia is by lattice vibrations (phonons) or by radiation (photons) [11].

In real crystal structures scattering of phonons occurs when they interact with lattice imperfections in the ideal lattice. Such imperfections include vacancies, dislocations, grain boundaries, atoms of different masses and other phonons. Ions and atoms of differing ionic radius may also scatter phonons by locally distorting the bond length and thus introducing elastic strain fields into the lattice [11].

Thermal conductivity of bulk 6 to 8 wt.% yttria partially stabilized zirconia is 2.2 to 2.9 W/mK, standards plasma sprayed zirconia coatings is typically 0.9 to 1.0 W/mK and standards EB-PVD coatings is typically 1.8 to 2.0 W/mK [3].

Dense zirconia based materials already exhibit low thermal conductivity. The introduction of a stabilizer, required to avoid the detrimental effect of monoclinic to tetragonal phase transformation is accompanied by the incorporation of a substantial amount of vacancies providing an efficient source of phonons scattering. Thermal conductivity decreases by the influence of stabilizers having different atomic mass and/or ionic radius [3].

Addition of niobia, as a co-dopant in the Y_2O_3 - ZrO_2 system, can reduce the thermal conductivity and improve mechanical properties of the coating. The 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 a reduction of internal cooling, reduce the metallic component temperature and extend their lifetime [12-14].

The addition of Ta_2O_5 , Nb_2O_5 , and HfO_2 to bulk Y_2O_3 -stabilized tetragonal ZrO_2 increases the transformability (t to 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 ZrO_2 , so the addition of these oxides increases the tetragonal distortion of the cubic lattice. The increase in the tetragonality due to alloying is consistent with the increase in the fracture toughness and the increase in the t to m transformation temperature. Evidently, $t\text{-ZrO}_2$ become unstable as their tetragonality increases toward 1.020, which corresponds to the c/b axial ratio of $m\text{-ZrO}_2$ at room temperature. On the other hand, they become stable as the tetragonality decreases toward unity, which corresponds to $c\text{-ZrO}_2$. This relationship allows the classification of oxides into either a stabilizer (decreasing tetragonality) or a destabilizer (increasing tetragonality) for the $t\text{-ZrO}_2$ phase [12-14].

When a trivalent oxide, e.g. Y_2O_3 , is added to ZrO_2 as a stabilizer, a certain amount of lattice defects, e.g. oxygen vacancies and negatively-charged solutes, are produced in the ZrO_2 lattice. The thermal conductivity of partially stabilized- ZrO_2 (PSZ) is determined by its defect structure and the association between defects. Pentavalent oxides are positively charged, opposite to the stabilizer, when dissolved in the ZrO_2 lattice, the addition of these oxides in the PSZ will definitely affect the original defect structure, thus also its properties. Ta_2O_5 has been found to affect the phase stability and the electrical properties of ZrO_2 , and Nb_2O_5 has also been found to dramatically change the grain boundary electrical conductivity [15].

The effect of doping with pentavalent oxides such as tantalum and niobia (cationic radii in the +5 oxidation state $\sim 0.68\text{\AA}$ for both) indicate that both ions reside as substitutional defects in the zirconium lattice (ionic radius of the Zr^{4+} ion is $0.79\text{\AA}$), annihilating oxygen vacancies generated by yttria doping. Thus, the defect chemistry generated by the two dopants is also identical and would be expected to scatter phonons due to the difference in ionic radius and atomic bonding [16]. Table I summarizes the effect of each type of dopant over zirconia thermal properties.

Another way to decrease the thermal conductivity of a material is by the introduction of microstructural defects such pores, voids, micro cracks which constitute obstacle against the heat transfer propagation [3]. Pores primarily decrease the net-section area through which heat can be transported by phonons and so the reduction in thermal conductivity depends not only on volume fraction of pores but also their aspect ratio and their spatial distribution.

Thus, the thermal and mechanical property differences of zirconia coatings results from differences in chemical composition and in the morphology of the porosity present within the TBC layer [17].

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, α , of a material is measured and subsequently related to thermal conductivity using the relationship:

$$k = \alpha \cdot c_p \cdot \rho \quad (1)$$

where c_p is the heat capacity at constant pressure and ρ is the specific mass of the material.

