Catalysis of Metallic and Ceramic TPS-Materials

By Georg HERDRICH and Markus FERTIG

Institut für Raumfahrtsysteme, Universität Stuttgart, Germany

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A facility for the determination of total and spectral emission coefficients is described. Values of measured total emission coefficients of the different high temperature ceramics such as HfO$_2$, Al$_2$O$_3$, Y$_2$O$_3$ and the metals/alloys Tungsten, TZM and PM1000 in the temperature regime of 750 – 1800 K are given. The drastic influence of the oxidation state of PM1000 on the emissivity is discussed. Additionally, results of an investigation of the influence of surface roughness and surface topology on emissivity are presented. Therefore, three SSiC samples with root-mean-squared roughness surface roughness from $R_q = 0.05$ to $R_q = 0.66$ have been prepared using common finishing operations. The tests showed that the emissivity increased about 10 % with an increase of the surface roughness even in the regime where $R_q$ values are in the same magnitude or much smaller than the maximum emitting wavelength. Knowledge on emissivity is a basis for the analysis of thermo-chemical behavior and related properties (i.e. recombination coefficients) as the two properties influence each other. In a second step a high enthalpy inductively heated plasma wind tunnel (PWK3) is described and a methodology to derive recombination coefficients is explained. Recombination coefficients for the above mentioned materials have been determined in pure oxygen plasma. The methodology for the determination of recombination coefficients of ceramic and metallic Thermal Protection System (TPS) materials in single species gases used at IRS and its latest improvements are presented. Test results for the recombination coefficients in oxygen plasma are shown between 1469 and 2072 K.

Key Words: catalysis, emission coefficient, high temperature materials

Nomenclature

- A: area ($m^2$)
- $c_p$: specific heat capacity ($J/(kg\cdot K)$)
- f: correction function (-)
- h: specific enthalpy ($J/kg$)
- $k_w$: recombination rate constant ($s^{-1}$)
- $L_e$: Lewis number (-)
- m: mass flow (rate) ($kg/s$)
- M: Molar mass ($kg/mol$)
- M: specific radiation ($W/m^2$)
- Ma: mach number (-)
- p: pressure ($Pa$)
- $q$: area specific heat flux ($W/m^2$)
- R: radius (m)
- $R_{eff}$: effective probe radius (m)
- $\Re$: universal gas constant ($J/(mol\cdot K)$)
- $S_e$: Schmidt number (-)
- S: Pyrometer signal (V)
- t: time (s)
- T: Temperature (K)
- u: velocity (m/s)
- x: axial coordinate (m)
- y: radial coordinate (m)
- $\beta$: accommodation coefficient (-)
- $\gamma$: recombination coefficient (-)
- $\epsilon$: emission coefficient (-)
- $\phi$: angle of the point (rad)
- $\lambda$: wavelength (nm)
- $\kappa$: isentropic exponent (-)
- $\mu$: dynamic viscosity ($kg/(ms)$)
- $\theta$: angle of bow shock (rad)
- $\rho$: density ($kg/m^3$)
- $\phi$: Goulard boundary layer model correction function for catalysis (-)
- $\Delta$: dissociation degree (-)

Subscripts

- a: apparent (related to temperature measurement)
- b: backside
- D: dissociation
- e: boundary layer edge (stagnation)
- fc: fully catalytic
- f: initial
- finit: finit catalytic
- Mat: material
- N: nitrogen
- L: structural loss
- O: oxygen
- Pl: plasma
- pos: position
- $S$: sample
- $tot$: total
- w: wall
- $\infty$: free stream

Abbreviations

- PAT: Passive to Active Transition
- APT: Active to Passive Transition
1. Introduction

Launch Vehicles and related entry vehicles encounter significant gas velocities and aero thermal heat loads during ascent and re-entry. To withstand these loads, the vehicle requires a thermal protection system (TPS). Within the ESA Winglet Launcher Studies (WLS), the Future European Space Transportation Investigation Programme (FESTIP) and the Future Launcher Preparatory Program (FLPP) the development of a hybrid hot load-carrying TPS, partly of Silicon based materials for hot regions like the nose and metallic alloys for colder parts like side panels has been advanced. Especially Oxide Dispersed Strengthened alloys like PM1000 have proven promising because of their high temperature strength, creep behavior and oxidation resistance.

