ABSTRACT

Catalytic recombination of dissociated atmospheric oxygen molecules on the surface of thermal protection systems (TPS) located on nose and leading edges can be a significant additional heat source during the atmospheric re-entry of a space vehicle. Typically, TPS of re-entry vehicles are designed considering the constituent materials as fully catalytic, a strongly conservative assumption that can lead to an over-sizing of the total mass required for the TPS. However, mass, performance, and cost considerations in future re-usable re-entry vehicles require a more sensible design approach based upon a more realistic assumption of partial catalicity.

Ground test simulation under atmospheric re-entry conditions is therefore necessary to characterize and select base materials for TPS. Very high temperature and low pressure air plasma are reproduced within the MESOX facility – out of equilibrium plasma – with a degree of dissociation of oxygen reaching 70% for an earth entry phase.

In this paper, experimental results are given on the catalytic properties of zirconium-based ceramics that represent a promising class of new TPS materials for the manufacturing of slender-shaped hot structures in hypersonic re-entry vehicles.

Two different zirconium-based compounds, produced by hot pressing and machined into their final shape by mean of electrical discharge machining or, alternatively, by diamond-tooling were tested in the temperature range 900-2500 K. Three kinds of zirconia different by their sintering additives were also tested in the same temperature range. The effects of the crystalline structure of zirconia materials and the one of surface machining for the zirconium-based ceramics are underlined and new experimental results on the recombination coefficient of atomic oxygen are obtained at high temperature on this class of new TPS.

1. MESOX SOLAR FACILITY AND DETERMINATION OF THE RECOMBINATION COEFFICIENT

The MESOX facility (Fig. 1) is described in details elsewhere [1, 2], here only its main features are outlined. The ceramic sample (25 mm diameter and 3 mm thickness) is put in a plasma reactor consisting of a silica tube (quartz), 50 cm length and 5 cm diameter with CaF2 viewports. The air plasma is generated by a 300 W microwave discharge surrounding the sample. The air plasma is generated by a 300 W microwave discharge surrounding the sample. The airflow is fixed at 4 l/h and is coming from to the top of the reactor and then pumped down. The sample is placed on a sample-holder at the centre of the plasma discharge. The reactor is positioned in such a way to let the sample be at 25 mm above the theoretical focus of the 6 kW solar furnace equipped with a variable opening shutter. Due to this shutter, the available incident concentrated solar flux can reach 5 MW.m⁻².

Fig. 1: MESOX solar facility and image of air plasma
The radial gradient in the reactor is 

The experiments are performed in steady state 

cylinder.

The recombination coefficient is the ratio of the flux of recombined atoms to the total flux of atoms impinging the surface:

\[ \gamma = \frac{O_{\text{rec}}}{O_{\text{tot}}} \]  

(1)

In this section, the method used for the measurement of the recombination coefficient \( \gamma \) of atomic oxygen on surface is briefly presented as it is detailed in [2].

OES and actinometry techniques were used to follow the relative atomic oxygen concentration profile along the discharge. A low known quantity of argon (5%) is introduced in the airflow and the evolution of the intensities ratio \( I_O/I_{Ar} \) of the 844.6 nm (O line) and 842.4 nm (Ar line) is measured along the discharge zone through the window (30 mm height and 9 mm width) performed in the waveguide. A cylindrical volume corresponding to the discharge zone is considered with every point represented by the coordinates (r, x). As the mean free path of oxygen atoms is 100 times less than the diameter of the reactor, the atom diffusion is given by the diffusion equation written in cylindrical coordinates that describes the variation of the oxygen concentration versus time for a fixed point (r, x) in the cylinder.

The experiments are performed in steady state conditions. The radial gradient in the reactor is negligible compared to the axial one, so the oxygen concentration is only function of x. Moreover, the stability of the \( I_O/I_{Ar} \) ratio in the reactor, measured without sample, allows neglecting the recombination in volume and on the reactor wall.

