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MODELING OF THE CATALYTIC PROPERTIES OF HIGH-TEMPERATURE SURFACE INSULATION IN A DISSOCIATED CARBON DIOXIDE – NITROGEN MIXTURE

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A model of the heterogeneous catalysis of a dissociated carbon dioxide – nitrogen mixture on high-temperature heat-shield coatings is developed; the model takes into account nonequilibrium adsorption-desorption reactions of nitrogen and oxygen atoms and carbon dioxide molecules and their recombination in the Eley-Rideal reactions. On the basis of a 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 catalysis model in question are chosen for three modern oxidant-resistant coating materials. The performances of these coatings are compared for the conditions of Mars Miniprobe entry into the Martian atmosphere. Their usability for the entry path considered is shown.

One of the main factors determining the heat transfer intensity during spacecraft entry into the Martian atmosphere is represented the recombination of the components of dissociated carbon dioxide, which constitutes about 96% of the atmosphere. Even at flight velocities of the order of 6 km/s, carbon dioxide is practically totally dissociated 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 the expense of using noncatalytic coatings, a fourfold reduction in the heat flux to the frontal surface of the vehicle could be achieved on most of the entry path, including the peak thermal load region.

High-temperature catalysis in dissociated air has been studied extensively, both experimentally and theoretically, in connection with the development of thermal insulation systems for Space Shuttle and Buran aeroassisted orbital transfer vehicles [1–4]. Originally, heterogeneous catalysis in theoretical models was described by first-order reactions with experimentally obtained rate constants. More recently, certain more accurate models [5–12] based on ideally adsorbed Langmuir layer theory [13] have been developed. These models made it possible adequately to describe – for a suitable choice of the relevant parameters – the aerodynamic heating on the windward side of reusable vehicles along the entire entry path.

At the same time, few studies have been devoted to high-temperature heterogeneous catalysis in dissociated carbon dioxide. In studying entry into the Martian atmosphere, the limiting cases of an ideal catalytic surface (with a maximum rate of heterogeneous recombination of the dissociated carbon dioxide components) and a noncatalytic surface [15–17] have mainly been considered in the literature. 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 [18, 19].

The first results of measurements of the dissociated carbon dioxide flow parameters, as well as of the heat fluxes to a catalytic surface and the temperature of the latter, were published in [20] for three types of coating materials and quartz. In that work, the effective rate constants of heterogeneous catalytic recombination of oxygen atoms and nitric oxide molecules on the surfaces of the coatings considered were also determined.

In this study, the approach developed in [5, 18, 19] is used to model the catalytic properties of heat-shield coatings in a dissociated CO_2–N_2 mixture. On the basis of an interpretation of the experimental data, explicit relationships between the catalytic activities and the near-surface conditions (temperature, pressure, and concentrations) are derived for the coatings studied in [20]. For each of these coatings, the heat fluxes at the Mars Miniprobe stagnation point are calculated along the vehicle's entry trajectory into the Martian atmosphere and the usability of the coatings in the thermal insulation system of the vehicle is established.

1. We will consider the flow of a dissociated carbon dioxide – nitrogen mixture past a catalytic surface; the mixture includes such species as O, N, C, O_2, N_2, NO, CO, and CO_2 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 Eley-Rideal reactions listed below:

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$$1.\ (\mathrm{O-S}) + \mathrm{O} \rightleftharpoons (\mathrm{S}) + \mathrm{O_2}, \qquad 2.\ (\mathrm{N-S}) + \mathrm{N} \rightleftharpoons (\mathrm{S}) + \mathrm{N_2}$$

$$3.\ (\mathrm{O-S}) + \mathrm{CO} \rightleftharpoons (\mathrm{S}) + \mathrm{CO_2}, \quad 4.\ (\mathrm{CO-S}) + \mathrm{O} \rightleftharpoons (\mathrm{S}) + \mathrm{CO_2}$$

and adsorption-desorption reactions of O and N atoms and CO molecules on active centers

$$5.\ \mathrm{O} + (\mathrm{S}) \rightleftharpoons (\mathrm{O-S}), \qquad 6.\ \mathrm{N} + (\mathrm{S}) \rightleftharpoons (\mathrm{N-S}), \qquad 7.\ \mathrm{CO} + (\mathrm{S}) \rightleftharpoons (\mathrm{CO-S})$$

No account has been taken of Langmuir-Hinshelwood recombination and adsorption of O_2, N_2, NO and CO_2 molecules. It is assumed that these processes are less probable on the temperature and pressure range considered ($300 \le T_w \le 2000$ K and $10^{-3} \le p \le 1$ atm). Heterogeneous reactions involving atomic carbon are also disregarded.