In contrast to the amount of work done in the field of mechanical properties characterization and engineering development, less experimental work has been conducted to characterize the catalytic and optical properties of such materials. However, these properties are of great importance because they are determining the thermo chemical behavior of the TPS during a given re-entry trajectory of a vehicle. Due to the high gas velocities in the re-entry phase, the oxygen and the nitrogen molecules passing through the bow shock become at least partly dissociated. Depending on the environmental conditions (e.g. pressure and temperature of the TPS material) these atoms will recombine at different rates following different mechanisms. In any case, the released recombination energy of this exothermal chemical reaction results in an additional heat flux on the TPS and the gas phase in the boundary layer. The increase in heat flux can be as much as 3 times for an air system, comparing a non-catalytic to a fully catalytic material.

Both catalysis and emissivity of a TPS material depend primarily on temperature. The heat flux onto a spacecraft itself becomes indirectly dependant on the TPS surface temperature. In case of common Silicon based TPS materials, the raised temperatures may trigger another surface phenomenon, which interacts with catalysis: passive and active Oxidation along with a further rapid temperature increase and consequently a much higher mass loss rate.

Fig. 1. Catalysis, emissivity and reaction scheme interaction

This overall interaction between emissivity, catalysis and reaction schemes is in principal shown in Fig. 1. It becomes clear that methodologies to assess surface reaction schemes require the precise knowledge of other material related properties. The emissivity is one of the most important of these parameters, see also section 3.5.

In order to develop and weight-optimized TPS for future, it is absolutely necessary to determine related material properties and closely investigate these surface phenomena and their interaction in ground tests and flight experiments. A promising assessment is the successful combination of experimental, in-flight data from the ballistic capsule MIRKA and numerical models as performed in Ref. 7). In a further step, a critical consideration of catalysis data with respect to the different methodologies to determine catalysis has to be performed. However, a survey of the different methods goes beyond this paper. This has been part of 6th European Symposium on Aerothermodynamics for Space in Versailles, Paris, France, November 2008, where specialist in gas surface interaction presented on both experimental and numerical assessment of catalysis and surface reactions.

2. Emissivity determination

Two approaches were realized at IRS to determine both total and spectral emissivities for typical high temperature materials.

The first type of emissivity determination can be considered as in situ determination. Here, a plasma wind tunnel probe equipped with a miniaturized pyrometer measuring the rear side temperatures of the specimen is used. The measured data are combined with simultaneously performed front side temperature measurements for which an external pyrometer is used. The application of simple analyses and the knowledge of the transfer functions of the pyrometers are the basis for the determination of the emissivity. Here, the resulting information is limited to external pyrometers that have a measurement wavelength which is undisturbed by the plasma of the operated plasma wind tunnel. The advantage of the method is that the emissivity values are representative for the used front side temperature pyrometer i.e. the data can be considered as to be individual values for the pyrometer that is usually used e.g. within plasma wind tunnel investigations. This method goes beyond this document. However, corresponding results were published in Ref. 8).

With the second type a more dedicated and flexible method is provided. Here, a modified black body source is used where the effective emissivity of the cavity of an electrically heated graphite rod which is close to one is compared with the real emissivity of the specimen to be investigated. This is done by a comparison of the two measured temperatures, one is the cavity temperature and the other is the specimen’s temperature. By analyses of the pyrometer signals the emissivities can be derived. The method allows the determination of both total and spectral emissivities. This property can be chosen by choosing the type of pyrometer i.e. either a spectral or a total radiation pyrometer.
2.1. Emissivity Measurement Facility (EMF)

The IRS emissivity measurement facility EMF has been qualified for total and spectral emissivities of ceramic and metallic TPS materials\(^1\). It is possible to test the same geometry (26.5 mm diameter i.e. the European Standard Sample) as in the plasma wind tunnel facilities, thus it is possible to test blank metal samples and samples that have been exposed to the thermo chemical loads during plasma wind tunnel testing. (Herein the samples from the Double probe measurements see section 3.5).

In its working principle the EMF has similarities to a variable blackbody source. However, the apparatus is much more complex, as a moveable sample support system within the black body cavity is required. The test setup of the facility is shown in Fig. 2.

