On experimental determination of the catalycity coefficient of heat-proof thermal protection materials

A A Shkuratenko
Moscow Aviation Institute (National Research University) Federal State Budget Educational Institution of Higher Professional Education
Mailing address: 4, Volokolamskoye Road, Moscow 125993
shkuratenko.anna@mail.ru

Abstract. This paper reviews the developed and tested algorithm of experimental determination of the catalycity coefficient of heat-proof thermal protection materials and determines the conditions which should be followed during the simulation process at high-temperature gas-dynamic testbeds within the experiment.

Introduction
The development of rocket and space technology is closely related to the creation of new heat-shielding materials that can protect the structure from thermochemical and mechanical erosion. To use such materials in construction, it is necessary to know the range of properties, such as: heat resistance, wear resistance, catalytic properties, etc.

The catalytic properties of materials are uniquely determined by the component composition of the incoming flow. It should be borne in mind that in the process of intensive aerodynamic heating, these properties change significantly.

1. Experiment simulation environment
At high flight speeds, a chemically active boundary layer is formed on the surface of the aircraft, in which chemical reactions of dissociation of molecules and recombination of atoms take place. The presence of chemical reactions causes a significant increase in heat flow in the structure due to heat and mass transfer processes. During the aerodynamic heating the surface catalycity is considered in terms of heterogeneous reactions of oxygen and nitrogen atom recombination.

\[
\begin{align*}
O + O + \text{catalyst} &\rightarrow O_2 + \text{catalyst} \\
N + N + \text{catalyst} &\rightarrow N_2 + \text{catalyst}
\end{align*}
\]

In the chemical nonequilibrium boundary layer these reactions play one of the crucial roles during the heat exchange process.

The surface catalycity is characterized either by the surface recombination rate constant \( k_w \) or recombination probability \( \gamma_w \).

By definition, parameter \( \gamma_w \) is a nondimensional coefficient which describes the ratio between the number of atoms recombined on the surface to the full number of atoms which have reached the
surface during the diffusion process. The analytical dependency between the above-given parameters is set with the following ratio:

$$k_w = \gamma_w \left( \frac{R \cdot T_w}{2\pi \cdot \mu_{ATOM}} \right)^{0.5}$$

(3)

For dissociated air in case of complete dissociation of oxygen molecules (the stream temperature on the boundary layer edge is $T_e \geq 5000K$) surface oxygen atom recombination catalyzes the homogeneous nitrogen atom recombination within the boundary layer. E.g., it is known that under absolute ambient temperature $T = 5000K$ the nitrogen atom weight percent is only 5% and under $T = 6000K$ it reaches 50%. In this regard during experimental tests air should be considered as a uniform gas with an effective rate of surface recombination of oxygen and nitrogen atoms $k_{w,1}$ [1].

Due to this it is reasonable to perform experimental tests not only on high-temperature ($T_w = 1700...2500K$), but also on low-temperature ($T_w \leq 600K$) surfaces of the tested samples considering that heterogeneous reactions of oxidation and nitridation of the materials tested for catalycity can cause significant inaccuracies in the test results. So during such tests one should take all efforts to exclude the surface reactions of the tested material with the mainstream atomic components.

During the experiment special attention should be also paid to the exchange reactions in the boundary layer. For excluding such reactions, the pressure in the boundary layer should be reduced to $P \leq 10^3...5 \cdot 10^3$ Pa or the size of the tested model made of the thermal protection materials should be decreased.

2. The procedure of experimental determination of thermal protection material catalycity in this study

During the experiment the pressure of the tested surface of the thermal protection material was kept within the above-given range for excluding both exchange reactions and homogeneous reactions of atom recombination in the boundary layer.

In fact, fulfilling the stated conditions during the experiment allowed “freezing” of the boundary layer. In this case the number of atoms delivered to the catalytic surface in the boundary layer by the diffusion process shall completely recombine there considering surface catalycity $k_w$. Then for each atomic stream of oxygen and nitrogen which reach the surfaces the following ratio will be true [1]:

$$\rho_w \cdot D_{1,2} \left( \frac{\partial C_w}{\partial y} \right)_w = (k_w \cdot \rho_w \cdot C_{i,w})^w$$

(4)

During the experiment the ratio taken from paper [1] was used for calculating the density of heat fluxes on the catalytically effective surface. The ratio was obtained for the forward stagnation point in the form of (ratio (5) obtained [1] by modifying the Goulard equation [2]):

$$q_0 = 0.665 \left[ \beta \cdot (\rho_w \cdot \mu_w)^{1/2} \right]^{0.17} \cdot \left( \frac{I_w}{I_0} \right)^{0.17} \cdot \Pr^{2/3} \left[ 1 + \left( \frac{I_w}{I_0} \cdot C_{\gamma} \right) \left( \frac{I_0}{I_w} - 1 \right) \right]$$