In accordance with the law of surface action, the mass rate of formation of an AB species in a j-th Eley-Rideal reaction

$$(\mathrm{A-S}) + \mathrm{B} = \mathrm{AB} + \mathrm{S}$$

is determined by the formula

$$r_{\mathrm{AB}} = k_j m_{\mathrm{AB}} (\rho/m)(\theta_{\mathrm{A}} x_{\mathrm{B}} - K_j x_{\mathrm{AB}} \theta), \qquad k_j = \gamma_j \sqrt{RT/2\pi m_{\mathrm{B}}}$$

Here, γ_j is the probability of formation of an AB particle in the collision of a B particle with a surface completely covered with adsorbed A particles; K_j is the equilibrium constant of this reaction, x_i are the molar concentrations of the species, θ_i are the degrees of occupancy of the surface by adsorbed substances, θ is the free surface fraction, ρ is the density, T is the temperature, R is the universal gas constant, and m_i and m are the molecular weights of i-th species and the gas mixture, respectively.

The mass rate of adsorption-desorption of an A particle in a j-th adsorption reaction

$$\mathrm{A} + \mathrm{S} = (\mathrm{A-S})$$

is equal to

$$r_{\mathrm{A}} = k_j m_{\mathrm{A}} (\rho/m) \left(x_{\mathrm{A}} \theta - \frac{K_j}{p} \theta_{\mathrm{A}} \right), \qquad k_j = \gamma_j \sqrt{\frac{RT}{2\pi m_{\mathrm{A}}}}$$

where p is the pressure and γ_j is the adsorption probability in the collision of an A particle with a totally free surface. The equilibrium constants K_j of the adsorption-desorption processes are expressed in terms of the statistical sums Q_k of the reagents and the adsorption energy E_A as follows:

$$K_j = \frac{Q_{\mathrm{A}} Q_{\mathrm{S}}}{Q_{(\mathrm{A-S})}} \exp\left(-\frac{E_{\mathrm{A}}}{RT} \right)$$

Taking into account the condition of stationary occupancy of the surface by adsorbed particles, the mass rates R_i of species formation in heterogeneous catalytic reactions can be expressed in terms of the deviations from equilibrium v_k (k=1, ..., 4) of the independent homogeneous reactions [5, 18, 19]

$$R_{\mathrm{O}} = -m_{\mathrm{O}} (\rho/m) \theta [2k_1 d_{\mathrm{O}} v_1 + (k_3 d_{\mathrm{O}} + k_4 d_{\mathrm{CO}}) v_3]$$

$$R_{\mathrm{CO}} = -m_{\mathrm{CO}} (\rho/m) \theta (k_3 d_{\mathrm{O}} + k_4 d_{\mathrm{CO}}) v_3$$

$$R_{\mathrm{CO_2}} = m_{\mathrm{CO_2}} (\rho/m) \theta [(k_3 d_{\mathrm{O}} + k_4 d_{\mathrm{CO}}) v_3 + l_{\mathrm{O}} k_3 K_3 d_{\mathrm{O}} v_4]$$

$$R_{\mathrm{N}} = -2m_{\mathrm{N}} (\rho/m) \theta k_2 d_{\mathrm{N}} v_2$$

$$d_{\mathrm{O}} = (l_{\mathrm{O}} x_{\mathrm{O}} + l_{\mathrm{O}}' x_{\mathrm{CO}} + K_5/p)^{-1}, \ d_{\mathrm{CO}} = (l_{\mathrm{CO}} x_{\mathrm{O}} + K_7/p)^{-1}, \ d_{\mathrm{N}} = (l_{\mathrm{N}} x_{\mathrm{N}} + K_6/p)^{-1}$$

$$v_1 = x_{\mathrm{O}}^2 - (K_{p1}/p) x_{\mathrm{O_2}}, \qquad v_2 = x_{\mathrm{N}}^2 - (K_{p2}/p) x_{\mathrm{N_2}}$$

$$v_3 = x_{\mathrm{O}} x_{\mathrm{CO}} - (K_{p3}/p) x_{\mathrm{CO_2}}, \qquad v_4 = x_{\mathrm{O}} x_{\mathrm{CO_2}} - K_{p4} x_{\mathrm{O_2}} x_{\mathrm{CO}}$$

Here, K_{pk} are the equilibrium constants of the corresponding gas-phase reactions.