The black body (BB) cavity is realized with a graphite rod \((\epsilon = 0.9)\) with a high length to diameter ratio which is resistively heated up for the measurements. The realized configuration has an apparent emissivity \(\epsilon > 0.999\), thus it can be regarded as a BB. The rod also has to maintain an isothermal profile to properly approximate a BB source. This was achieved by an optimization process, were the outline and the wall thickness of the rod was varied over its length.

Inside the rod the material sample is mounted on a graphite sample holder which is itself fixed on a Molybdenum stick. On the back side of the vacuum vessel (see right side of Fig. 2) the stick is guided through a special flange. The flange houses a sealing assembly that allows the axial shift of the stick while maintaining the vacuum characteristic of the tank. For the measurement it is of importance, that the time for the shift of the sample is as short as possible to minimize the temperature drop in the sample. The utilized pneumatic piston drive takes about 0.25 s for a shift and has a special stop dynamic to minimize the forces on the sample. The two stage vacuum system consists of a mechanical pump and an oil diffusion pump. The minimum pressure achieved is about \(10^{-1}\) Pa. The power supply system is capable of a maximum current of 1000 A. During operation the current is controlled. Fig. 3 shows a typical power and current profile for a desired temperature within the BB. For temperatures higher than 1800 K, an inert gas atmosphere is required inside the vessel to protect the graphite rod of being damaged by chemical reactions.

Therefore, an argon supply system is installed, providing an inert overpressure atmosphere during high temperature measurements. Moreover, it has been found that the inert atmosphere also minimizes e.g. oxidation processes related to the sample materials, hence keeping test conditions more stable and reproducible. As a consequence, all tests were carried out in an argon atmosphere. During the experiment a pyrometer is used for the temperature measurement. Depending on the purpose of the test, the detector can be changed to either a wavelength non-selective device for total emissivity measurements or a spectral pyrometer for spectral emissivity measurements. As the total emissivity of a material is the decisive parameter for the radiation characteristic of a TPS according to the well known Stefan-Boltzmann-Equation and necessary for the determination of the catalysis related properties this paper focuses on total emissivity measurements.

This type of measurement postulates a pyrometer device which detects all wavelengths of Planck’s radiation distribution. As this is technically infeasible, one has to make the cut back to a most possible broadband detector type and accept a certain part of the intensity lost for detection. Respectively, a broadband thermopile type pyrometer with a sensitive wavelength interval of 1.1–22 \(\mu m\) with a measurement rate of 5 Hz was used. Hence at 750 K the detected radiation fraction of Planck’s Distribution is 99.4 %, at 1500 K it is still 97.9 % and at 1800 K it is 93.5 %. A suitable optical window material was found to be KRS-5, that is used to provide optical access though the front end of the vacuum vessel into the BB cavity (see Fig. 4, left).

As shown in Fig. 4, KRS-5 glass has a good transmittance at wavelengths up to 35 \(\mu m\). As KRS-5 has a very low melting point of about 690 \(K\), a hybrid water/air cooling system had to be installed to protect the KRS-5 window from exceeding its working temperature.
2.2. Measurement Principle

The measurement procedure has the following action:

1. The sample is placed in the sample holder at the bottom of the cavity (Pos 1, Fig. 5). The design of the cavity defines an apparent emissivity close to unity at Pos. 1.

![Figure 5. Cut through BB-Cavity and moveable Sample Support System](image)

2. The vacuum vessel is evacuated and then refilled with an inert argon atmosphere.

3. The cavity is resistively heated up to the desired temperature at which emissivity has to be measured. The electrical current can be adjusted hence emissivity can be measured at different temperatures. The temperature is constantly (5 Hz) taken via the pyrometer. Due to radiation exchange the sample comes in thermal equilibrium with the cavity.

4. When the nominal temperature is stable, the sample is rapidly shifted in Pos. 2 via the pneumatic piston. As the shift is quick, it can be considered isothermal.

