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Characterisation of thermal barrier coatings and ultra high temperature composites deposited in a low pressure plasma reactor

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Abstract

A low pressure plasma process working at 600–800 Pa was used to deposit from aqueous solution ZrO_2–4 mol% Y_2O_3 (Yttria partially stabilized Zirconia–YpSZ) layers and stacks of Ta_2O_5/YpSZ layers for use as thermal barrier coatings (TBC). The observation of the cross section revealed a high porosity. The thermal diffusivity of the layers (1×10^{-7} m^2 s^{-1}) was measured by a laser flash technique and compared with values obtained on air plasma sprayed material (3×10^{-7} m^2 s^{-1}). The plasma reactor were also used to deposit ZrB_2–ZrO_2–SiC layers used as Ultra High Temperature Composite (UHTC) from aqueous solutions of zirconyl and Boron nitrates containing suspensions of SiC. Layers up to 100 μm thick were obtained on SiC substrates. XRD was used to study the crystallinity of the layer. The presence of ZrB_2 and SiC phases was confirmed after the deposition. XRD analysis showed that heat treatment at 1073 K under oxidizing conditions led to the loss of ZrB_2 and the appearance of ZrO_2 phases. To understand the behaviour of the layers to interaction with atomic oxygen (combustion for TBC and spacecraft re-entry phase for UHTC), we have measured the atomic oxygen recombination coefficient to determine the number of adsorption sites on the surface of the coatings. This was accomplished by using a low pressure plasma reactor coupled with optical spectroscopic measurements as a diagnostic technique.

Keywords: Traditional ceramics; Composites; Nanocomposites; Porosity; Thermal properties

1. Introduction

Research to reduce the consumption of fuel and the emissions of pollutants by turbines is a current subject of interest in aeronautics. For example, increasing the temperature of combustion leads to more efficient conversion of fuel into energy. The lifetime of materials used in turbines need to be increased by augmenting their resistance to corrosion phenomena at high temperature. Such improvements can also decrease the cost of turbines. One of the solutions consists in covering the combustion chamber and the blades with a thermal barrier coating (TBC). A TBC is a thick oxide layer used to protect the alloy of the blades and the combustion chamber against high temperatures. The oxide generally used is zirconia partially stabilized with yttrium (YpSZ).[1] This oxide has a low thermal diffusivity (2.5 W/m K with 1273 K as well as a good coefficient of thermal expansion ($\sim 10^{-5}$/°C).[2] These characteristics naturally make it a good material for use as a TBC. Several deposition techniques are used to obtain YpSZ layers such as EBPVD,[3] but also APS,[4] sol–gel,[5] PECVD,[6] and SPS[7]... In all cases, the YpSZ TBC should be highly porous in order to decrease the thermal diffusivity of the layers. For example, the SPS technique permits the deposition of 20% porous YpSZ. Covering YpSZ by Ta_2O_5 is envisaged to increase the lifetime of the TBC,[8] The tantalum oxide, porous or not, can act as a protective layer against the chemical attack of CaO–MgO–Al_2O_3–SiO_2 dusts which are present in the combustion chamber.[9] B.A. Nagaraj[8] has reported that a tantalum oxide deposited by EBPVD or Plasma Spray onto the thermal barrier coating has dielectric properties such that the CMAS deposits are less able to adhere to the exposed surface of the outer layer. As a result, the CMAS are unable to infiltrate the porous surface structure of the thermal barrier coating, and thus cannot attack and destroy YpSZ.

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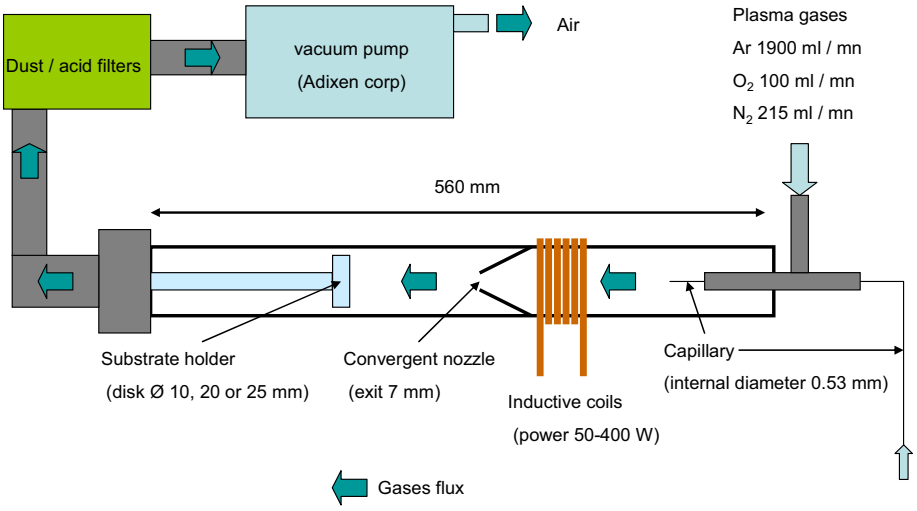


Fig. 1. Description of the low pressure plasma process developed to deposit thick ZrB_2–ZrO_2–SiC coatings.