The quantities l_i are equal to the ratios of the rate constants of the Eley-Rideal processes to those of the adsorption reactions

$$l_{\mathrm{O}}=k_1/k_5, \qquad l_{\mathrm{O}}'=k_3/k_5, \qquad l_{\mathrm{N}}=k_2/k_6, \qquad l_{\mathrm{CO}}=k_4/k_7$$

The free surface fraction θ is determined from the formula

$$1/\theta=1+(x_{\mathrm{O}_2}l_{\mathrm{O}}K_1+x_{\mathrm{CO}_2}l_{\mathrm{O}}'K_3+x_{\mathrm{O}})d_{\mathrm{O}}+(x_{\mathrm{N}_2}l_{\mathrm{N}}K_2+x_{\mathrm{N}})d_{\mathrm{N}}+(x_{\mathrm{CO}_2}l_{\mathrm{CO}}+x_{\mathrm{CO}})d_{\mathrm{CO}}$$

Considering that at $T_w \leq 3000$ K the quantities $K \ll 1$, the mass rates of recombination of oxygen atoms and carbon dioxide molecules in heterogeneous catalytic reactions can be written in the approximate form:

$$R_{\mathrm{O}}=-\rho(k_{\mathrm{O}}^{(1)}c_{\mathrm{O}}+k_{\mathrm{O}}^{(3)}c_{\mathrm{CO}}+k_{\mathrm{O}}^{(4)}c_{\mathrm{O}}), \qquad R_{\mathrm{CO}}=-\rho(k_{\mathrm{CO}}^{(3)}c_{\mathrm{CO}}+k_{\mathrm{CO}}^{(4)}c_{\mathrm{O}})$$

$$k_{\mathrm{O}}^{(1)}=2\gamma_1^*\sqrt{\frac{RT}{2\pi m_{\mathrm{O}}}}, \qquad k_{\mathrm{O}}^{(3)}=\frac{m_{\mathrm{O}}}{m_{\mathrm{CO}}}\gamma_3^*\sqrt{\frac{RT}{2\pi m_{\mathrm{CO}}}}, \qquad k_{\mathrm{O}}^{(4)}=\gamma_4^*\sqrt{\frac{RT}{2\pi m_{\mathrm{O}}}}$$

$$k_{\mathrm{CO}}^{(3)}=\gamma_3^*\sqrt{\frac{RT}{2\pi m_{\mathrm{CO}}}}, \qquad k_{\mathrm{CO}}^{(4)}=\frac{m_{\mathrm{CO}}}{m_{\mathrm{O}}}\gamma_4^*\sqrt{\frac{RT}{2\pi m_{\mathrm{O}}}}$$

$$\gamma_1^*=\gamma_1\theta_{\mathrm{O}}^*, \qquad \gamma_3^*=\gamma_3\theta_{\mathrm{O}}^*, \qquad \gamma_4^*=\gamma_4\theta_{\mathrm{CO}}^*$$

$$\theta_{\mathrm{O}}^*=\theta x_{\mathrm{O}}d_{\mathrm{O}}, \qquad \theta_{\mathrm{CO}}^*=\theta x_{\mathrm{CO}}d_{\mathrm{CO}}$$

where c_i are the mass concentrations of the species. The coefficients γ_1^*, γ_3^*, and γ_4^* represent the probabilities of oxygen atom and carbon dioxide molecule recombination in the corresponding Eley-Rideal reactions with allowance for the occupancy of the active centers by adsorbed particles.

2. In order to describe the catalytic properties of a surface within the framework of the catalysis model suggested, it is necessary to establish the temperature dependence of the quantities γ_j ($j=1, ..., 7$) and the equilibrium constants K_j of the adsorption reactions ($j=5, ..., 7$). In this study we will use a model representation of these functions with experimentally obtained parameters.

We considered the experimental data [20] for three types of siliconized coating materials, namely, the glassy coating of the Buran orbiter tile heat shield based on the SiO_2–B_2O_3–SiB_4 system (coating I); an oxidant-resistant carbonaceous coating based on aluminoborosilicate glass with a $MoSi_2$ admixture (coating II) , and a coating made of a new composite material [21] based on the Hf–Si–C–B system (coating III). For these materials, experimental data on the heat fluxes in three regimes of subsonic flow past the model were obtained using a high-frequency plasma generator [20]. Since the experiments were performed with carbon dioxide, nitrogen adsorption and heterogeneous recombination were not taken into account in the data processing.

To minimize the number of model parameters, the following simplifying assumptions were made on the basis of an analysis of data found in the literature: (1) the statistical sums $Q_{(\mathrm{A-S})}$ and Q_{S} coincide and (2) the recombination probabilities can be represented in the form of an Arrhenius temperature dependence $\gamma_j(T)=a_j\exp(-E_j^{ER}/RT)$ with adsorption proceeding with zero activation energy (γ_5=const and γ_7=const).

3. The available experimental data do not allow the unequivocal determination of all the parameters of the catalysis model. Hence, their values were varied within reasonable limits, subject to the condition that the r.m.s. deviation of the calculated heat fluxes from the measured ones did not exceed 5 per cent. In this study, the heat fluxes were calculated in the same way as in [20], that is, within the framework of the finite-thickness boundary layer problem using the gaseous medium model described in detail in [22]. 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^f to a cold, ideal catalytic surface (T_w=300 K, $\gamma_i^*=1$) coincide. The measured values were chosen on the basis of an analysis of the experimental data for copper and silver surfaces [20, 23] and are given in Table 1. 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 Δp are also given for three flow regimes.