There are several classical techniques to measure the thermal properties of a material. These classical methods, which involved the fitting of steady state and non-steady-state experimental temperature data to theoretical models, were usually time expendable. Additionally, the large size of the 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 minimizes the heat losses by making the measurement time short enough so that very little cooling can take place. This method consists of heating the front surface of a thermally insulated specimen with a high-intensity short-duration radiative heat pulse and measuring the temperature evolution on the back surface by the use 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 [18].

The present work analyzes the addition of niobia, as co-dopant in the yttria-zirconia coating system. 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. Research in zirconia co-doped with yttria and niobia sintered tablets show low thermal conductivity and high tenacity [19,20]. The purpose of this work is to show the influence of the addition of niobia on microstructure and on thermal properties of ceramic coatings.

2. Experimental

SAE 304 stainless steel plates with 12.7 mm of diameter and 1.59 mm of thickness were used as metallic substrates. Both bond layer and ceramic top coating were EB-PVD deposited using one source 30 kW electron beam equipment. It consists of an electron gun with an accelerating voltage of 25 kV and beam current variation from 0 to 1.2 A. The vacuum system has an ultimate pressure of 10^{-6} torr ($\sim 10^{-4}$ 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 ($\sim 900^{\circ}\text{C}$), 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 targets (cylinders of 20 mm diameter and mass of 20 gram) was prepared from cold compacted powder mixtures and sintered at 1700°C under vacuum (10^{-4} Pa). The bond layer was Ni-31Cr-11Al-0.65Y alloy (wt.%) 25 μm thick.

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. 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, 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).

For coatings thermal properties determinations, the laser technique was used (Thermal Flash 2000/Holometrix equipment). The values of thermal diffusivity (average of three measurements, for each samples at each temperature) had been calculated in accordance with the Degiovaninni model [21].

From the results of thermal diffusivity, values of the specific masses and the thermal capacity of the substrate and the layers, disregarding the interfaces (contact resistance) and considering that the energy of the laser is used only for heating the sample, it is possible to calculate the coatings thermal conductivity, using the following equation:

$$\left(\frac{e_a^2}{\alpha_a} \right) = \left(\frac{e_m^2}{\alpha_m} \right) \left[1 + \frac{\rho_c c_c e_c}{\rho_m c_m e_m} \left(1 + \frac{3 e_c / k_c}{2 e_m / k_m} \right) \right]^2 \quad (2)$$

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

3. Results and discussions

Two ceramic coatings formulations was used, one with ZrO₂ + 8 wt.% Y₂O₃ and other with ZrO₂ + 8 wt.% Y₂O₃ + 6 wt. % Nb₂O₅ (Figure 1). Figure 2 shows optical micrograph TBC polished cross section with Vickers microhardness indentations and Table II shows the microhardness values. The niobia and yttria co-doped zirconia coating shows a lower microhardness value.

The surface roughness is about 0.1 μ m for both ceramic coatings. The lower values of surface roughness of EB-PVD ceramic coatings when compared with plasma spray coatings (10.0 μ m), reduces aerodynamic drags of the vanes coated with these TBCs [11]. The influence of niobia on the surface roughness of ceramic coatings was not observed.

The thermal diffusivity, specific heat and specific mass values of the material, allow the calculation of the thermal conductivity (Equation 2). The technique of interferometry of thermal waves (laser technique) was used for determination of the thermal diffusivity of coatings. Figure 3 presents the samples used for determination of the thermal diffusivity of the coatings.

In all the samples were used colloidal graphite covering of for optimisation of the energy absorption of the laser energy and to make uniform infra-red sensor data acquisition in the sample backside. The graphite layer, about 30 μ m, was not considered in the calculations.

Table 3 presents the results of the thermal diffusivity (cm²/s) of the samples and Figure 4 presents the results of the thermal diffusivity variation with the temperature for the three samples.

With the results of the thermal diffusivity of the sample without coating and coated samples, the specific masses values, the heat capacities of the substrate (0,5 J/g.K) and the layers and the thermal conductivity of the substrate, it is possible to calculate the thermal conductivity of coatings using Equation 2. The results of these calculations are presented in Table 4. Figure 5 shows the results of the variation of the thermal conductivity with the temperature for the coatings.

From the analyses of the results of thermal properties, it is observed that the values of thermal conductivity of the yttria doped zirconia coating (average value: 1.171 W/mK) are next to those indicated by literature for EB-PVD coatings (1,5 to 1,9 W/mK) [3]. It is observed a reduction of 50% in the thermal conductivity of yttria niobia co-doped zirconia coating (average value: 0,542 W/mK) when compared with yttria doped zirconia coating.