High temperature composite layers are also investigated for aerospace applications, especially for the protection of re-entry vehicles against high temperature during re-entry into the earth's atmosphere. Due to the high temperature created by the interaction between vehicle and the atmosphere ($T > 1773$ K), UHTC materials (Ultra High-Temperature Composite) are now being studied.[10–13] For example, ZrB_2 presents an unique combination of mechanical and physical properties, including a high melting point (>3273 K), high thermal and electric conductivity, chemical inertia which counters molten metals, and very great impact resistance.[14] These characteristics of ZrB_2 make it an excellent candidate for a standard UHTC material. However, it may be very difficult to synthesize this kind of material as a thick layer with strong adhesion to the substrate.

In this work, a deposition technique developed in Chimie ParisTech was studied to deposit both YpSZ layers for TBC applications and ZrB_2–ZrO_2–SiC coatings to be used as UHTC materials. The principle of the deposition technique consists of introducing an aqueous solution of a nitrate salt or a solid suspension in water into a low pressure plasma discharge.[15–17] The aim of this work was to study the possibility of obtaining thick ceramic coatings using a plasma power of less than 0.5 kW. This power value was less than one tenth of that used for the "usual" deposition techniques such as Solution Plasma Spray and EBPVD (Power > 10 kW).[3,7] After the deposition, coatings were annealed and analyzed by several techniques (SEM, XRD, Laser Flash Technique, catalicity measurements) to study the stability, the morphology, the properties and the resistance of the deposited material.

2. Description of the low pressure plasma process and analyses performed on the oxide coatings

2.1. Principle of the plasma process

The deposition process consists of using the oxidizing properties of an Ar/Oxygen discharge to transform precursor nitrate salts into oxide layers. For example, a ZrO_2 coating can be obtained on a substrate when an aqueous solution containing zirconyl nitrates is injected into the plasma reactor. The plasma reactor consisted of a pyrex tube equipped with a convergent nozzle (pressure: 600–800 Pa). The injection system used for the deposition of YpSZ and Ta_2O_5 was described previously and additional information can be found in the literature.[17] Another injection system was developed for the deposition of ZrB_2–ZrO_2–SiC from an aqueous solution containing a SiC suspension. All the characteristics of the deposition technique are summarized in Fig. 1.

The chemical reactions which occur in the discharge lead to the formation of oxidant species such as O (from O_2) and $OH^{\bullet}$ (from the water of the aqueous solution) which are favorable reagents to transform precursor nitrate salts into oxide layers. One of the advantages of inductive plasma is the purity of the products which is high because the discharge is generated without internal electrodes which could otherwise pollute due to consumption and corrosion.

The coating deposition consisted of two steps. The synthesis of YpSZ was described previously.[17] For the deposition of ZrB_2–ZrO_2–SiC, the aqueous solution was injected during 1 min into a 120 W plasma discharge by means of a capillary as shown in Fig. 1 (step 1). As the liquid exits the capillary, the formation of aerosol occurs and the nitrate salt reacted with the oxidant species of the plasma to form a deposit on a substrate. The second step consisted of a 10 min post treatment using a 180 W plasma discharge, in which only air flowed through the capillary. The oxidant reagents present in the plasma discharge then eliminated residual water from the deposit and finished the transformation of the nitrates into the oxide layer. The cycle was repeated until the desired thickness of oxide was obtained. It is essential to note that the temperature of the substrate during the post treatment is less than 573 K. After the synthesis, a heat treatment was performed on the oxides to complete the elimination of nitrate and water and to crystallize the layers. This heat treatment was performed as follows: 1273 K for 4 h in air (heating and cooling rate: 473 K h^{-1}).

2.2. Aqueous solution used for the deposition of coatings

2.2.1. ZrO_2–Y_2O_3 and ZrO_2–Y_2O_3/Ta_2O_5

The precursors used for the deposition of YpSZ on 25 mm alumina disk consisted of a mixture of ZrO and Y nitrate powders dissolved in water in order to obtain YpSZ containing 5.26 mol% Y_2O_3. The characteristics of the nitrates are following:

- Zirconyl nitrates Acros Organics 99.5%: $[ZrO(NO_3)_2] = 0.34\ mol\ L^{-1}$,
- Yttrium nitrates Acros Organics 99.9%: $[Y(NO_3)_3] = 0.04\ mol\ L^{-1}$.