In Fig. 1 we have plotted the surface-temperature dependence of the calculated heat fluxes to coating I at the stagnation point of the test model for the first (lower set of curves) and third (upper set) test regimes for various groups of catalysis model parameters in the experimental conditions [20]. Points *1* relate to the experimental results in accordance with which the model parameters were chosen, while curves N correspond to the heat fluxes to a noncatalytic surface.

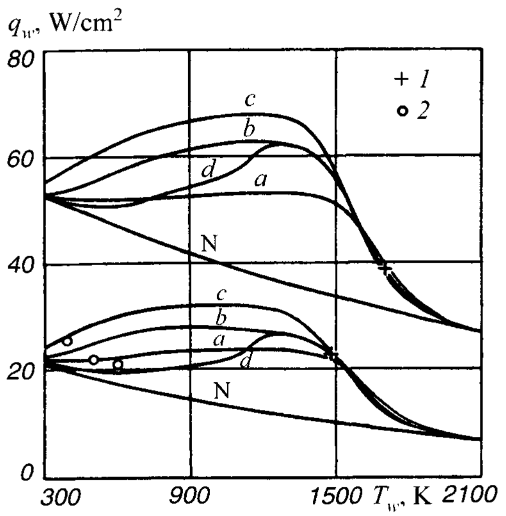

Fig. 1

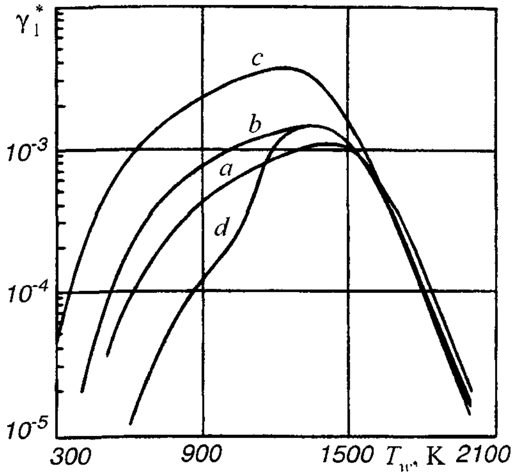

Fig. 2

Fig. 1. Temperature dependence of the heat fluxes to coating I at the stagnation point for the first and third test regimes and different sets of model parameters under the conditions specified in [20]. Curves N correspond to the heat fluxes to a noncatalytic surface; curves *a*, *b*, and *c* were obtained without and curve *d* with allowance for CO molecule adsorption; curve *b* corresponds to the model in which O atom adsorption is assumed to be equilibrium. The values of the model parameters for which the corresponding curves were obtained are given in Table 2. Points *1* and *2* relate to the results of [20] and [23], respectively.

Fig. 2. Temperature dependence of the probability of O atom recombination in the Eley-Rideal reactions for coating I. The notation is the same as in Fig. 1.

TABLE 1

Parameters	Regimes		
	1	2	3
p_e, gPa	100	100	100
T_e, K	3320	4360	5800
V_s, m/s	47.3	76.1	105.6
q_w^I, W/cm^2	46.4	74.4	103.7
N, kW	29	37	44
Δp, Pa	10.5	17.5	24.5

Curves *a*, *b*, and *c* were obtained without taking CO molecule adsorption into account, while curve *d* was obtained with account for this reaction. Curve *c* corresponds to the model in which O atom adsorption is near-equilibrium. The values of the parameters for which the curves were obtained are given in Table 2, where the activation energies and adsorption heats are indicated in kJ/mole. In the same table, the values of the model parameters chosen for coatings II and III are also given.

Note that at low temperatures the predicted heat fluxes to the surface with coating I are in satisfactory agreement with the experimental values for quartz (points *2*) [23], which mainly determines the catalytic properties of this coating. At the same time, on the intermediate temperature range, $400 < T < 1400$ K, the difference in the heat fluxes obtained for different sets of model parameters can be as high as 50%. The model parameters could be refined if additional experimental information on this temperature range was to hand.

In Fig. 2 we have plotted the temperature dependence of the probability γ_1^* of oxygen atom recombination in the Eley-Rideal reaction for collision with a surface with coating I for the same model parameter sets. The recombination probability is the product of two functions: $\gamma_1^*=\gamma_1\theta_O^*$. One of these increases with temperature, while the other, as the calculations showed, decreases sharply at high temperatures. Thus, a clearly defined maximum is formed at $T_w \approx 1350$ K.