The reduction of almost 50% in the coating thermal conductivity promoted by the niobia can be attributed to three factors that, and orderly in importance are: the increase in the level of porosity inferred by reduction of the Vickers microhardness in the yttria niobia co-doped zirconia coating; the phonons scattering promoted for the differences of ionic rays and chemical bonds between matrix (zirconia) and dopants (niobia and yttria) and, in lesser degree, to the small reduction of the specific mass promoted by the niobia addition.

4. Conclusion

The single-phase tetragonal niobia and yttria co-doped zirconia coatings shows 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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References

- [1] Funatani, K. Emerging technology in surface modification of light metal. *Surface and Coatings Technology*, n. 133 - 134, p. 264-272, 2000.
- [2] Xu, H., Goug, S., Deng, L., *Thin Solid Films*, 334, p.98-102, 1998.
- [3] Schulz, U. et al., *Surface and Coating Technology*, 133-134, p. 40-48, 2000.
- [4] Evans, A. G. et al., Mechanics-based Scaling Laws for the Durability of TBC, *Progress in Materials Science*, 46, p. 249-271, 2001.
- [5] Zhu, D. et al., *NASA/TM-2000-210238*.
- [6] Goward, G. W., *Surface and Coating Technology*, 108-109, p. 73-79, 1998.
- [7] Nicholls, J.R., Deakin, M.J., Rickerby, D. S., *Wear*, 233-235, p. 352-361, 1999.
- [8] Czek, N. et al., *Surface and Coating Technology*, 113, p. 157-164, 1999.
- [9] Hass, D.D., *Doctor Degree Thesis*, University of Virginia, May, 2001.
- [10] Almeida, D. S. et al., *Anais do Congresso Brasileiro de Engenharia e Ciência dos Materiais*, Natal, 2002.

- [11] Nicholls, J. R.; Lawson, K. J.; Johnstone, A.; Rickerby, D. S. Surface and Coatings Technology, n. 151-152, p. 383-391, 2002.
- [12] Kim, D. J., J. Am. Ceramic Soc., 73[1] 115-20 (1990).
- [13] Kim, D. J. e Tien, T. Y., J. Am. Ceramic Soc., 74[12]3061-65 (1991).
- [14] Lee, D. Y., et al, J. Materials Science Letters, 17 (1998) 185-187.
- [15] Guo, X. and Wang, Z., J. European Ceramic Society, 18 (1998) 237-240.
- [16] Raghavan, S. et al, Acta Materialia, 49 (2001) 169-179.
- [17] Hass, D.D.; Slifka, A. J.; Wadley, H. N. G. Acta Materialia, n. 49, p. 973-983, 2001.
- [18] Couto, P.; et al. Metrologia-2003. Anais. Recife, Pernambuco, Brasil, 2003.
- [19] Guo, H.; Bi, X., Gong, S., Xu, H., Scripta Materialia, n. 44 (2001) 683-687.
- [20] Raghavan, S.; et al., Scripta Materialia, 39 [8] (1998) 1119-1125.
- [21] Degiovaninni, A.; Lament, M. Revue Phys. Appl., v. 21, n. , p. 229-237, 1986.
- [22] Beddoes, J. Introduction to Stainless Steel - ASM International. J. G. Pars, 1999. 315 p.

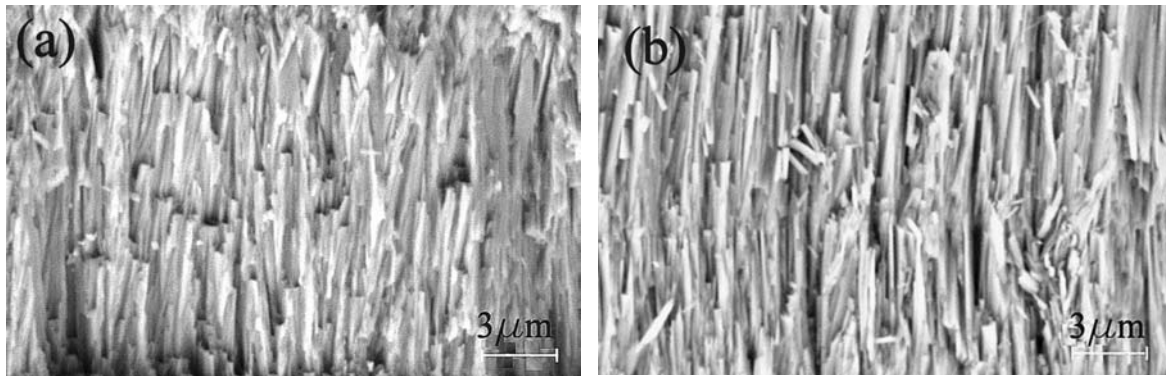


Figure 1: SEM of EB-PVD ceramic coatings fractured cross section.