The solution containing Tantalum used to obtain Ta2O5 was home made at ONERA. The composition of the solution of Tantalum was $10\ g\ L^{-1}$ of Ta, $40\ g\ L^{-1}$ $H_2C_2O_4$ and 0.4% H_2SO_4. Concerning the deposition of YpSZ/Ta_2O_5 layer stacks, an aqueous solution containing ZrO and Y nitrates was first injected into the reactor. When the YpSZ coating was thick enough, the solution of Ta was introduced in order for it to then be covered by a thin layer of Ta_2O_5.

2.2.2. ZrB_2–ZrO_2–SiC

The aqueous solution was prepared in order to obtain a 20 vol% ZrB_2–SiC on a 25 mm SiC disk. The characteristics of the precursors used to prepare the solution are summed up here:

- Zirconyl nitrate Acros Organics 99.5%,
- Boron solution used for the calibration of ICP (Sigma–Aldrich), 10,034 ppm of B in water, 0.1% NH_4OH,
- SiC powder, β phase, $\rho = 3.217\ g\ cm^{-3}$, Alfa Aesar.

The aqueous solution obtained from the mixture of precursors contained a very high concentration of suspended SiC and exhibited a high viscosity.

2.3. Analyses used to study the morphology, structure and properties

Scanning Electron Microscopy (SEM) was used to study the morphology of the coatings. The observation of the cross section revealed the porosity and the attachment of the coatings to the substrate. X-ray diffraction (XRD) was employed to study the crystallinity, purity, thermal stability and the composition of the deposited coatings. For the case of the YpSZ layer, the thermal diffusivity was measured by a CO_2 laser technique as a function of the temperature.[18,19] The thermal diffusivity was compared to values acquired on two other YpSZ samples synthesized by other techniques. The aim was to determine if the TBC obtained in the low pressure plasma process was of the same quality as those deposited by an industrial plasma technique (APS).[19]

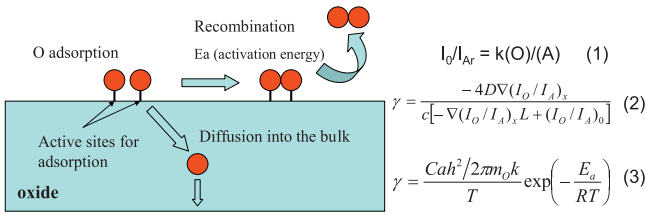


Fig. 2. Reactivity of oxide with atomic oxygen (recombination/diffusion) and equation used to determine the number of active sites and the γ coefficient for the recombination of O_2.

2.4. Properties of the surface: measure of the recombination of oxygen

The surface of the oxide layers used as TBC in aeronautics and as UHTC in aerospace are in contact with O at high temperature. The atomic oxygen results from the dissociation of O_2 due to the high temperatures in the combustion in a turbine or is produced in the plasma surrounding a spacecraft during re-entry in the atmosphere. It is important to investigate the recombination of atomic oxygen on the surface of the coating. By considering Ta_2O_5, which is envisaged to function as a protective layer against CMAS attack, the aim of the analysis was to determine if the interaction with O was similar to that observed for YpSZ. Concerning the ZrB_2–ZrO_2–SiC coating, the objectives of such analyses was to compare with the SiC material usually employed to protect the space shuttle.

The samples were placed in a low pressure plasma reactor which produces atomic oxygen.[20–22] As shown in Fig. 2, the number of adsorbed O depends on the number of active sites. It can be supposed that the atomic oxygen is eliminated from the surface by two possible pathways:

- Recombination to form O_2 (depends on the number of active recombination sites: Ca),
- Diffusion into the bulk (favored if γ are low) or the oxidation of the coating if it is not yet complete.

The recombination coefficient was calculated using the actinometry spectroscopic method. O atom concentration had been monitored with optical emissions from O (844.6 nm) and Ar (811.5 nm). The ratio I_O/I_{Ar} was proportional to the concentration ratio of O and Ar according to the following relation:

$$\frac{I_O}{I_{Ar}} \propto \frac{(O)}{(Ar)} \quad (1)$$

The movement of oxygen atoms in the boundary layer near the sample was controlled by diffusion and described by the general diffusion equation. The recombination coefficient γ was calculated from the atomic oxygen concentration profile along the reactor by using Eq. (2):

$$\gamma = \frac{-4D\nabla(I_O/I_A)_x}{c\left[-\nabla(I_O/I_A)_x L + (I_O/I_A)_0\right]} \quad (2)$$

where D is the binary coefficient ($m^2\ s^{-1}$), c the atomic velocity ($m\ s^{-1}$), L the width of the boundary layer (m), $\nabla(I_O/I_{Ar})_x$