TABLE 2

Curve	a_1^{ER}	a_2^{ER}	a_3^{ER}	γ_5	γ_7	E_O^{ad}	E_{CO}^{ad}	E_1^{ER}	E_3^{ER}	E_4^{ER}
a	0.015	0.015	0	0.025	0	300	0	25	15	0
b	0.038	0.038	0	0.025	0	280	0	25	15	0
c	0.018	0.018	0	1.0	0	280	0	15	10	0
d	0.038	0.038	0.038	0.025	0.013	280	280	25	15	25
Coating I	0.016	0.016	0	0.016	0	380	0	20	25	0
Coating II	0.042	0.042	0	0.025	0	400	0	15	25	0

The reason for this behavior is that at sufficiently low temperatures the surface is fully occupied by adsorbed species; however, the recombination rate in the Eley-Rideal reaction is low.

The recombination rate increases with temperature; simultaneously, the catalytic activity also grows. At sufficiently high temperatures (specific to each type of coating) thermic 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 [24]. It can be seen from Fig. 2 that the maximum value of γ_1^* does not exceed 10^{-2} and, depending on the choice of the model parameters, may vary over an order of magnitude.

In Fig. 3 the effective coefficients of heterogeneous recombination, γ_O^{ef} and γ_{CO}^{ef}, determined from the formulas

$$R_O=-\rho\gamma_O^{ef}\sqrt{\frac{RT}{2\pi m_O}}\,c_O,\qquad R_{CO}=-\rho\gamma_{CO}^{ef}\sqrt{\frac{RT}{2\pi m_{CO}}}\,c_{CO}$$

are plotted against the inverse temperature for a coating I in the first test regime for various model parameter sets. The points in this figure relate to the approximation derived in [23] on the basis of a comparison of the calculated heat fluxes with the experimental ones using a simpler catalysis model, in which it was assumed, in particular, that $\gamma_O^{ef}=\gamma_{CO}^{ef}$.

Clearly, on the $T_w < 1500$ K range there is a considerable scatter of the calculated values of γ_O^{ef} and γ_{CO}^{ef}, depending on the chosen set of model parameters. The approximation [23] is in fairly good agreement with curves *a* lying between γ_O^{ef} and γ_{CO}^{ef}.

The analogous results for coating III are presented in Fig. 4 for three test regimes (curves *1*, *2*, and *3*, respectively). The measured-calculated results [20] also lie between our calculated curves for γ_O^{ef} and γ_{CO}^{ef}. Note a certain stratification of the curves obtained in different test regimes due to the fact that the effective coefficients of heterogeneous recombination depend not only on the temperature but also on other surface flow parameters, such as concentrations and pressure. The different behavior of the γ^{ef} plots in the high-temperature region for coatings II and III, on the one hand, and for coating I, on the other, as noted in [20], can be explained by the difference in the adsorption heats for these coatings which determine the positions of the maximum for these quantities as a function of temperature. It is clear from Figs. 3 and 4 that for coating I the experiments were run on the temperature range to the left of the value at which the maximum of γ^{ef} is reached, while for coating III they were run to the right of this point. The situation with coating II is the same as for coating III.

4. To evaluate the influence of the catalysis model chosen on the calculated heat fluxes to the surface of a Martian vehicle, we calculated the flow past a spherical bluntness of radius R_0=0.38 m under conditions corresponding to the entry path of a Mars Miniprobe vehicle having the same radius of the aerobrake bluntness [25]. The freestream parameters for several points of the entry trajectory used in the calculations are given in Table 3. The flow was calculated within the framework of the viscous shock layer approximation. The gaseous medium model and the method of solving the governing equations are described in detail in [22]. It was assumed that the Martian atmosphere consists of 95.7% carbon dioxide, 2.7% nitrogen, and 1.6% argon. In view of the additive nature of the structural formulas, the results [5, 6] obtained by investigating the heat transfer on reusable silica coatings in dissociated air were used for describing the heterogeneous recombination of nitrogen atoms. The surface was assumed to be equilibrium emissive. The blackness coefficients of the surface were determined in accordance with the recommendations given in [20].

In Fig. 5 the heat fluxes at the stagnation point of coating I are plotted against the flight altitude *H* for the above-mentioned versions of the catalysis model. Note that the effect of variation of the model parameters on the maximum heat flux does not exceed several per cent. This can be explained, first of all, by the fact that the experimental conditions [20], on the basis of which these parameters were chosen, were close to the full-scale flight conditions at which the peak thermal loads are attained.