(5)

where parameter $\varphi$ with rate of surface recombination of atoms $k_w$ is represented by ratio:

$$\varphi = \left( 1 + 0.6565 \cdot c^{-2/3} \cdot \left[ \beta \cdot \left( \frac{\mu_w}{\rho_w} \right) \right]^{1/2} \cdot \left( \frac{I_w}{I_0} \right)^{0.17} \right) \cdot \left( \frac{I_0}{I_w} \cdot C_{\gamma} \right)$$

(6)

$I_0$ and $I_w$ are enthalpy of mainstream diffusion and gas enthalpy under wall temperature of the $T_w$, correspondingly.

Let us denote the set of parameters:
\[
0.665Sc^{-\frac{2}{5}} \cdot \left[ \beta \cdot \left( \frac{\mu_w}{\rho_w} \right) \right]^{\frac{1}{2}} \cdot \left( \frac{I_w}{I_0} \right)^{0.17} = S
\]  

(7)

Then equation (8) will be written as:

\[
\varphi = \frac{1}{1 + \frac{S}{k_w}}
\]

(8)

From here it follows that

\[
k_w = \frac{\varphi \cdot S}{(1 - \varphi)}
\]

(9)

So values \(k_w\) can be determined if \(S\) and \(\varphi\) are known.

It is obvious that set \(S\) is determined upon the results of the experimental diagnostics of the parameters of high-temperature mainstream such as: static pressure \(p\), diffusion pressure \(p_0\), diffusion enthalpy \(I_0\), mainstream rate \(V_\infty\), surface temperature of the tested sample \(T_w\), rate gradient in the forward stagnation point \(\beta\), etc. The parameter numerical value \(\varphi\) is determined by calculation with experimental data substituted in the ratio (5).

The experiment at the high-temperature gas-dynamic testbed is based on the use of cooled and uncooled calorimetric sensors. The surface of their heat-receiving element is covered with a thin layer (5...10 µm) of a tested heat-proof composite for determining \(k_w\) [3]. The thin layer on the surface of the heat-receiving element of the calorimeter can be formed in different ways. However, it shall provide the possibility to fulfill the following requirements:

- the coating shall be highly adhesive;
- the composition shall not be changed during the technological process of forming the coating.

So the calorimeter with the thin layer of catalytically effective coating shall be installed in the reference section of the dissociated mainstream. Then the heat flux density shall be measured with the heat-receiving element of the calorimeter. During the experiment the surface temperature of the heat-receiving element of the calorimeter shall be measured using a thermal imaging system. Provision of a “frozen” (without exchange reactions) or equilibrium boundary layer on the calorimeter surface during the experiment allows determining the heat flux density considering the coating surface catalycity [4].

In such case using equation (5) it is rather simple to calculate parameter value \(\varphi\) if the rest of parameters of this equation are known. The only issue which offers difficulties is unknown set

\[
\sum_{i=1}^{n} C_{i,\epsilon} \cdot h_i^0
\]

(10)

For calculating the value of the set an additional experiment is required. It shall involve a calorimeter with a heat-receiving element made of a material with absolute catalycity i.e. copper.

So it follows from (6) that under \(k_w \rightarrow \infty\) parameter is \(\varphi \rightarrow \infty\). In such a case, equation (5) will be written as:

\[
q_w = 0.665\left[ \beta \cdot (\rho_w \cdot \mu_w) \right]^{\frac{1}{2}} \cdot \left( \frac{I_w}{I_0} \right)^{0.17} \cdot Pr^{-\frac{2}{5}} \left[ 1 + \left( \frac{Le^{-\frac{2}{5}}}{1} \right) \frac{\rho_0}{\rho_0} \cdot C_w \right] \left( I_0 - I_w \right)
\]

(11)

The calculated value of this value shall be substituted in equation (5) and the parameter value \(\varphi\) shall be calculated for this experiment, i.e. for the tested catalytically effective coating.

Further if value \(\varphi\) is known, the catalytic recombination reaction rate \(k_w\) for the chosen composition of the thermal protection coating can be calculated simply.