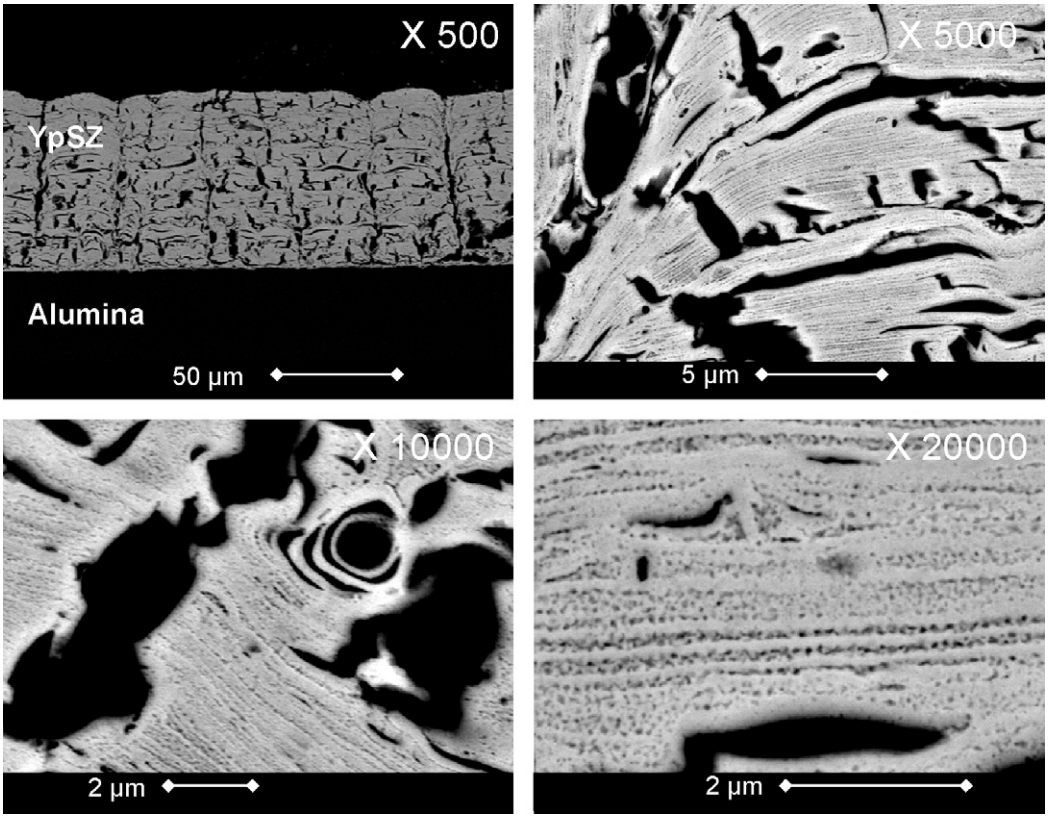


Fig. 3. Cross section of YpSZ layer deposited on alumina and heat-treated at 1273 K for 4 h.

the axial concentration gradient and $(I_O/I_{Ar})_0$ the steady state concentration.

The recombination coefficient is a function of the surface temperature according to the following Eq. (3):

$$\gamma = \frac{C_a h^2/2\pi m_O k}{T} \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where C_a is the number of active sites (atoms m^{-2}), h the Planck constant (6.626×10^{-34} J s), m_O mass of an oxygen atom (kg), k the Boltzmann constant ($1.380\,65 \times 10^{-23}$ J K^{-1}), T the temperature in K, E_a is the activation energy of the surface reaction (J mol^{-1}) and R the gas constant (8.314 J mol^{-1} K^{-1}. The activation energy of the process and the number of active sites could be deduced by calculating γ with Eq. (2) and by plotting ln (γT).[2]

3. Characteristics of YpSZ and YpSZ/Ta_2O_5 coatings

3.1. YpSZ layers deposited on alumina substrate

The observation of the cross section of YpSZ after the heat treatment revealed a thick porous coating up to 80 µm thick as shown in Fig. 3. By considering the time needed for the deposition of YpSZ (injection and post treatment), the growth rate was calculated to be around 10 µm h^{-1}. It can be seen that the YpSZ/alumina interface is typical of a coating adhering strongly on the substrate. Cracks are present between pores in the cross section and some of them seem to extend from the surface all the way down to the alumina substrate. These cracks are a favorable feature to increase the thermo-mechanical resistance of the YSZ coating. The SEM shows that the YpSZ layer exhibits pores with micrometric and nanometric sizes. By considering only the micrometric pores, and by using software called Visilog, the porosity was estimated to be around 25% (similar to SPS technique[7]). Water porosimetry was performed to measure the total porosity of the YpSZ coating. The total porosity was found to be 50% and the density was 3.1 g cm^{-3}. It is the presence of many nanometric pores which permits the coating to be highly porous. By observing the nano-pores under higher magnification, it can be seen in Fig. 3 that their size is less than 100 nm. The nano-porosity exhibits a horizontal lamellar nano-structure as shown at high magnification (×20,000). Such nano-structure could be a favorable feature to decrease the thermal diffusivity of the TBC.