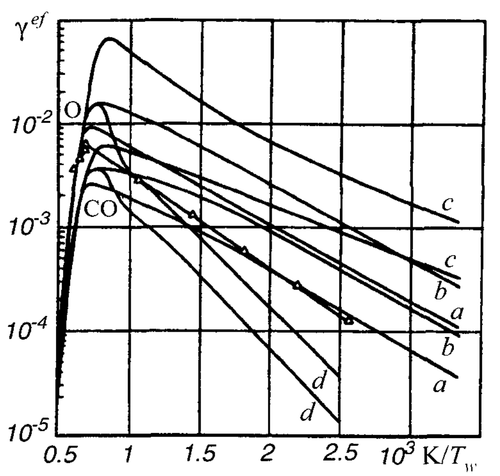

Fig. 3

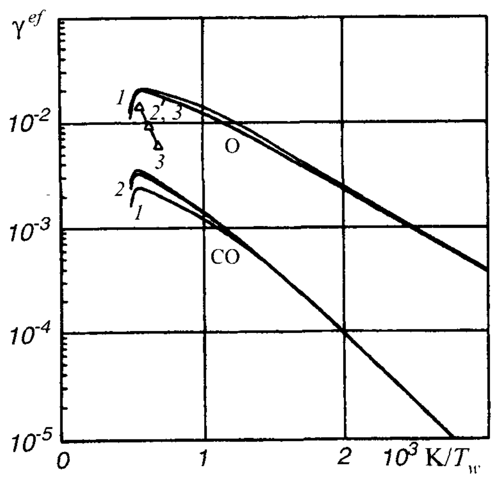

Fig. 4

Fig. 3. Temperature dependence of the effective coefficients of heterogeneous recombination, γ_O^{ef} and γ_{CO}^{ef}, for coating I. The points relate to the approximation [23]. The rest of the notation is the same as in Fig. 1.

Fig. 4. Temperature dependence of the effective coefficients of heterogeneous recombination, γ_O^{ef} and γ_{CO}^{ef}, for coating II. Curves *1*, *2*, and *3* relate to the corresponding test regimes. The points relate to the results of [20].

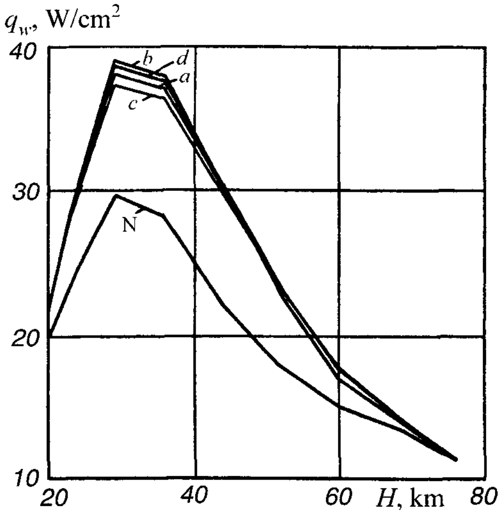

Fig. 5

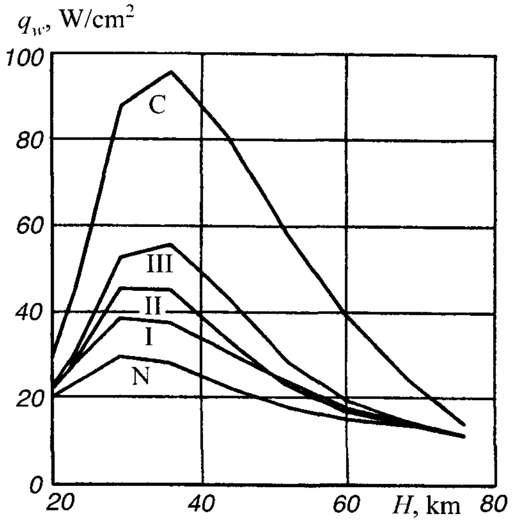

Fig. 6

Fig. 5. Flight altitude dependence of the heat fluxes at the stagnation point for different sets of parameters of the model describing the catalytic properties of a surface under Mars Miniprobe entry conditions. The trajectory parameters are given in Table 3. The notation is the same as in Fig. 1.

Fig. 6. Flight altitude dependence of the heat fluxes at the stagnation point for different coatings under Mars Miniprobe entry conditions. The trajectory parameters are given in Table 3. The Roman numbers correspond to the coatings, N is an ideal noncatalytic surface, and C is an ideal catalytic surface.

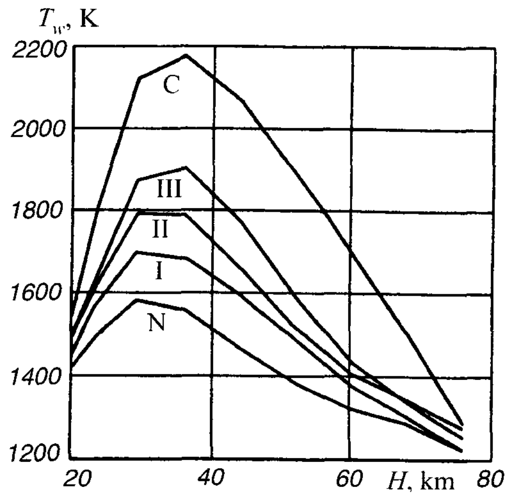

Fig. 7. Flight altitude dependence of the equilibrium surface temperature for different coatings under Mars Miniprobe entry conditions. θhe notation is the same as in Fig. 6.