5. After another temperature is taken at Pos. 2, the sample is re-shifted to Pos. 1 for further measurements.

The total emissivity is evaluated by the obtained apparent temperature drop perceived by the linear pyrometer that has been used within this work. According to the Stefan-Boltzmann-Law:

\[ S_{Pos 1} \sim \Phi_{Pos 1} \sim M_{Pos 1} \sim \sigma \cdot \varepsilon_{Pos 1} \cdot T_{Pos 1}^4 \]  

(1)

The ratio of the obtained signals (\( \varepsilon_{Pos 1} \approx 1 \)) yields in:

\[ \frac{S_{Pos 2}}{S_{Pos 1}} = \frac{\varepsilon_{Pos 2} \cdot T_{Pos 2}^4}{T_{Pos 1}^4} \]  

(2)

As the shift is isothermal (\( T_{Pos 1} = T_{Pos 2} \)) the emissivity can be determined by the ratio of the two signals or can be evaluated by the apparent temperature drop (\( \rightarrow \) Subscript a). Independently from Eq. 1 and 2, neglecting the offset values the used pyrometer, calibrated on a BB, allows for:

\[ S \sim T^4, \text{ consequently } S_a \sim T_a^4 \]  

(3)

Hence the emissivity can also be obtained through:

\[ \varepsilon_{Pos 2} = \frac{T_{a, Pos 2}^4}{T_{a, Pos 1}^4} \]  

(4)

2.3. Results and Discussion

For all tests, the surface of each sample has been honed to a surface roughness of about \( R_q = 0.5 \). Additionally, all samples were weighted and the thickness was determined with a micrometer screw before and after the tests. The oxidation of metallic samples was conducted during the Double Probe measurements (see section 3.5), where a blank sample was exposed to oxygen plasma for about 30 min. at high temperatures (see Fig 16). An analysis of the accuracy has been conducted, taking calibration uncertainties and non-linear effects of the pyrometer into account. It predicts an uncertainty of the emissivity of \( \pm 5 \% \) from the nominal value. In Fig. 6-10 the results for the total emissivities of the ceramic and metallic candidate catalytic sample materials are given. A quantitative comparison of the measurement result shows a reasonable agreement to the values found in literature for \( \text{Al}_2\text{O}_3 \), see Fig. 6. No References could be found for \( \text{HfO}_2 \) and \( \text{Y}_2\text{O}_3 \). Interestingly, three different behaviours whit rising temperature could be observed: The emissivity of \( \text{Y}_2\text{O}_3 \) rises whereas the emissivity of \( \text{HfO}_2 \) stays nearly constant and the emissivity of \( \text{Al}_2\text{O}_3 \) decreases with increasing temperatures.

![Figure 6. Total Emissivities of the Ceramic Materials](image)

The investigation of PM1000 is of great importance as it is foreseen as material for the side panels of the EXPERT capsule\(^ {13} \).

![Figure 7. Total Emissivities of PM1000](image)

The measurements (Fig. 7) showed that the emissivity for the blank/clean material deviate more than a factor of two in some temperature ranges. The emissivity of the clean material (Fig. 8 A) is below 0.4 whereas it rises steeply towards 0.72 at temperatures above 1100 K, where oxidation processes start taking place. In comparison, the pre-oxidized sample had an emissivity of 0.7 at low
temperatures rising to about a near constant value of 0.9 at temperature levels above 1100 K. The pre-oxidized sample showed a brown-greenish camouflaged surface (see Fig. 8 B) after the oxidation in the pure oxygen plasma flow of the inductively driven plasma wind tunnel PWK3. The colour and pattern indicates that a layer of Cr$_2$O$_3$ has formed. This hypothesis is supported by a decrease of weight and an increase of thickness (see Table 1) which could be due to the low density of a forming Cr$_2$O$_3$ layer. Additionally, one value of the emissivity of Cr$_2$O$_3$ of 0.6 could be found in rather rare literature which reasonable fits to the value of 0.7 at the beginning of the measurement.

![Fig. 8. Surface Changes of the PM1000 Samples](image)

During the emissivity measurement of this pre-oxidised sample a further oxidation of the relatively soft Cr$_2$O$_3$ layer has probably taken place. After the measurement the colour had homogenously changed to dark grey, together with a thickness decrease and a mass increase. This might indicate a formation of an Al$_2$O$_3$ layer (density, colour) but then is in contrast to the emissivity measurement of Al$_2$O$_3$ (Fig. 6) and could be closer investigated via Secondary Ion Mass Spectroscopy (SIMS).

<table>
<thead>
<tr>
<th>Table 1 Weight and Thickness Changes of the PM1000 Sample</th>
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<tbody>
<tr>
<td><strong>mass m ±0.00005 [g]</strong></td>
</tr>
<tr>
<td>blank (new material)</td>
</tr>
<tr>
<td>after pre-oxidation</td>
</tr>
<tr>
<td>after emissivity measurement</td>
</tr>
</tbody>
</table>

*) referring to the mass at beginning of each test

The significant decrease of emissivity at temperatures above 1500 K may be explained with by melting of material at the surface.

