Effect of Physical Adsorption on Heat Fluxes to Catalytic Surfaces in Carbon Dioxide

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Abstract. A model of the heterogeneous catalysis of a dissociated carbon dioxide mixture on high-temperature heat shield coating has been developed. The model takes into account both chemical and physical adsorption and desorption of oxygen atoms at vacant active sites on the surface; recombination of chemisorbed oxygen atoms with gas phase of O atoms and of CO molecules (Eley – Rideal recombination) and with physisorbed atoms (Langmuir – Hinshelwood recombination). Note that the physisorbed atoms either are desorbed from the surface or diffused to the nearest chemisorbed site. Therefore some of these diffusing atoms will be able either to occupy vacant active sites or to react with chemisorbed atoms. The developed here kinetic model for surface reactions provides closed expression for effective probabilities of heterogeneous reactions \( \text{O} + \text{O} \rightarrow \text{O}_2 \), \( \text{CO} + \text{O} \rightarrow \text{CO}_2 \) and \( \text{C} + 2\text{O} \rightarrow \text{CO}_2 \) on the quartz surface in terms of the rate constants and the activation energies of the elementary studies of these reactions. Based on comparison of the calculated heat fluxes in dissociated carbon dioxide with those measured on the VGU-4 plasma generator of the Institute for Problems in Mechanics of the RAS, the parameters of the present catalysis model were chosen for \( \text{SiO}_2 \) - based coating materials. The different mechanisms effect of above-mentioned heterogeneous reactions on recombination probabilities and heat fluxes to coatings was investigated.

INTRODUCTION

One of the main factors determining the heat transfer intensity during a space vehicle at the Martian atmosphere entry is represented the recombination of the components of dissociated carbon dioxide, which consists of about 96% of the atmosphere. Even at flight velocities of the order of 6 km/s, carbon dioxide has been dissociated practically totally in crossing the bow shock. At the same time, owing to the high rarefaction of the atmosphere, the gas-phase recombination in the vicinity of the vehicle surface is near-frozen. Theoretically, at using noncatalytic coatings, a fourfold reduction in the heat flux to the frontal surface of the vehicle may be achieved on most part of the entry path, including the peak thermal loaded region.

High-temperature catalysis in dissociated air has been studied extensively experimentally and theoretically, in connection with the development of thermal protection systems for Space Shuttle and Buran aero assisted orbital transfer vehicles [1-4]. Originally, heterogeneous catalysis in theoretical models was described by first-order reactions with experimentally obtained rate constants. Recently, more accurate models [5-13] based on ideally
adsorbed Langmuir layer theory [14] were developed. These models describe adequately the aerodynamic heating on the windward side of reusable vehicles along the entry path [15].

At the same time, few studies have been devoted to high-temperature heterogeneous catalysis in dissociated carbon dioxide. In studying the Martian atmosphere entry, mainly the limit cases of an ideal catalytic surface (with a maximum rate of heterogeneous recombination of the dissociated carbon dioxide components) and a noncatalytic surface were considered in the literature [16-18]. Phenomenological models of the catalytic properties of heat-shield coatings of spacecraft entering the Martian atmosphere based on a detailed analysis of the heterogeneous catalytic reaction mechanism were suggested in [19, 20].

The first results of measurements of the dissociated carbon dioxide flow parameters, as well as the heat fluxes to a catalytic surface and the temperature of the latter, were published in [21, 22] for three coating materials types and quartz. The approach developed in [5, 19, 20] was used to model the catalytic properties of heat-shield coatings in a dissociated CO₂ - N₂ mixture in [23, 24]. On the basis of the experimental data interpretation, explicit relationships between the catalytic activities and the near-surface conditions (temperature, pressure, and concentrations) were derived for the coatings studied in [21,25]. For each of these coatings, the heat fluxes at the Mars Miniprobe stagnation point were calculated along the vehicle's entry trajectory into the Martian atmosphere and the coatings usability in the thermal protection system of the vehicle was established.