TABLE 3

H, km	V_∞, m/s	ρ_∞, kg/m^3	T_∞, K
75.92	5800	$3.01\cdot10^{-6}$	129
67.89	5791	$9.51\cdot10^{-6}$	130
59.87	5769	$2.89\cdot10^{-5}$	134
51.84	5690	$8.37\cdot10^{-5}$	140
43.82	5536	$2.27\cdot10^{-4}$	148
36.79	5172	$5.81\cdot10^{-4}$	158
28.95	4539	$1.23\cdot10^{-3}$	167
23.16	3471	$2.27\cdot10^{-3}$	174
17.89	2549	$3.84\cdot10^{-3}$	182

In Figs. 6 and 7 plots of the heat flux and the equilibrium radiation temperature at the stagnation point on the surface versus the flight altitude are presented for coatings I (variant *a*) and II and III, as well as for a noncatalytic (curve N) and an ideal catalytic (curve C) surface. These results show that the catalytic activity is lowest for coating I. By using this coating the maximum heat flux could be reduced by a factor of 2.5 as compared with that to an ideal catalytic surface. The corresponding decrease in the equilibrium radiation temperature of the surface is about 500 K. For reference, by using a noncatalytic surface, the maximum heat flux could be reduced by a factor of 3.2.

When coatings II and III are used, higher values of the heat fluxes and surface temperatures are realized. Nevertheless, for all the coatings studied, the maximum surface temperatures on the trajectory under consideration do not exceed the greatest permissible temperatures for these coatings in prolonged use (1800 K for coatings I and II and 1900 K for coating III).

Summary. On the basis of ideal adsorbed Langmuir layer theory, a model of the interaction of dissociated carbon dioxide – nitrogen mixture with a catalytic surface is developed; the model takes into account the nonequilibrium nature of the adsorption-desorption reactions and the Eley-Rideal reactions. The structural formulas for the catalytic activity coefficients as a function of the surface conditions (temperature, pressure, and species concentrations) are derived. By interpreting the experimental data obtained on an inductive plasma generator [20], model parameters are determined for three high-temperature heat-shield coatings. The studies show that additional experimental data over a wider temperature range are needed for adequately modeling the catalytic properties of the surface.

The performances of the above-mentioned coatings are compared for the conditions of entry of a Mars Miniprobe into the Martian atmosphere. The results obtained show they could be used in the thermal insulation system of the vehicle. It is established, in particular, that using the glassy coating of the Buran orbiter tile heat shield would result in a 2.5-fold reduction in the maximum heat flux to the vehicle nose along the entire trajectory as compared with an ideal catalytic surface and in a reduction of the maximum surface temperature from 2170 to 1695 K.