The intensities ratio profile leads to the determination of the recombination coefficient \( \gamma \) from the following equation:

\[ \gamma = \left( \frac{I_O}{I_{Ar}} \right)_{T=0} \frac{T_x}{T_L} - 1 \]

\[ \frac{4D_{O,air}}{V.L} \]  

(2)

with \( D_{O,air} \) the binary diffusion coefficient of O in air, V the mean square atomic oxygen velocity and L the thickness of the recombination boundary layer determined experimentally. Due to the temperature gradient between the sample (\( T_s \)) and the plasma bulk (\( T_L \)), the relative oxygen concentration ratio is related to the measured intensities ratio \( I_O/I_{Ar} \) respectively at the entrance of the reactor (x = L) and at the surface sample (x = 0). The partial pressure of the actinometer gas is assumed constant. The accuracy on \( \gamma \) has been estimated to be ± 30 %.

For the determination of the gas temperature \( T_L \), we used a method based on the comparison between experimental and calculated spectra for two N\(_2\) bands (0-2) and (1-3) in the second positive system of N\(_2\) (C\(_2^1\)\(T_u^+\) - B\(_3\)\(T_l^+\)). Calculated spectra are a powerful tool for the determination of temperature especially when the bands are complex. This technique allows taking into account physical phenomena as well as apparatus characteristics in order to derive temperatures (rotational and vibrational). The purpose to get accurate measurements is to find the couple of rotational temperature and apparatus function values (two free parameters) that minimizes the sum of the square differences between both experimental and calculated spectra. Accurate temperature values may then be derived by using a least mean square method with iterations on the rotational temperature and apparatus function values (two free parameters). The recombination coefficient of atomic oxygen on zirconia temperature values are used after to calculate the recombination coefficient \( \gamma \).

2. EXPERIMENTAL RESULTS FOR THE RECOMBINATION COEFFICIENT

There is no data in the open literature for the recombination coefficient of atomic oxygen on zirconia at high temperature. There are only few data on zirconium- and hafnium-based diboride ceramics obtained by Marschall [3] up to 923 K and our team [4, 5] up to 2000 K as these ceramic compounds represent a promising class of new heat shield materials for the manufacturing of slender-shaped hot structures in hypersonic re-entry vehicles [6]. Most of the published data for the recombination of atomic oxygen were focused only on silica and reaction-cured glass (detailed in [2]).
Three stabilized zirconia containing $\text{Y}_2\text{O}_3$ (YSZ), CaO (CSZ) or MgO (MSZ) as sintering aids (3-5%) were used to measure the recombination coefficient. The choice of these zirconia samples to study the recombination of atomic oxygen was made according to the fact that we have previously shown that the crystal lattice is an important parameter to take into account for the catalycity; for example, $\beta$-cristobalite is more catalytic than quartz by nearly one order of magnitude [2]. So, we chose zirconia with different microstructures due to the presence of several impurities in low content to see if it is an influential parameter on catalycity as we have already shown on alumina samples [7]. Moreover, zirconia is a high stable refractory oxide that allows to perform measurement of the recombination coefficient until very high temperatures (2500 K) to eventually measure a change in the curve $\log \gamma = f(1/T)$. Zirconia is also part of the oxides formed during the oxidation of Ultra-High Temperature Ceramics (UHTC) like $\text{ZrB}_2/\text{SiC}$ and $\text{ZrB}_2/\text{HfB}_2/\text{SiC}$ that can be used as protective materials during atmospheric re-entry at high speed [6].

$\text{ZrB}_2$-based UHTC materials with different composition and surface finishing were also used: $\text{ZrB}_2/\text{SiC}$ (A) and $\text{ZrB}_2/\text{HfB}_2/\text{SiC}$ (B). These materials were elaborated in Italy (CNR-ISTEC, Faenza). The two sintered materials were cut and shaped in billets of 25 mm diameter and 2 mm thickness for catalycity measurements using either diamond-loaded tools (DLT) or electrical discharge machining (EDM).

All the materials are characterized using several techniques (XRD, XPS, SEM and AFM) before and after test. In order to understand the results obtained on the recombination coefficient, some analyses after test are presented here.