The measured emissivities of clean Tungsten and TZM show very similar values of about 0.3 at low temperatures constantly rising to values of about 0.43 at 1800 K, see Fig. 9. In contrast, the oxidized metals showed a clearly different behavior: While the pre-oxidized Tungsten only changed slightly color, the TZM nearly became black, indicating that the conditions during the plasma wind tunnel tests were severe enough to heavily oxidize the TZM while the Tungsten sample withstand visibly better. Investigating the measured emissivities this hypothesis is fortified. While the emissivity of the pre-oxidized Tungsten sample is only little higher: 0.35 at 720 K and 0.48 at 1800 K the emissivity of the pre-oxidized TZM is about 2.5 times higher than that of the blank metal.

![Fig. 9. Total Emissivities of Tungsten and TZM](image)

Despite the research done in the field of emissivity and reflectivity dependence on roughness parameters, little is known about the influence of surface roughness and surface topology on the emissivity of typical TPS materials. Therefore, three SSiC samples have been prepared, each with a different degree of surface roughness, using common finishing operations: “as fired” (R$_q$ = 0.67), grounded (R$_q$ = 0.24) and polished (R$_q$ = 0.05). The surface roughness was determined after production. Using Wien’s Law, the maximum wave-length in the temperature range between 750 and 1800 K is between 1.61 and 3.75 μm, thus being in the same magnitude or much taller than the surface roughness. In optics a surface where R$_q$/λ$_{max}$ << 1 can be considered smooth, thus approaching the properties of a perfectly smooth surface. For the cases where R$_q$ ≈ λ$_{max}$ classical diffraction models could be applied to describe the radiative properties of the surface. They predict the independence of the hemispherical emissivity to the value of R$_q$. However, it has been found in Refs. 17, 19, 20 that experimental results show the emissivity to be very sensitive to the state of the surface in the optical roughness range. Also the results of the SSiC related measurements (see Fig. 10) show a clear trend. The lowest emissivities were obtained for the smoothest surface (polished), which is compliant to the results of Ref. 17.

**Fig. 10. Surface Roughness Influence on Emissivity of SSiC**

3. Determination of recombination coefficients

The inductively driven plasma wind tunnel PWK3 is used at IRS for both basic investigation in the field of catalysis, reaction schemes and entry simulation for
celestial bodies such as Mars or Venus\textsuperscript{21). The basis for this capability was provided with the development of the high enthalpy inductively coupled plasma generators IPG3, IPG4 and IPG5\textsuperscript{22a}. The electrode-less plasma sources use self-field based MHD effects allowing for the generation of high enthalpy plasma flows in a wide range of operational parameter. With the combination of the related properties e.g. the electrode-less high enthalpy plasma generation and the potential to generate high enthalpy plasmas of single gases such as oxygen or nitrogen became basis for the aforementioned capabilities.

3.1. Methodology for Determination of Recombination Coefficients

As mentioned in the beginning, the determination of the recombination coefficient is of great importance for the characterization of TPS materials. The methodology to determine the recombination coefficients at IRS was first reported in Ref. 23). Within this work, it is used for the determination of oxygen related recombination coefficients. The supporting techniques, especially concerning the probe measurements in the inductively driven PWK3-IPG3 facility\textsuperscript{24} at IRS will be discussed. A scheme of the interaction of all steps involved in the determination methodology is shown in Fig. 11.

![Fig. 11. Determination of Recombination Coefficients (scheme)](image)

The determination of recombination coefficients is carried out adapting Goulard’s boundary layer theory\textsuperscript{25} and inverse heat flux calculation of material double probe temperature measurements of the investigated materials in the stagnation point of oxygen (or nitrogen) plasmas. It has been found, that structural heat losses due to conductivity of the samples and the probe have to be taken into account for this inverse calculation. Further necessary plasma parameters (e.g. stagnation enthalpy, Pitot pressure and Mach number) have been derived using various Probe techniques\textsuperscript{6, 26} developed at IRS. Numerical data such as transport coefficients, dynamic viscosity and effective probe radii were calculated with the Upwind Relaxation Algorithm for Nonequilibrium flows of the University of Stuttgart (URANUS)\textsuperscript{27}. Most physical properties of the candidate materials and gases were supported by the supplier or can be found in literature. The emissivities were measured using the IRS emissivity measurement facility (EMF), see section 2.