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REFERENCES

1. P. N. Baronets, A. N. Gordeev, A. F. Kolesnikov, *et al.*, "Developing heat shield materials for the "Buran" orbital vehicle using an inductive plasma generator," in: *Gagarin Scientific Studies on Aviation and Cosmonautics, 1990, 1991* [in Russian], Nauka, Moscow (1991), p. 41.
2. G. E. Lozino-Lozinskii, "'Buran' flight," in: *Gagarin Scientific Studies on Aviation and Cosmonautics, 1989* [in Russian], Nauka, Moscow (1990), p. 6.
3. C. D.Scott, "Effect of nonequilibrium and wall catalysis on Shuttle heat transfer," *J. Spacecraft Rockets*, **22**, 489 (1985).
4. O. Yu. Polyanskii, M. M. Kuznetsov, V. L. Men'shikova *et al.*, *Effect of the Real Gas Properties on the Aerodynamic and Thermal Characteristics of Hypersonic Vehicles* [in Russian], Central Aerohydrodynamics Institute, Department of Scientific and Technological Information, Review No. 676 (1987).
5. V. L. Kovalev and O. N. Suslov, "Model of the interaction between partially ionized air and a catalytic surface," in: *Investigation of Hypersonic Aerodynamics and Heat Transfer with Allowance for Nonequilibrium Chemical Reactions* [in Russian], Moscow University Press, Moscow (1987), p. 58.
6. V. L. Kovalev and O. N. Suslov, "Simulation of the interaction between partially ionized air and the catalytic surface of high-temperature reusable thermal insulation," *Izv. Ross. Akad. Nauk. Mekh. Zhidk. Gaza*, No. 5, 179 (1996).
7. G. N. Zalogin and V. V. Lunev, "Catalytic properties of materials in a nonequilibrium dissociated air flow," *Izv. Ross. Akad. Nauk, Mekh. Zhidk. Gaza*, No. 5, 161 (1997).
8. E. J. Jumper and W. A. Seward, "Model for oxygen atom recombination on silicon-dioxide surfaces," *J. Thermophysics Heat Transfer*, **5**, 284 (1991).
9. R. J. Willey, "Comparison of kinetic models for atom recombination on high-temperature reusable surface insulation," *J. Thermophysics Heat Transfer*, **7**, 55 (1993).
10. O. Deutschmann, U. Riedel, and J. Warnatz, "Modeling of nitrogen and oxygen recombination on partial catalytic surfaces," Universität Stuttgart, Institut für Technische Verbrennung, Preprint No. 23 (1994).
11. F. Nasuti, M. Barbato, and C. Bruno, "Material-dependent catalytic recombination modeling for hypersonic flows," *J. Thermophysics Heat Transfer*, **10**, 131 (1996).
12. A. Daiss, H. H. Frühauf, and E. W. Messerschmidt, "Modeling of catalytic reactions on silica surfaces with consideration of slip effects," *J. Thermophysics Heat Transfer*, **11**, 346 (1997).
13. I. Langmuir, "Monolayers on solids," *J. Chem. Soc.*, **4**, 511 (1940).
14. V. L. Kovalev, A. F. Kolesnikov, A. A. Krupnov, and M. I. Yakushin, "Analysis of phenomenological models describing the catalytic properties of high-temperature reusable coatings," *Izv. Ross. Akad. Nauk, Mekh. Zhidk. Gaza*, No. 6, 133 (1996).
15. Y.-K. Chen, W. D. Henline, D. A. Stewart, and G. V. Candler, "Navier-Stokes solution with surface catalysis for Martian atmospheric entry," *J. Spacecraft Rockets*, **30**, 32 (1993).
16. R. A. Mitcheltree and P. A. Gnoffo, "Wake flow about the Mars Pathfinder entry vehicle," *J. Spacecraft Rockets*, **32**, 771 (1995).
17. R. N. Gupta, K. P. Lee, and C. D. Scott, "Aerothermal study of Mars Pathfinder Aeroshell," *J. Spacecraft Rockets*, **33**, 61 (1996).
18. V.L.Kovalev, "Phenomenological models of the catalytic properties of the thermal insulation of vehicles entering the Martian atmosphere," in: *Proceedings of the 14th International Workshop on Models in the Continuum Mechanics* [in Russian], Moscow Physical and Technical Institute (1998), p. 83.
19. V. L. Kovalev, "Modeling of the catalytic properties of heat-shield coatings on entry into the Martian atmosphere," *Vestn. MGU, Ser. 1, Mat. Mekh.*, No. 1, 37 (1999).
20. N. G. Bykova, S. A. Vasil'evskii, A. N. Gordeev, A. F. Kolesnikov, I. S. Pershin, and M. I. Yakushin, "Determination of the effective probabilities of catalytic reactions on the surfaces of heat shield materials in dissociated carbon dioxide flows," *Izv. Ross. Akad. Nauk, Mekh. Zhidk. Gaza*, No. 6, 144 (1997).
21. G. A. Kravetskii, A. V. Kuznetsov, B. I. Kostikov, and V. V. Rodionov, "Heat-resistant non-oxidizing shield coating made from carbon-carbon and carbon-silicate-carbide materials and structural elements made from these materials for aeronautical and rocket engineering," in: *Proceedings of the 1st International Aerospace Symposium "Man-Earth-Space", 1992, Vol. 5, Materials and Production Technology of Aerospace Engineering* [in Russian], Engineering Academy Press, Moscow (1995), p. 249.
22. N. E. Afonina and V. G. Gromov, "A viscous shock-layer study of the flow in the stagnation region of a vehicle entering the Martian atmosphere," Moscow State University, Institute of Mechanics, Preprint No. 31–97 (1997).
23. A. F. Kolesnikov, I. S. Pershin, S. A. Vasil'evskii, and M. I. Jakushin, "Study of quartz surface catalycity in dissociated carbon dioxide subsonic flows," *AIAA Paper*, No. 2847 (1998).
24. P. Kolodziej and D. A. Stewart, "Nitrogen recombination on high-temperature reusable surface insulation and the analysis of its effects on surface catalysis," *AIAA Paper*, No. 1637 (1987).
25. V. Rubio Garcia, L. Marraffa, G. Scoon, R. Roumeas, and R. Seiler, "Mars Miniprobes. Elements of aerothermodynamics and entry trajectories," in: *Proceedings of 3d European Symposium on Aerothermodynamics for Space Vehicles. ESTEC. Noordwijk, the Netherlands. 24–26 November 1998* (1998), p. 155.