- (a) Sample 1 ($\text{ZrO}_2 + 8 \text{ wt.}\% \text{ Y}_2\text{O}_3$)
- (b) Sample 2 ($\text{ZrO}_2 + 8 \text{ wt.}\% \text{ Y}_2\text{O}_3 + 6 \text{ wt.}\% \text{ Nb}_2\text{O}_5$)

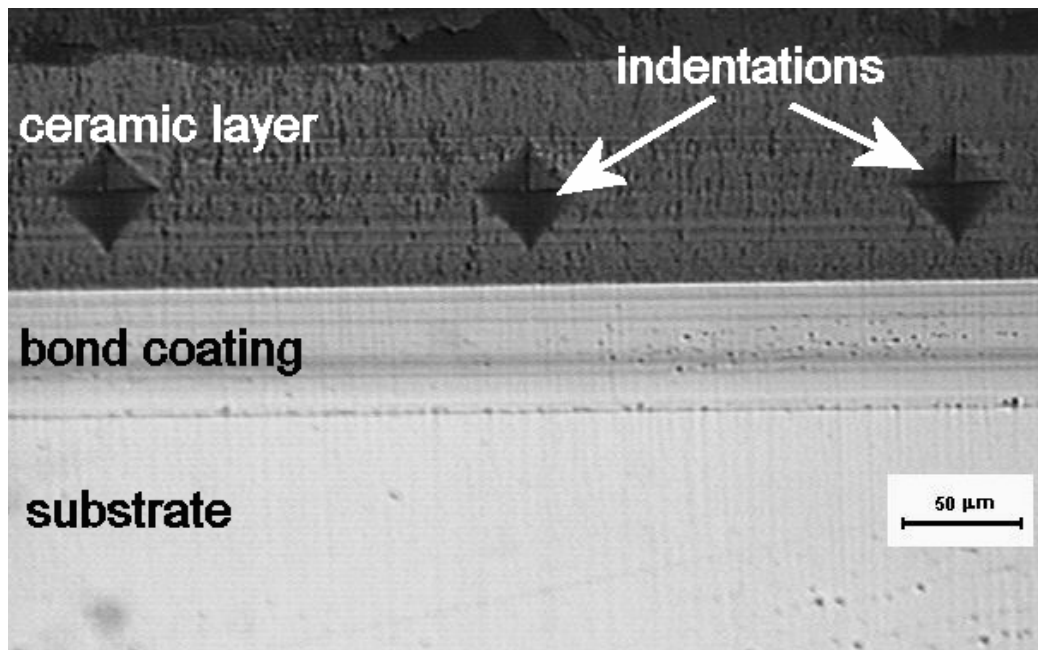


Figure 2: Optical micrograph TBC polished cross section with Vickers micro hardness indentations