Based on Goulard’s Theory (Eqs. 5-7), the recombination rate $k_w$ and hence the recombination coefficient $\gamma_w$ of a material can be determined from the ratio of the fully catalytic to the measured finite catalytic heat flux. The assumption of complete energy accommodation to the TPS surface ($\beta = 1$) was made.

\[
k_w = \frac{2 Y_w \phi_w (T_w)}{2 - Y_w \phi_w (T_w)} \sqrt{\frac{\gamma_w}{2 \pi M_w}} \tag{5}
\]

\[
\phi_w = \left[ 1 + \frac{0.665}{S\phi_{\text{eff}} \rho_{\text{eff}} k_{\text{eff}} \tau_{\text{eff}}} \left( \frac{\mu_{\text{eff}} \rho_{\text{eff}}}{\rho_{\text{eff}}} \right) \right]^{\frac{1}{2}} \frac{(2 - \rho_{\text{eff}})}{\rho_{\text{eff}}} \tag{6}
\]

\[
\dot{q}_w = q_{\text{ref}} \left( 1 - \frac{L_{\text{eff}}^{25} \frac{2}{\rho} \left( \frac{h_{\text{ref}}}{h_{\text{w}}}, \frac{\gamma_{\text{ref}}}{\gamma_{\text{w}}} \right)}{1 + \left( L_{\text{eff}}^{25} - 1 \right) \frac{2}{\rho} \left( \frac{h_{\text{ref}}}{h_{\text{w}}}, \frac{\gamma_{\text{ref}}}{\gamma_{\text{w}}} \right)} \right) \tag{7}
\]

The fully catalytic heat flux was calculated measuring the heat flux on cooled oxidized copper and a correlation introduced by Pope\textsuperscript{28}:

\[
q_{\text{ref}} = 1.25 \cdot q_{\text{CuO}} \tag{8}
\]

In the case of oxygen, the HF measured was set equal to the fully catalytic HF as proposed in Refs. 6, 23).

3.2. Calorimetric Heat Flux and Pitot Pressure

For the measurements the IRS calorimetric HF-Pitot pressure double probe (Fig. 12) was used. The probe employs an insulated sample of oxidised copper which is kept at a constant temperature of about 300 K by a separate high pressure water cooling circuit.

![Fig. 12. Calorimetric HF – Pitot Pressure Double Probe](image)

The inlet and the outlet temperatures of the water are measured by PT100 resistance thermometers. A flow controller determines the flow rate and hence the mass flow can be calculated. The HF is then derived according to:

\[
\dot{q}_{\text{ref}} = c_{\text{pu}} \dot{m} \left( T_{\text{inlet}} - T_{\text{wheat}} \right) / A_{\text{sample}} \tag{9}
\]

The probe can be turned by $180^\circ$ such that the other side (Fig. 12) can be used for the Pitot pressure measurements. The radial and axial mapping of the HF and the Pitot pressure of the plasma plume is taken for the estimative calculation of the local stagnation enthalpy at the boundary layer edge\textsuperscript{24}.
To ensure the reliability of this approach the relation expressed by equation (10) was cross-checked with different independent optical measurement techniques such as laser-induced fluorescence and diode laser absorption spectroscopy. The reference condition investigated in these literatures was under the plasma condition used for this work, see also table 2.

Based on the measured radial \((y_{Pos})\) profiles of heat flux and total pressure at distinguished axial distances from the plasma source outlet \((x_{Pos})\) a radius \(R_{Pl}\) of the plasma plume of roughly 100 mm was determined. The total enthalpy was previously measured with a cavity calorimeter described in Refs. 22, 24).

3.3. Mach Number and Velocity

Free stream values of the Mach number and respectively the plasma speed where calculated using the Rayleigh-Pitot Equation and the Pitot pressure measurements

\[
Ma_{\infty} = \left( \frac{P_{\infty}}{P_{w}} \right)^{\frac{\gamma - 1}{2\gamma}} M_{a,\infty} + \left( \frac{2}{\gamma + 1} \right) \left( \frac{P_{\infty}}{P_{a}} \right)^{\frac{\gamma + 1}{\gamma - 1}} = 0 \quad (11)
\]

or obtained via probe measurements with the cone probe described e.g. in Ref. 30). The isentropic exponent in equation (11) is usually taken from numerical data or from measurements where wedge or cone probes were combined with the Pitot pressure measurements. Corresponding data can be found in Refs. 22 and 24.