### 2.1 Stabilized zirconia samples

The experimental results of the recombination coefficient $\gamma$ versus the reciprocal temperature are obtained for the three zirconia YSZ, CSZ and MSZ in the temperature range 900-2500 K, for 200 Pa total air pressure, and presented on Figs. 4 (YSZ), 5 (CSZ) and 6 (MSZ). The recombination coefficients $\gamma$ have been calculated for zirconia with the measured concentration profiles, obtained in steady-state conditions. The recombination coefficients for atomic oxygen are plotted on a logarithmic scale as a function of the reciprocal temperature for analysis by the Arrhenius equation:

$$\gamma = B \exp (-E_a/RT) \quad (3)$$

where $B$ is the pre-exponential coefficient, $E_a$ is the activation energy of the oxygen recombination process, $R$ the gas law constant, and $T$ is the temperature.

These results show the strong catalytic activity of zirconia when compared to the previous results obtained on silica [2].

We have to notice that, for both the zirconia stabilized with yttria (YSZ) or CaO (CSZ) around 1600 K, there is a change in the slope of the curves, due to the irreversible phase transformation from monoclinic (file 83-0944) to tetragonal (file 80-0965), as confirmed by the XRD patterns (Figs 7 and 8).

After catalycity measurement at the higher temperature level, the monoclinic zirconia is transformed into the tetragonal phase (and this is an irreversible process due to the sintering additives) as the temperature reached during the measurement is higher than the temperature of the sintering elaboration process. In that case when zirconia is mainly in the tetragonal phase, the recombination coefficient can be correlated by a unique Arrhenius fit (dotted lines in Figs. 5 and 6).

![Fig. 4: Recombination coefficient for the yttria-stabilized zirconia (YSZ) versus reciprocal temperature (black triangles: 1st measurement, open triangles: 2nd one after the high temperature exposure)](image1)

![Fig. 5: Recombination coefficient for the CaO-stabilized zirconia (CSZ) versus reciprocal temperature (black squares: 1st measurement, open squares: 2nd one after the high temperature exposure)](image2)

We obtain the following expressions for the recombination coefficient $\gamma$ and the respective activation energies $E_a$:

$$\gamma = B \exp (-E_a/RT) \quad (3)$$
For the zirconia stabilized with Y₂O₃ (YSZ):
\[ \gamma \approx 8.10^{-2} \] until 1600 K (before the M->T phase transformation) then,
\[ \gamma = 1.315 \exp(-4796/T) \] with \( E_a \approx 40 \text{ kJ/mol} \) above 1600 K.
When zirconia is mainly in the tetragonal phase, then in the temperature range 900-2300 K,
\[ \gamma = 0.579 \exp(-3347/T) \] with \( E_a \approx 21 \text{ kJ/mol} \).

For the zirconia stabilized with CaO (CSZ):
\[ \gamma = 0.148 \exp(-804/T) \] and \( E_a \approx 7 \text{ kJ/mol} \) before the M->T phase transformation.
When zirconia is mainly in the tetragonal phase, then in the temperature range 900-2500 K,
\[ \gamma = 0.768 \exp(-3347/T) \] and \( E_a \approx 28 \text{ kJ/mol} \).

For the zirconia with MgO (MSZ):
\[ \gamma = 0.18 \exp(-849/T) \] and \( E_a = 7 \text{ kJ/mol} \) for \( 900 \leq T \leq 1600 \) K. Only measurements up to 1600 K have been done on this material due to the crack of the samples occurring during the M->T phase transformation.

These results show the strong catalytic activity of zirconia if we compare with our previous results obtained on silica [2]. Table 1 presents the mean experimental values obtained for the recombination coefficient for the monoclinic (M) and tetragonal (T) phases. For example, for the yttria-stabilized zirconia YSZ when the T phase is present in the sample, the \( \gamma \) coefficient goes from 0.040 to 0.108 as it is almost constant when the M phase is still present (8.10^{-2}). On this table, we can see that the \( \gamma \) coefficient increases with temperature until a maximum value of 0.20 for 2400 K for both YSZ and CSZ zirconia ceramics. At this temperature level, zirconia is less catalytic than alumina [7] and materials forming an oxide layer partly composed of zirconia will be better as protective materials for atmospheric re-entry than aluminum-based materials.