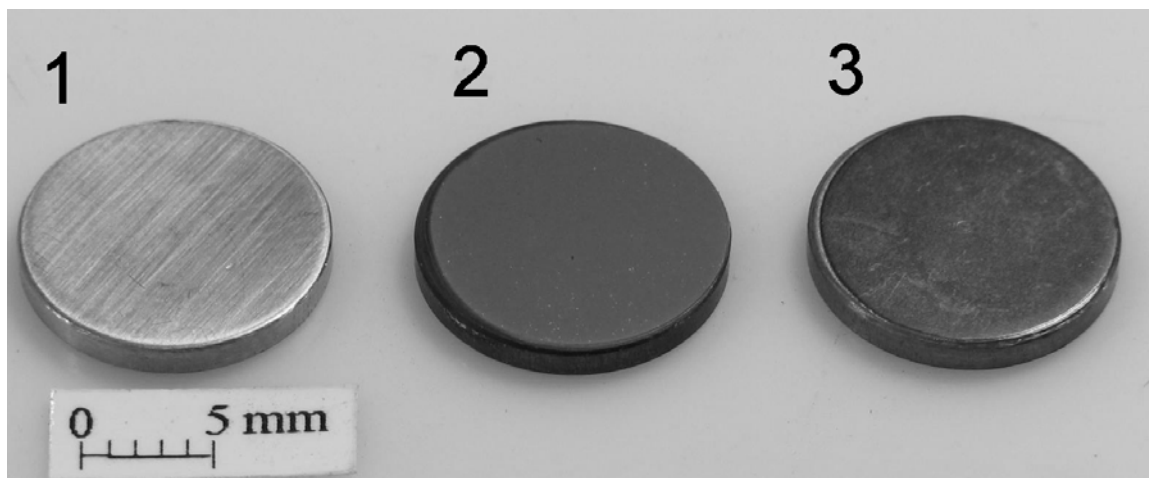


Figure 3: Samples used for thermal diffusivity determination. (1) without coating, (2) with coating of $\text{ZrO}_2 + 8 \text{ wt.}\% \text{ Y}_2\text{O}_3$, (3) with coating of $\text{ZrO}_2 + 8 \text{ wt.}\% \text{ Y}_2\text{O}_3 + 6 \text{ wt.}\% \text{ Nb}_2\text{O}_5$.

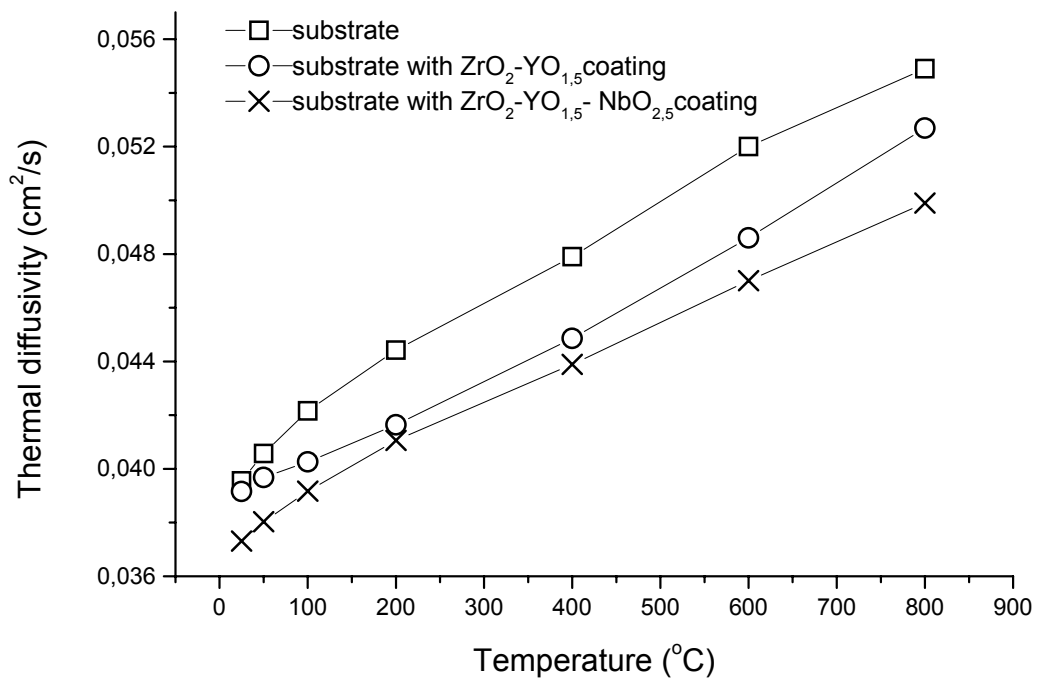


Figure 4: Results of the thermal diffusivity variation with the temperature for the samples.