3.4. Plasma Parameters

The dissociation degree of the plasma was determined using thermo-chemical data of the gas species (oxygen and nitrogen) of the NIST online databases. With the measured stagnation enthalpy at the boundary layer and the corresponding total pressure, the temperature, the gas constant and the molar mass can be derived under the assumption of thermo-chemical equilibrium. Compared to \(^{23}\), this procedure makes the determination of recombination coefficients much more flexible concerning axial distances from the generator and the temperature regime, especially towards colder temperatures. The effective probe radius has been estimated by iterative comparison of two URANUS calculations, one with the European Standard Probe geometry and one with a hemispherical blunt body of varying radius, both under the same free stream conditions. The effective radius of the probe is determined by the consistency of the two flow fields (e.g. \(R_{eff} = 2.42 \, R_{probe}\)) at the final iteration. Lewis and Schmidt numbers as well as the viscosity have been determined according to Ref. 27.

3.5. Pyrometric Heat Flux Experiment

The heat flux and the wall temperatures of the TPS materials under investigation are determined through measurements with the IRS Pyrometric Double Material probe. The probe (Fig. 13) is equipped with two PYREX mini pyrometers, measuring the rear side sample temperatures during the plasma wind tunnel tests.

![Pyrometric Material Double Probe](image)

Fig. 13. Pyrometric Material Double Probe (LHS: Scheme, RHS: in operation, IRS PWK2)

From analysis it could be derived that despite high temperature insulation of the material sample the structural heat losses into the probe have to be taken into account to calculate the correct heat flux. The transient heat flux onto a sample can then be expressed through

\[
\dot{q}_w(T, t) = \varepsilon(T) \sigma T_w^4 + \eta(T) \rho_s f(T) \frac{dT_w}{dt} + \dot{q}_F(T).
\]

During plasma wind tunnel test the probe is hold at a constant axial position until thermal equilibrium between the environment and the sample is reached. This simplifies Eq. 12 to steady state. The HF loss term can further be written as a proportion of the load term on the sample:

\[
\dot{q}_w(T, t) = f(T) \dot{q}_F(T, t).
\]

The function \(f(T)\) then represents the loss factor of the heat load density on the sample depending on the temperature \(T\). It has been estimated by a transient thermal analysis of the PYREX probe \(^{33}\). Fig. 14 shows the result for \(f(T)\) representatively for a SSIC sample. From the analysis data, the regression function \(f(T)\) was derived.

![Structural Heat Loss for Pyrometric Double Probe](image)

Fig. 14. Structural Heat Loss for Pyrometric Double Probe (here SSIC)

It is evident, that especially for recombination coefficient determination at lower temperature regimes, which, e.g., are typically encountered on metallic TPS applications, the structural heat loss has to be taken into account. Further it can be seen from Eq. 12 that a calculated heat flux is directly proportional to the total emissivity. Therefore, the knowledge of the temperature dependant total emissivity of the sample material is essential to accurately calculate heat fluxes.
3.6. Test conditions and Results

The tests were conducted in the inductively driven test facility PWK3 - IPG3, which operates electrode free and thus generates plasmas without impurities due to cathode erosion. All metallic species were blank polished to a surface finish of about $R_a = 0.5$ previous to the tests. Table 2 shows the test conditions for the recombination coefficient determination.

<table>
<thead>
<tr>
<th>Table 2 Test condition in PWK3-IPG3 facility$^{(2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass flow rate [g/s]</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>3</td>
</tr>
</tbody>
</table>

$^{(2)}$ More detailed information on facility and parameters can be found in$^{22, 24}$

From the temperature histories obtained with the Double Material Probe tests (section 3.5) the HF was recalculated at the stationary points and corrected for structural losses as described. Thereby, the results of the temperature dependent emissivities obtained in section 2 were used. Due to the improvements of the pyrometric HF measurements, the error could be reduced to 5 % (mainly the error of emissivity) compared to the approximated 12 % of$^{24}$. The obtained axial HF profiles are shown in Fig. 15 and 16.