Figs. 7 and 8 present the XRD patterns of the samples YSZ and CSZ respectively before and after the measurement of \( \gamma \) at high temperature. On these two figures, the monoclinic (M) phase has nearly disappeared for the YSZ material (Fig. 7) and is very reduced for the CSZ one (Fig. 8) after high temperature exposure, in agreement with the results obtained for the recombination coefficient. These results confirm the influence of the crystalline structure of the material upon its catalycity as we have already proved on silica polymorphs [2].

### Table 1: Experimental mean values of the recombination coefficient obtained for the three stabilized zirconia samples for the two phases M and T.

<table>
<thead>
<tr>
<th>Samples (T/K)</th>
<th>( \gamma ) YSZ M-T</th>
<th>( \gamma ) CSZ M-T</th>
<th>( \gamma ) MSZ M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.084 - 0.040</td>
<td>0.061 - 0.036</td>
<td>0.073</td>
</tr>
<tr>
<td>1400</td>
<td>0.090 - 0.043</td>
<td>0.071 - 0.056</td>
<td>0.095</td>
</tr>
<tr>
<td>1600</td>
<td>0.079 - 0.108</td>
<td>0.085</td>
<td>0.109</td>
</tr>
<tr>
<td>1800</td>
<td>0.094 - 0.123</td>
<td>0.102</td>
<td>-</td>
</tr>
<tr>
<td>2000</td>
<td>0.123 - 0.155</td>
<td>0.120</td>
<td>-</td>
</tr>
<tr>
<td>2200</td>
<td>0.163 - 0.209</td>
<td>0.186</td>
<td>-</td>
</tr>
<tr>
<td>2400</td>
<td>0.210</td>
<td>0.202</td>
<td>-</td>
</tr>
</tbody>
</table>
2.2 ZrB$_2$-based UHTC samples

Dense ceramics were obtained by hot pressing of the following two powder compositions (vol %):

- Material A: ZrB$_2$ + 15 SiC
- Material B: ZrB$_2$ + 15 SiC + 10 HfB$_2$

with 2 vol.% MoSi$_2$ as a sintering aid in both compositions.

The catalycity data are hereby discussed by comparing the two materials A and B (different composition) and, for EDM and DLT (different surface finish).

Figs. 9 and 10 reproduced the results obtained for the recombination coefficient on the four materials: A-EDM and A-DLT (Fig. 9), B-EDM and B-DLT (Fig. 10).

In the temperature range 900-2000 K, A-DLT (ZrB$_2$-SiC) shows higher catalytic activity than the A-EDM material. This behavior is due to the presence of a thin oxide layer formed during EDM, which is consistent with reports showing that amorphous and crystalline silicon oxides have low catalytic activity for oxygen recombination. As can be seen on Fig. 9, at about 1200 K, the gamma curve of A-EDM exhibited a change in the slope: at temperatures lower than 1200 K, the recombination coefficient is almost constant (around 8.10$^{-3}$ close to the quartz one [2]). It is evident that the function ln $\gamma = f(1/T)$ does not follow an Arrhenius type law that predicts a linear behavior in all the temperature range. This catalytic behavior of the A-EDM sample confirms the analogous experimental data published in our previous work [4] and is probably related to the M-$\rightarrow$T phase transformation of the zirconia present in the oxide layer if we compare to the results presented before for zirconia. It is important to point out that this double-slope trend does not occur in the A-DLT sample, thus suggesting that the surface finish and/or the surface micro-damage and oxidation occurring during EDM may play a significant role in defining the catalytic behavior of this UHTC composition. This is confirmed by the XPS analyses of the surfaces of the two samples A-EDM and A-DLT after $\gamma$ measurement.