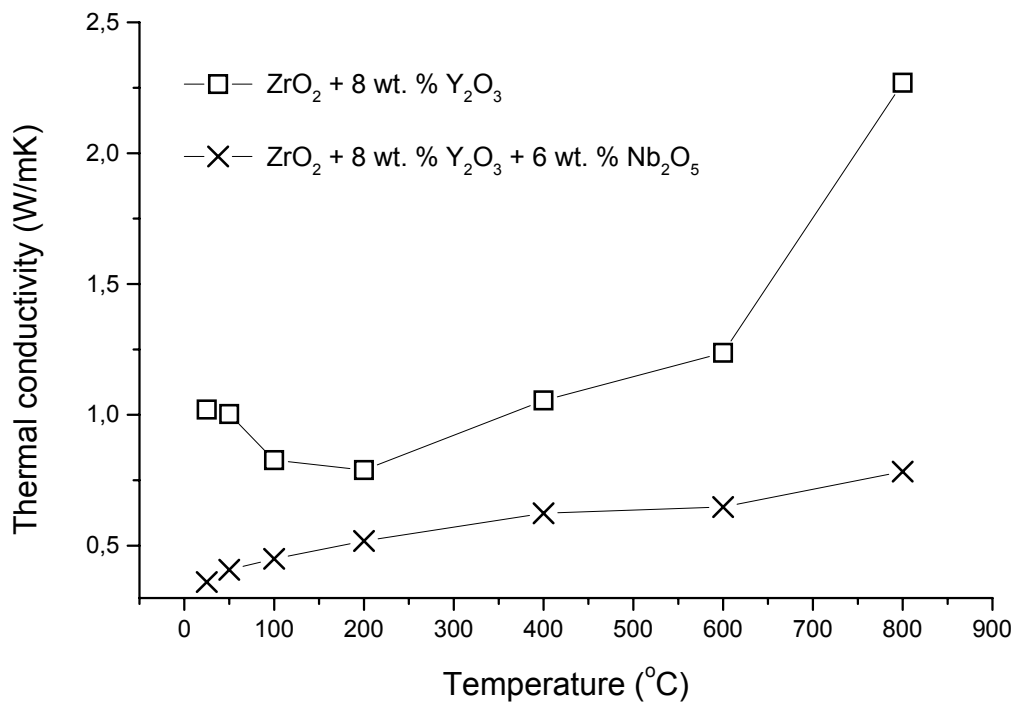


Figure 5: Coatings thermal conductivity with temperature.

Table I Effect of metallic oxide dopants in the zirconia thermal conductive reduction.

Dopant	Effect
Subtetravalent (Y_2O_3 , CaO , MgO)	- Oxygen vacancies are produced to maintain charge balance; - Cations effect is secondary;
Tetravalent (CeO_2)	- Ce ions are responsible for the thermal conductive reduction;
Supertetravalent (Ta_2O_5 , Nb_2O_5)	- Ions and atoms of differing ionic radius scatter phonons.

Table II Sample characteristics.

Sample	Diameter (mm)	Total thickness (mm)	Ceramic layer thickness (μm)	Specific mass (g/cm^3)	Vickers microhardness (Hv)	Material
1	12,7	1,579	-	8,00	-	SAE 304
2	12,7	1,603	60	6,06	363	ZrO_2 + 8 wt.% Y_2O_3
3	12,7	1,669	55	6,02	240	ZrO_2 + 8 wt.% Y_2O_3 + 6 wt. % Nb_2O_5

Table II Thermal diffusivity (cm^2/s) of sample (average of three measurements).

Temperature ($^{\circ}C$)	Sample 1		Sample 2		Sample 3	
	average	deviation	average	deviation	average	deviation
25	0,03955	0,00040	0,03916	0,00002	0,03731	0,00017
50	0,04057	0,00019	0,03968	0,00023	0,03803	0,00008
100	0,04216	0,00006	0,04026	0,00028	0,03917	0,00010
200	0,04442	0,00033	0,04164	0,00094	0,04106	0,00005
400	0,04790	0,00075	0,04486	0,00047	0,04389	0,00025
600	0,05200	0,00027	0,04860	0,00031	0,04701	0,00013
800	0,05490	0,00026	0,05269	0,00014	0,04990	0,00012

Table III Heat capacities and coatings thermal conductivity.

Temperature (°C)	Zirconia heat capacity (J/g.K)*	Thermal conductivity SAE 304 ** (W/m.K)	Coatings thermal conductivity (W/mK)	
			ZrO ₂ +8 wt. % Y ₂ O ₃	ZrO ₂ +8 wt. % Y ₂ O ₃ + 6 wt. % Nb ₂ O ₅
25	0,400	15,2	1,020	0,361
50	0,450	15,5	1,003	0,408
100	0,500	16,2	0,827	0,450
200	0,540	17,5	0,789	0,518
400	0,590	20,2	1,055	0,624
600	0,610	22,8	1,237	0,648
800	0,620	25,5	2,269	0,783

* Sintered yttria doped zirconia heat capacity [Raghavan, 1998].

**Substrate thermal conductivity.