The thermal diffusivity of the YpSZ coating was measured using a laser CO_2 flash technique. The results are summarized in Fig. 4. The highest diffusivity values were obtained from a single crystal, that is for a dense material.[18] The curves with intermediate values are typical of air plasma sprayed materials.[19] The curve exhibiting lower values corresponds to the YpSZ coating deposited in the low pressure plasma process after a heat treatment of 2 h at 1273 K. The results are in accordance with the SEM observation. The nano porosity probably leads to a decrease of the thermal diffusivity values. The voids and the lamellar nano structure contribute to a decrease in the heat flow that goes from the surface to the substrate. Further work will consist of the study of the thermal stability of the nano pores at high temperature (more than 1373 K) and the measurement

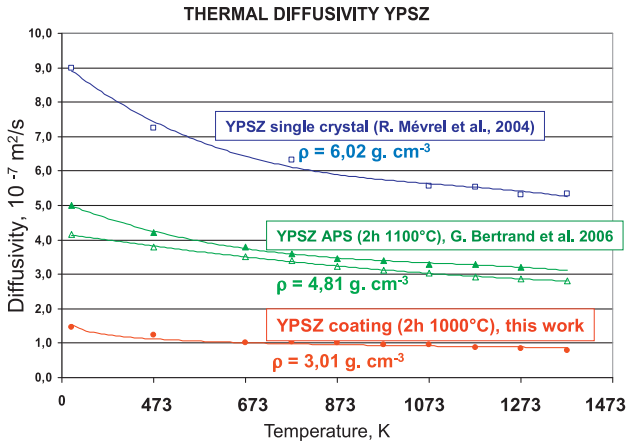


Fig. 4. Thermal diffusivity of YpSZ measured as a function of the temperature by a laser CO_2 flash technique.[18,19]

of the thermal conductivity of YpSZ in order to compare with classical techniques such as EBPVD and SPS.

3.2. Deposition of YpSZ/Ta_2O_5 stack

Fig. 5 presents the cross section of a stack of thin YpSZ/Ta_2O_5 layers observed by SEM. As expected, the nano pores previously described can be seen in the YpSZ layers. It can be observed that porous Ta_2O_5 fully covers the surface of YpSZ. EDX analyses performed on the cross section of the stack confirmed the presence of Ta on the partially stabilized zirconia. No Tantalum was detected in the YpSZ coating.

3.3. Recombination of oxygen at the surface of YpSZ and Ta_2O_5

In a turbine, the TBC is deposited onto a bondcoat layer, which permits the YpSZ coating to adhere to the super-alloyed blade. It is well-known that YpSZ contributes to the formation of a thin alumina coating (thermally grown oxide–TGO) between the TBC and the boundary layer due to the dissociation and the diffusion of O into the zirconia at high temperature. An alumina coating which is too think leads to the delamination and destruction of the TBC. Covering YpSZ by Ta_2O_5 could be a favorable feature to protect the TBC against CMAS, but it could also increase the dissociation and the diffusion of oxygen to the zirconia/boundary interface. The objective is then to determine if the reactivity of YpSZ and Ta_2O_5 with oxygen atom is the same by measuring the recombination of O_2 at the surface.

Fig. 6 shows the evolution of the recombination coefficient as a function of the surface temperature measured on the alumina substrate, YpSZ and Tantalum oxide. By comparing the three different samples, it can be observed that the recombination coefficient increases with the temperature, but that the Ta_2O_5 exhibits the higher γ coefficient at 1073 K. The analyses show that the coatings exhibit different surface properties upon reaction with oxygen. The surface of Ta_2O_5 exhibits a lower number of active sites than YpSZ which is a favorable feature to limit the adsorption of O. At the same time the recombination of O_2 is higher for the tantalum oxide. It could be supposed that the small quantity of adsorbed O is eliminated under O_2 instead of diffusing into the bulk of the material. Currently, it is not possible to definitively determine whether the Tantalum oxide is able to increase or decrease the diffusion of oxygen into the bulk and additional studies must be done. Further work will consist of coupling measurement of the γ coefficient using labeled O^{18} oxygen as the working gas with SIMS analyses to understand the mechanism for the diffusion of oxygen into YpSZ and Tantalum oxide. Employing Ta_2O_5 as a protective coating and as a diffusion barrier would be interesting to improve the lifetime of the TBC.