If this algorithm is used in experiments, the following recommendations should be strictly abided:
• the testbed shall allow generation of clear dissociated nonturbulent air stream with a range of changing the stagnation temperature $2500 \leq T_0 \leq 8000$ K and pressure $10^3 \leq P_0 \leq 5 \cdot 10^3$ Pa for providing a chemically “frozen” boundary layer;
• the calorimeters with small-size diameters are allowed for the experiment;
• during the calculation of the material catalycity rate $k_w$ the temperature of the surfaces of both heat-receiving elements of calorimetric sensors shall be controlled within the range of the same measurement allowance[1].

2.1. Remeasurement in case of difference between temperature values of the calorimeter surfaces
If the condition of equal temperatures of the heat-receiving elements of calorimetric sensors is not fulfilled during the experiment, it is necessary to perform a remeasurement using calorimeters of different levels of heat fluxes for aligning their values with one surface temperature. Then after such remeasurement value $k_w$ shall be calculated according to the following algorithm. The heat fluxes are remeasured according to the following algorithm. E.g., let us assume that during the experiment the surface temperature of the calorimeter with the tested material $T_{w, k_w}$ is higher than such temperature of the material with absolute catalycity $T_w$, $k_w \rightarrow \infty$. In such case the heat flux to the hot wall shall be aligned (remeasured) with the lower temperature using the following ratio:

$$q_{0,k_w} = q_{0,k_w \rightarrow \infty} \left( \frac{I_0 - I_{W,k_w}}{I_0 - I_{W,k_w \rightarrow \infty}} \right)$$  \hspace{1cm} (12)

where $I_w$ is mainstream stagnation enthalpy, $I_w$ is air enthalpy under wall temperature. Specifically

$$I_{W,k_w} = C_p \left( T_{W,k_w} - T_{HAT} \right)$$ \hspace{1cm} (13)

and

$$I_{W,k_w \rightarrow \infty} = C_p \left( T_{W,k_w \rightarrow \infty} - T_{HAT} \right)$$ \hspace{1cm} (14)

This algorithm and the above-given experiment simulation environment allow us to calculate the catalycity coefficient without any difficulties and this, in turn, allows determining the heat flux to the wall of the thermal protection material considering its catalycity.

3. Some experimental data
Using the method described above, the values of catalytic activity coefficients and heat fluxes for carbon-carbon composite materials were obtained. Some experimental data are presented in table 1.

| Material            | $q_w$, W/m² | $T_w$, C | $k_w$, m/c |
|---------------------|-------------|---------|-----------|
| N₂                  | 1405        | 2169    | >100      |
| Si -Ti -Mo- Cr      | 1650        | 1800    | 0.88      |
| Si -Ti-Mo- B        | 1460        | 1780    | 0.18      |
| Si -Ti-Mo- B - Y - Al| 1480        | 2000    | 0.38      |
| Si -Ti-Mo- B - Y - Hf| 1750        | 2100    | 0.35      |
Conclusion
The proposed variant of the experimental determination of catalytic properties of heat-resistant coatings will help to define the values of thermal swats and $k_\alpha$ of any materials, and further studies will give the possibility of creating a new thermal insulation purposes (such as based on carbon-carbon and carbon - ceramic composite materials).

References
[1] Nikitin P V Shkuratenko A A 2016 Impact of the Catalytically Effective Surface on the Intensity of Convective Heat Transfer (Moscow: Trudy MAI No.88).
[2] Goulard R 1959 On Catalytic Recombination Rates in Hypersonic Stagnation (Journal Issues of Rocket Technology No. 5) p.3-23.
[3] Halpern B Rosner D E 1978 Chemical Energy Accomodation at Catalytic Surfaces (Chem. Soc. Farad. Trans. J. V.74) p.1833-1912.
[4] Shkuratenko A A 2018 Diagnostics of Heat Exchange in Hypersonic Streams for Determining Catalycity and Radiation Properties (Moscow: Publishing house MAI) p.171.
[5] Nikitin P V Tushavina O V Shkuratenko A A 2019 Calculation of aircraft units using film cooling with regard to unsteady heat conductivity (Bucharest: INCAS BULLETIN vol. 11) p.191-201.
[6] Koshkin V K Mikhailova T V 2007 Technical thermodynamics (Moscow: Publishing house MAI) p. 386.
[7] Bashilov S A Nikitin P V 2010 Method of formation of heat-resistant protective coatings on the surface of carbon-carbon heat-protective materials (Moscow: Proceedings of MAI No. 37) p. 16.
[8] Kolychev A V 2012 Active thermal protection of hypersonic design elements aircraft on new physical principles at aerodynamic heating (Moscow: Publishing house MAI vol.51).