On the contrary, a less evident difference is recorded between the $\gamma$ values of B-DLT and B-EDM samples (Fig. 10). Both samples exhibit $\gamma$ values ranging from 10$^{-2}$ and 10$^{-1}$ across the investigated temperature range and follow Arrhenius-like temperature dependence, just like the sample A-DLT.

X-ray Photoelectron Spectroscopy (XPS) was used to analyze the surfaces of the reference and tested samples after the measurement of the recombination coefficient $\gamma$. The elementary compositions have been calculated from the area of each photoelectron peak O 1s, C 1s, Si 2p, Zr 3d, B 1s and Hf 4f, using the effective ionization cross sections given by Scofield [8] and corrected by the square root of the kinetic energy of each photoelectron.

The quantitative results were obtained on the surfaces after Ar$^+$ ion etching during 15 min under 1 kV. This treatment allows to partially remove the atmospheric carbon contamination and to carry out analysis on the atomic layers located at around 30 nm under the first contaminated layer. It has to be noticed that the carbon contamination is not totally removed. This incomplete decontamination can be due to the surface roughness (the arithmetic roughness $R_a$ is equal to 0.58 $\mu$m for A-EDM and 0.98 for B-EDM; for A and B-DLT samples, it is lower and equal to 0.14 $\mu$m) and/or to the lower efficiency of the ion etching on insulating materials.

Table 2 presents the elementary composition of the UHTC samples before and after treatment at high temperature under air plasma. For the ZrB$_2$/SiC EDM reference sample (A-EDM ref), the elementary

Table 2: elementary composition (%) on reference and tested samples determined by XPS analysis

<table>
<thead>
<tr>
<th>elem_comp</th>
<th>C 1s</th>
<th>O 1s</th>
<th>Si 2p</th>
<th>Zr 3d</th>
<th>B 1s</th>
<th>Hf 4f</th>
</tr>
</thead>
<tbody>
<tr>
<td>samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-EDM ref</td>
<td>21.4</td>
<td>53.2</td>
<td>9.0</td>
<td>12.9</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>G (1820 K)</td>
<td>2.6</td>
<td>65.2</td>
<td>26.8</td>
<td>3.4</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>K (1980 K)</td>
<td>12.2</td>
<td>59.2</td>
<td>3.3</td>
<td>25.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B-EDM ref</td>
<td>38.6</td>
<td>41.9</td>
<td>3.5</td>
<td>10.6</td>
<td>4.7</td>
<td>0.7</td>
</tr>
<tr>
<td>S (1820 K)</td>
<td>31.6</td>
<td>41.9</td>
<td>16.5</td>
<td>3.8</td>
<td>6.2</td>
<td>-</td>
</tr>
<tr>
<td>B-DLT ref</td>
<td>23.0</td>
<td>38.4</td>
<td>5.4</td>
<td>15.9</td>
<td>15.8</td>
<td>1.5</td>
</tr>
<tr>
<td>W (1800 K)</td>
<td>1.7</td>
<td>64.3</td>
<td>28.7</td>
<td>2.9</td>
<td>2.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>
composition close to the surface shows that it contains mainly ZrB₂ and SiC and few oxides SiO₂ and ZrO₂. After heat treatment at 1820 K (sample G), the surface is mainly composed of SiO₂ and few ZrO₂ and B₂O₃ (borosilicate glass). When the temperature is increased to 1980 K (sample K), silica vaporizes and finally the surface is mainly composed of ZrO₂. This is confirmed by the morphology of the SEM images of Fig. 11.