In this paper the effect of the physisorbed atoms recombination in Eley – Rideal and Langmuir – Hinshelwood mechanisms and evaluated recombination of C atoms on the surface is investigated.

**CATALYTIC MODEL**

We consider the flow of a dissociated carbon dioxide mixture past a catalytic surface body. The mixture includes such species as O, C, O₂, CO, and CO₂ and simulates the gas in the shock layer at the vehicle entry into the Martian atmosphere with velocities as high as 8 km/s. The heterogeneous catalytic reaction mechanism consists of the following reactions listed below:

1. O + Sᵥ ↔ O⁺, 2. O⁺ + O ↔ Sᵥ + O₂, 3. O⁺ + CO ↔ Sᵥ + CO₂, 4. O + Fᵥ ↔ Oᶠ,
5. Oᶠ + Sᵥ ↔ O⁺ + Fᵥ, 6. O⁺ + Oᶠ ↔ O₂ + Fᵥ + Sᵥ, 7. O⁺ + O⁺ ↔ O₂ + 2Sᵥ, 8. O⁺ + C ↔ CO + Sᵥ,

where O⁺ and Oᶠ are chemisorbed and physisorbed atoms respectively; Sᵥ and Fᵥ denote vacant chemisorption and physisorption sites.

In our model we neglected a number of other possible reactions such as, for example, interaction either between two physically adsorbed atoms, as well as processes involving adsorbed molecules and dissociative chemisorption of molecules. Ignoring the dissociative chemisorption is justified for the relatively low surface density of active sites and low wall temperatures, due to high-energy thresholds associated with such reactions. For the same reason we can discount reaction between two chemically adsorbed atoms (reaction 7). The other processes, due to the lack of pertinent data on rate constants, are overlooked here for simplicity. The effect of this reaction is investigated on the
basis of data on rate constant [11, 12]. Reaction 8 is considered in two limit cases: when it is frozen or when it is fast.

Rate constants of adsorption and Eley – Rediel reaction are determined by the formula

$$k_i^+ = \gamma_i \left( \frac{1}{4N_v} \right)^\frac{8kT}{\pi M_m},$$

where \( \gamma_i \) is reaction probabilities; \( \left\langle v_m \right\rangle \) denotes the mean velocity of the gas phase particle \( m \) near the surface; \( N_v \) is \( N^f_v \) or \( N^s_v \); \( N^f_v \) is active sites number for physical adsorption and \( N^s_v \) is active sites number for chemical adsorption per unit area; \( M_m \) is molecular weight.

Rate constants of Langmuir – Hinshelwood reactions are determined by the formula

$$k_i^+ = \gamma_i D_m, D_m = \frac{V_{Dm}}{4N_v} \exp\left(-\frac{E_{Dm}}{T}\right),$$

here \( V_{Dm} \) is frequency factor and \( E_{Dm} \) activation energy of surface diffusion. For reactions 5 and 6 \( V_{Dm} = 10^{13} \text{ cm}^{-1} \) [26, 27], for reaction 7 \( V_{Dm} = C_D \left\langle v_m \right\rangle \), where \( C_D = 2.2 \cdot 10^{10} \text{ m}^{-1} \) [11]. It is assumed that \( N^f_v = 10^{20} \text{ m}^{-2} \), and \( N^s_v = 5 \cdot 10^{18} \text{ m}^{-2} \) (See [11,26,27]).