4. Characteristics of ZrB_2–ZrO_2–SiC coatings

4.1. Deposition of ZrB_2–ZrO_2–SiC coatings

A 100 μm thick ZrB_2–ZrO_2–SiC coating was obtained by using the low pressure plasma reactor (growth rate 60 μm h^{-1}). The variation of the composition of the layer was studied by X-ray diffraction analysis (Fig. 7), both after a simple heat treatment (1273 K—4 h) and after heat treatment coupled to oxidation by plasma exposure during the measurements of the recombination coefficient (1073 K during 2 min). The indexation of the peaks was performed using values found in the literature.[23] In the first case, peaks of high intensity were found for silicon carbide and ZrB_2. In the second case, the oxidation due to the air plasma treatment under thermal condition (1073 K) changed the deposited layer into a ZrB_2–ZrO_2–SiC composition (appearance of peaks corresponding to ZrO_2: angle $2\theta = 22, 59$)

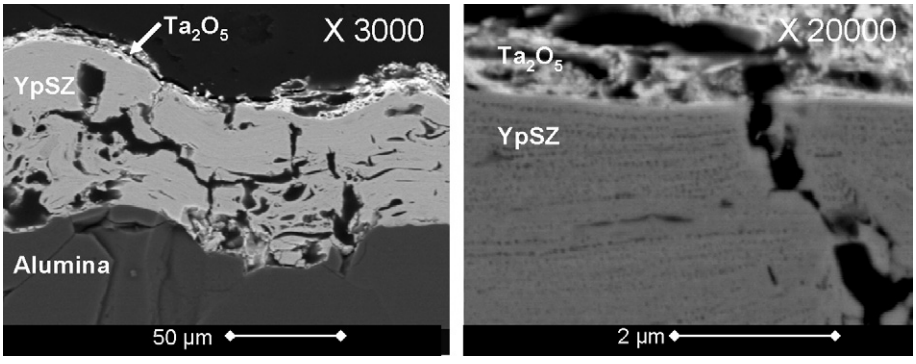
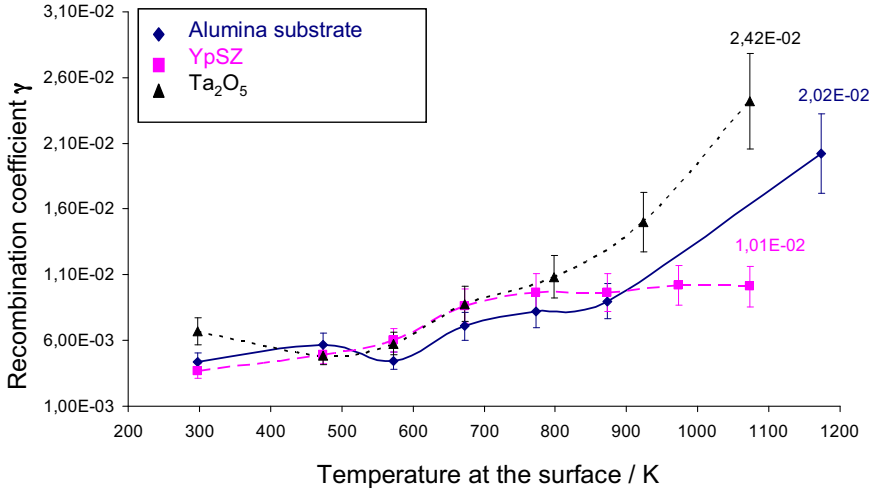


Fig. 5. Cross section of the YpSZ/Ta_2O_5 stack observed by SEM (after the heat treatment at 1273 K for 4 h).



	γ (±15%) 300 K	Active sites, Ca (atomes.m^{-2}) (±15%) 300K	γ (±15%) 1100 K or 1200 K
Alumina	4,38.10^{-03}	3,30.10^{19}	20.2.10^{-03}
YpSZ	3,65.10^{-03}	5,70.10^{19}	10,1.10^{-03}
Ta_2O_5	6,70.10^{-03}	2,97.10^{19}	24,2.10^{-03}

Fig. 6. Recombination coefficient γ and number of active sites estimated on alumina substrate, YpSZ and Ta_2O_5 coatings.

but no silica layer was observed. This transformation involves the formation of boron oxides. B_2O_3 can fill any cracks forming and thus prevent the diffusion of oxygen during atmospheric re-entry phase.