![Fig. 11: SEM images of the A-EDM reference sample (top), and the two samples after γ measurement: left down, 1820 K and right down, 1980 K.](image)

On Fig. 11, the micrographs of the samples A-EDM before and after high temperature and air plasma exposure are reported. The A-EDM image in Fig. 11 shows different surface morphology according to the maximum temperature used for the γ measurement. The sample after 1820 K presents a surface with a borosilicate glassy layer composed mainly of silica with small part of boron and zirconium oxides (2-3% at. detected by XPS) present as crystalline islands on the SEM image. After the γ measurement at 1980 K, the surface of the sample is mainly constituted by zirconia (crystalline as revealed by XRD) with only few traces of silica (3% at. as detected by XPS). This is due to the fact that this sample was exposed at a maximum temperature of 1980 K at which silica disappeared. Although the mechanism was not studied, the silica loss could be due to decomposition into volatile SiO.

On Fig. 12, B-EDM and B-DLT exposed in air plasma at a maximal temperature of 1800 K show the formation of a uniform glassy layer that was confirmed to be a borosilicate glass. XPS analyses have indeed shown that the composition of the layer was mainly silica with small amounts of boron oxide (2-6 at.%), zirconia (3-4 at.%) and very small amounts of hafnia (0.2 at.%).

Even if this is not evident from the SEM micrographs, we can suppose that the different catalytic behavior of the A-EDM is related to the nature of the surface modification induced by the electrical discharge machining on this material only. Probably, the higher refractoriness of the HfB₂ included in material B limits the surface alterations occurring during EDM.

![Fig. 12: SEM images of the B-EDM reference sample (left top) and after γ measurement at 1820 K (right top), and of B-DLT reference sample (left down) and after γ measurement at 1800 K (right down).](image)

With regards to catalytic measurements, the obtained results show for all the tested UHTC samples a low catalytic activity in the examined temperature range with a maximum measured value for atomic oxygen recombination coefficient γ of about 0.1 for the ZrB₂/HfB₂-based material. DLT ZrB₂/SiC, and both EDM and DLT ZrB₂/HfB₂/SiC follow an Arrhenius type law in the whole temperature range, and they also show similar gamma values ranging from 10⁻² about at 800 K to 10⁻¹ at 1800 K. The catalytic behavior appears to be dictated again by the oxide scale that develops on the samples exposed in high temperature air plasma, regardless of the samples composition and surface finish.

On the contrary, the EDM ZrB₂/SiC sample is characterized by a peculiar catalytic behavior: in fact, at about 1200 K the kinetic equation related to the atomic oxygen recombination mechanism on the surface of EDM ZrB₂/SiC changes: for higher temperatures, the sample follows an Arrhenius type law while for lower temperatures γ becomes almost constant. This sample exhibits a minimum value of γ of about 8.10⁻³ for
temperatures up to 1200 K and a maximum value of $3.10^{-2}$ at 1980 K. This result can be linked to the behavior observed for the $\gamma$ evolution versus reciprocal temperature of the stabilized zirconia (YSZ and CSZ) due to the presence of the monoclinic phase.

3. CONCLUSIONS
The experimental determination of the recombination coefficient on stabilized zirconia and on UHTC materials of different composition and surface mechanical treatment has been realized in the MESOX set-up. Zirconia samples were used to show the influence of sintering aids, but finally, the main influence observed is the one due to the irreversible phase transformation from monoclinic to tetragonal. Sintered zirconia samples present recombination coefficient ranging from $8.10^{-2}$ at 900 K to 0.2 at 2400 K after stabilization of the tetragonal phase.

The use of UHTC to manufacture thermal protection systems (TPS) and increase the heat resistance of structural for sharp-shaped hypersonic re-entry vehicles needs the complete characterization of their radiative and catalytic properties. The recombination coefficient of atomic oxygen for sintered zirconium diboride-based composite ceramics - ZrB$_2$/SiC and ZrB$_2$/HfB$_2$/SiC - was measured as a function of temperature. Moreover, in order to describe the effect of the machining method on catalycity, two kinds of surface manufacturing were considered: samples manufactured by electrical discharge machining (EDM) and machined by diamond-loaded tools (DLT). Finally, these samples present a low catalytic activity when a borosilicate glassy layer with small parts of zirconia is formed on the surface – below 1800 K – and when zirconia is present in higher quantity, then the recombination coefficient can be close to 0.1 at 2000 K.

4. REFERENCES