![Fig. 15. Axial HF profile of the ceramic materials](image1)

![Fig. 16. Axial HF profile of the metallic materials](image2)

The HF's allow for a qualitative comparison of the catalytic behavior of the investigated materials. Thus the catalytic efficiency for the ceramics can be provided by $\gamma(Y_2O_3) > \gamma(HfO_2) > \gamma(Al_2O_3)$, where the extremely high HF of $Y_2O_3$ thereby indicates highest $\gamma$ of all tested materials. The hierarchy for the metallic species can be tabulated as following: $\gamma(PM1000) > \gamma(TZM) > \gamma(Tungsten)$ at lower temperatures whereas the catalytic efficiency of tungsten exceeds TZM at rising temperatures.

In the case of the ceramic samples, the previously made qualitative comparison could be verified by the quantitative results (recombination coefficients). The uncertainty has been assessed to be well within one order of magnitude of the calculated values. It has indeed been found that $Y_2O_3$ has with values between 0.3 and 0.4 the highest oxygen recombination coefficients of all tested samples. In this temperature regime $Y_2O_3$ can be regarded to be close to fully catalytic behavior. For the metallic specimens the initial impression, which e.g. could be derived from qualitative considerations, may lead to falsified statements as long as the high variety in the emissivities of the concerned materials have not been taken into account. This becomes clear, comparing PM1000 to the other materials in Fig. 7 and 9. However, the results for PM1000 show a good agreement with the results of Ref. 8, taking into account that in Ref. 8) the HF was not corrected for structural losses. With the overestimated HF on PM1000 in Ref. 8) the slightly higher values for the recombination coefficients can be explained.

![Fig. 17. Oxygen Recombination Coefficients of ceramic Materials](image3)

![Fig. 18. Oxygen Recombination Coefficients of metallic Materials](image4)

4. Conclusion

Methodologies and facilities allowing for the determination of emissivities and recombination coefficients were introduced.

Based on this, total emissivities of $HfO_2$, $Y_2O_3$, $Al_2O_3$, PM1000, TZM and Tungsten were determined in the temperature range between 750 and 1800 K. In the case of the metallic specimen experimental investigations with clean and pre-oxidized metals/alloys were conducted. It was found that the emissivities of PM1000 and TZM are highly affected within the investigated temperature regime through the surface oxidation that was brought to the materials using a high enthalpy oxygen plasma flow in the inductively heated plasma wind tunnel PWK3. For TPS applications of these materials (e.g. PM1000 is foreseen as metallic TPS material of the European Re-entry capsule EXPERT$^{34}$) a “full” pre-oxidation state like shown in Fig. 8C seems necessary for a predictable and optimal radiation based cooling behavior ($\epsilon_{net}$ constant at $@ 0.9$) of the TPS. The investigation of surface roughness influence on TPS emissivity values showed a clear trend of rising
emissivity with an increased surface roughness for SSIC. Since this behavior is apparently difficult to predict with common theory, further experiments for broader roughness and topology range should be conducted in the future. This work should include C/C-SiC and metallic species due to the special interest for TPS applications.

Oxygen recombination coefficients of the investigated materials have been derived using a combined numerical and experimental methodology. The obtained results could be summarized as follows: \( Y_2O_3 \) can be regarded close to fully catalytic in the investigated temperature regime. The other ceramics show a rather moderate and very constant catalytic behavior. Especially together with a nearly constant emissivity of \( HfO_2 \) within broad temperature levels, this makes the thermo-chemical performance of these materials more predictable. The metallic specimen showed temperature dependant individual behavior from highly catalytic to rather low catalytic behavior. The results of PM1000 showed a good agreement with previously found results, justifying the recent improvements within the pyrometric HF measurement.

Meanwhile, an enlargement of the temperature regime for the emissivity measurement has been realized using a purpose- build broadband thermopile detector with an all-CaF\(_2\) optical path. This will allow for measurements from 1450 K to 2600 K with a detected radiation fraction of Plank’s Distribution from 95 % at 1450 K to 99 % at 2600 K, thus further improving accuracy at medium temperatures and extending the measurement range. As for the determination of the recombination coefficient the methodology could be improved by the elimination of the CuO-based heat flux as a reference which will be a further contribution to reduce the fairly high uncertainties or inaccuracies of such methods.

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