These results are in agreement with the SEM observation (Fig. 8). First of all, the thickness of the deposit is larger than one hundred microns and there is no problem of adhesion, even after exposure to an oxygen flux at 1273 K. The surface has a porous aspect, confirming the formation of ZrO_2. A multilayer system (SiO_2, ZrO_2, SiC + ZrO_2 layer) was not observed as expected.[12,14] This result be explained by several factors. The first one is the nature of the deposit. A plasma spray test was performed on the silicon carbide sample, whereas samples used in the literature[24] were obtained by hot pressing of ZrB_2 and SiC powders. The second factor is the difference in the thermal treatment in this work and other work. The maximum temperature and time of sample processing (2 h at 1273 K) are lower than those in the literature (temperature from 1473 K to 2473 K for treatment times between 30 and 60 min).

4.2. *Recombination of oxygen at the surface of ZrB_2–ZrO_2–SiC coatings*

Due to the high exothermicity of the atomic oxygen recombination reaction during the space shuttle re-entry process, it is interesting to follow the evolution of gamma coefficient from 473 K to 1073 K. As shown in Fig. 9, the recombination coefficient increases with temperature and exhibits higher values than those measured on the other SiC samples (SiC + Chromium).[25,26]

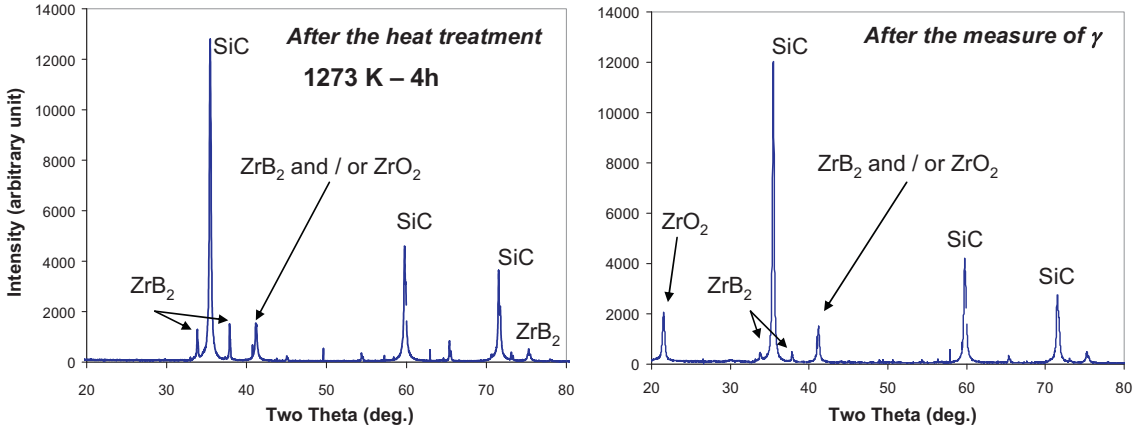


Fig. 7. XRD patterns of ZrB_2–ZrO_2–SiC performed after the heat treatment and the measure of γ.