Reaction probabilities are determined by the formula \( \gamma_i = A_i \exp\left(-\frac{E_i}{RT}\right) \). Adsorption activation energy \( E_i \) is assumed equal zero. Note that activation energies \( E_{Dm} \) and \( E_i \) of Langmuir – Hinshelwood appear in exponent term as sums. Thus it may be assumed that \( E_{Dm} = 0 \). Equilibrium constants \( K_j \) are expressed in terms of statistic sums of reagents [23, 24], then for \( k_j^- \) we have \( k_j^+ / k_j^- = K_j \). It is supposed that statistic sums adsorbed particles and free sites are equal. Catalytic model parameters are given in Table 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>E, KJ/mol</th>
<th>Q, KJ/mol</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.025</td>
<td>0</td>
<td>300</td>
<td>[23, 24]</td>
</tr>
<tr>
<td>2</td>
<td>0.015</td>
<td>25</td>
<td>-</td>
<td>[23, 24]</td>
</tr>
<tr>
<td>3</td>
<td>0.015</td>
<td>15</td>
<td>-</td>
<td>[23, 24]</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0</td>
<td>20</td>
<td>[26, 27]</td>
</tr>
<tr>
<td>5</td>
<td>0.53</td>
<td>0</td>
<td>-</td>
<td>[26, 27]</td>
</tr>
<tr>
<td>6</td>
<td>0.53</td>
<td>0</td>
<td>-</td>
<td>[26, 27]</td>
</tr>
<tr>
<td>7</td>
<td>0.02</td>
<td>125</td>
<td>-</td>
<td>[12]</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>1.0</td>
<td>500</td>
<td>-</td>
<td>[11]</td>
</tr>
</tbody>
</table>

For reaction 1–3 parameters \( A_i \) and \( E_i \) were determined in [24] ground a comparison of the calculated heat fluxes in dissociated carbon dioxide with those measured on VGU–4 plasma generator of the Institute for Problems mechanics of RAS [21, 28]. Catalytic model parameters for reactions 4–6 were determined from analysis data [27].

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and from comparison calculated and measured heat fluxes in the third regime of subsonic flow past the model at low temperature (Table 2).

**COMPARISON WITH EXPERIMENTAL DATA**

In this study, the heat fluxes were calculated the same way as [21], that is described in details in [29,30], within the framework of the finite-thickness boundary layer problem using the gaseous medium model. In this approach, the gas composition at the outer edge of the boundary layer is assumed to be equilibrium. The gas temperature at the outer edge of the boundary layer is found from the condition that the calculated and measured heat fluxes \( q_w \) to a cold, ideal catalytic surface (\( T_w = 300^\circ K, \gamma_i^* = 1 \)) coincide. The measured values are chosen around an analysis of the experimental data for copper and silver surfaces [21, 28] and are given in Table 2. In this table the velocity \( V_s \) of the subsonic jet at the center of the exit section of the plasma generator discharge channel, the measured pressure \( P_e \) at the outer edge of the boundary layer, the power \( N \) supplied to the induction coil, and the ram pressure \( \Delta p \) are given for six flow regimes also.

**TABLE 2. Regimes of subsonic flow past the model.**

<table>
<thead>
<tr>
<th>Regimes/Parameters</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_e, K )</td>
<td>3320</td>
<td>4360</td>
<td>5800</td>
<td>6256</td>
<td>6600</td>
<td>6875</td>
</tr>
<tr>
<td>( V_s, m/c )</td>
<td>47,3</td>
<td>76,1</td>
<td>105,6</td>
<td>118,0</td>
<td>145,0</td>
<td>164,0</td>
</tr>
<tr>
<td>( q_w^f, Wt/cm^2 )</td>
<td>46,4</td>
<td>74,4</td>
<td>103,7</td>
<td>130</td>
<td>175,0</td>
<td>208,0</td>
</tr>
<tr>
<td>( N, kWt )</td>
<td>29</td>
<td>37</td>
<td>44</td>
<td>52</td>
<td>64</td>
<td>72</td>
</tr>
<tr>
<td>( \Delta p, Pa )</td>
<td>10,5</td>
<td>17,5</td>
<td>24,5</td>
<td>26,2</td>
<td>33,75</td>
<td>38,8</td>
</tr>
</tbody>
</table>

In Fig. 1 it is shown the surface temperature dependence of calculated heat fluxes to coatings based on SiO\(_2\) for different test regimes. The curves number correspond regimes number in Table 2. The calculation results, ignoring processes with physisorbed atoms, are marked by dotted lines. Points 1 (\( \times \)) relate to the experimental results in accordance with which the rate constants of reactions 1-3 are chosen in [23]. Note that at low temperature the predicted heat fluxes are in good agreement with the experimental values for quartz (points 2–•) for all regimes. Neglecting processes with physisorbed atoms at low temperature decrease the heat fluxes significantly.

In Fig. 2, 3 the effective coefficients of heterogeneous recombination \( \gamma_{O}^{ef} \) and \( \gamma_{CO}^{ef} \) determined by the formula

\[
R_O = -\rho \gamma_{O}^{ef} \sqrt{\frac{RT}{2\pi m_o}} c_o, \quad R_{CO} = -\rho \gamma_{CO}^{ef} \sqrt{\frac{RT}{2\pi m_{CO}}} c_{CO}
\]

are plotted according to the inverse temperature for different test regimes. Note that the calculations are carried out taking into account the reactions of chemisorbed atoms both with physisorbed atoms (Hinshelwood-Hinshelwood mechanism) and gas phase atoms (Eley-Rideal mechanism).

Taking into consideration both mechanisms allow to explain the non-Arrhenius temperature dependencies \( \gamma_{O}^{ef} \) and \( \gamma_{CO}^{ef} \) in a wide temperature range, from 300 up to 2000 K. This can be seen especially on Fig. 2. Thus, a clearly defined maximum is formed at \( T_w \approx 1350^\circ K \). The reason for this behavior is that at sufficiently high temperatures (specific to each type of coating) thermal desorption processes predominate, the degree of occupancy of the surface diminishes, and
the resulting rate constant for the heterogeneous recombination of oxygen atoms also decreases. This was discovered earlier for dissociated air [5,6] and confirmed experimentally in [32]. Here you see minimum of $\gamma'_O$ at $T_w \approx 600^\circ K$ also. It may be explained by intensification processes with physisorbed atoms.

In Fig. 4 the surface temperature dependence of calculated heat fluxes to coatings based on SiO$_2$ is plotted for different test regimes when fast reaction 8 is also considered. One can see that this reaction effect on heat fluxes is too large if the power N supplied to the induction coil.

In Fig. 5 the heat flux is presented (at the stagnation point on the surface versus the surface temperature when we have used rate constants for reaction 7 from [12] (dotted lines). Note a certain stratification of the curves at high temperatures. Taken from [11] the rate constants for this reaction provide the same results as in the case the reaction is absent. The investigations show that additional experimental data are needed over a wider temperature range for adequately modeling the Langmuir-Hinshelwood processes with chemisorbed atoms on catalytic surfaces.

**SUMMARY**

On the basis of ideal adsorbed Langmuir layer theory, an interaction model of dissociated carbon dioxide mixture with a catalytic surface has been developed. The model takes into account both chemical and physical adsorption and desorption of O atoms at vacant active sites on the surface; recombination of chemisorbed of O atoms with gas phase of O atoms and of CO molecules (Eley – Rideal recombination) and with physisorbed atoms (Langmuir – Hinshelwood recombination). The structural formulas for the catalytic activity coefficients as function of the surface conditions (temperature, pressure, and species concentrations) are derived. By interpreting the experimental data, obtained on an inductive plasma generator, model parameters are determined for SiO$_2$ - based coating materials. Comparison the calculated and measured heat fluxes shows, that the model may predict heat-transfer in a wide temperature range, from 300 up to 2000 K.

**ACKNOWLEDGMENTS**

The study was carried out with the support of the Russian Foundation for Basic Research (project No.02-01-00759) and A.M. Liapunov Franco-Russian Institute (Project 02-06).

**REFERENCES**