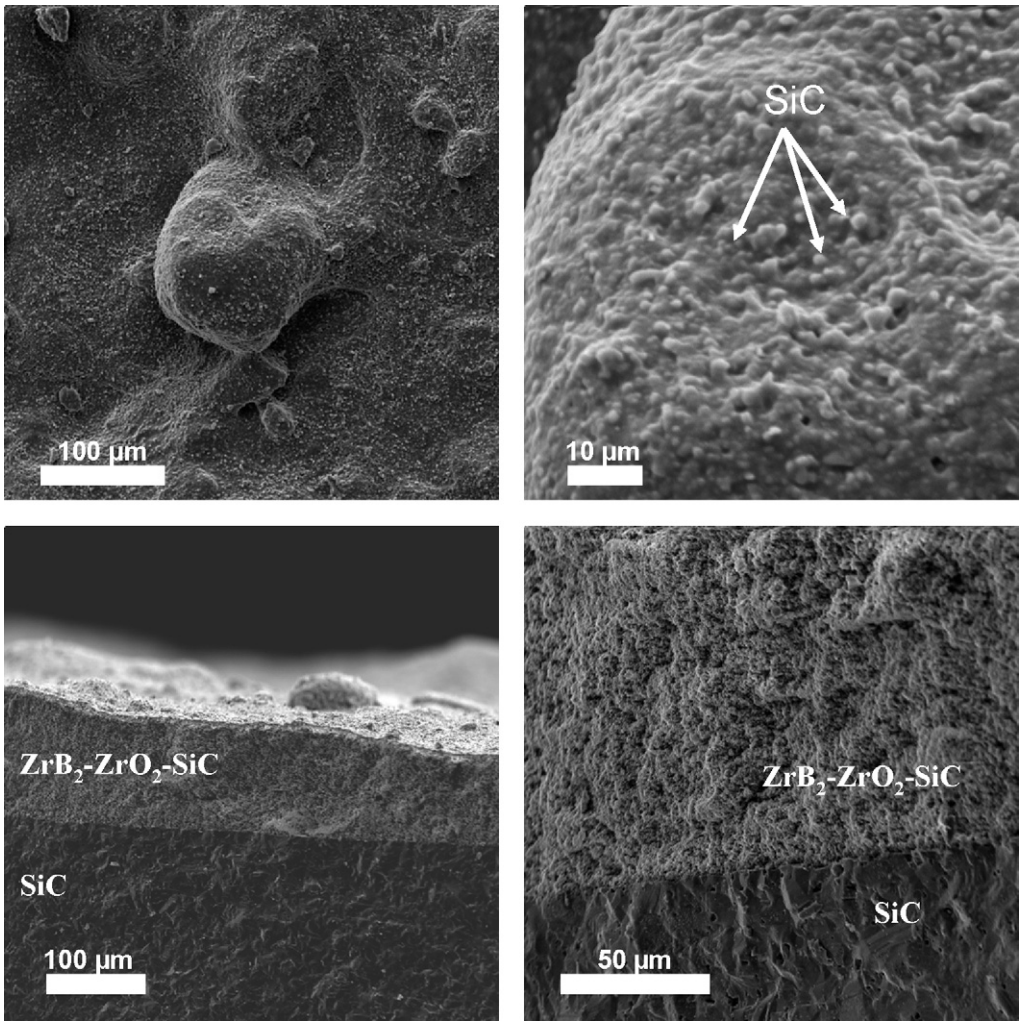


Fig. 8. Surface morphology and cross section of ZrB_2–ZrO_2–SiC observed by SEM after plasma exposure during the measurement of the recombination coefficient.

This behaviour can be explained by the fact that the nature of the surface changes during treatment. It has already been shown that the deposits of ZrB_2 turned into ZrO_2 and B_2O_3, thus greatly reducing the diffusion of oxygen. This change is found at 700 K which corresponds to the melting temperature of B_2O_3 and the oxidation of ZrB_2 into ZrO_2. At higher temperature, stabilization of the recombination coefficient is observed. At 1073 K, the value of recombination is lower than the value of that for blank silicon carbide, close to that of the thermal barrier YpSZ but higher than that of Cr + SiC deposition. This is certainly due to a lack of silica on surface (less recombinant).

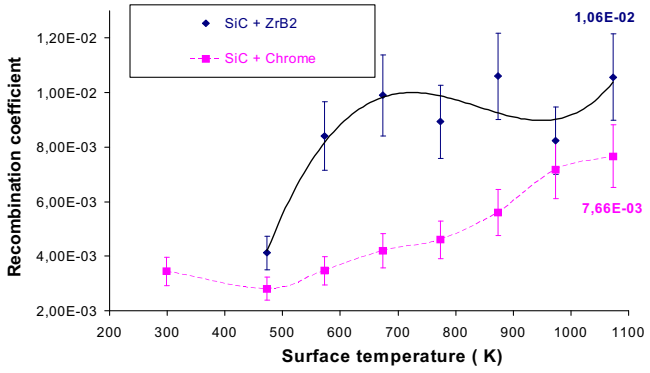


Fig. 9. Recombination coefficients γ versus surface temperature for ZrB_2–ZrO_2–SiC coatings.

5. Conclusion

A low pressure plasma process has been developed for the deposition of complex ceramic oxides under low temperature conditions. The injection system of the reactor permits the injection of aqueous solutions and aqueous solution with solid suspensions. By using this technique, it was possible to obtain YpSZ and YpSZ/Ta_2O_5 coatings for application as thermal barrier coatings (TBC) (growth rate: 10 µm h^{-1}). In particular, YpSZ exhibited micro and nano porosity which decreases the thermal diffusivity of the layer. The thermal diffusivity values obtained at high temperature are about one third of those obtained from plasma sprayed material. Measuring the recombination coefficient of both YpSZ and Ta_2O_5 underlined the fact that the surface properties of the layers are quite different. Ta_2O_5, which is envisaged as a protective layer against atmo-

spheric dust, could increase the diffusion of oxygen into the bulk of the coatings, which could lead to delamination of the TBC.

The deposition of complex ultra-high temperature composite material has also been achieved using the same process. A ZrB_2–ZrO_2–SiC coating up to 100 μm thick was deposited onto a SiC substrate (60 μm h^{-1}). No problem of adhesion was noted for the coating over a temperature range from 298 K to 1100 K. In comparison with the literature, no silica layer was observed despite the probable loss of silicon carbide. The formation of B_2O_3 seems to be key for the prevention of the diffusion of oxygen during atmospheric re-entry phase. Moreover, treatments at higher temperatures seem necessary to validate the deposition technique (at least up to 2000 K) and more work on the diffusion of oxygen (using O^{18} in the plasma) in this type of layer would also be helpful.

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