

ANALYSIS OF A NUMBER OF ELEMENTS IN THE MECHANISM OF MASS ENTRAINMENT OF CARBON MATERIAL WITHIN THE FRAMEWORK OF THE COMPLETE THERMOCHEMICAL MODEL OF ITS DESTRUCTION

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The results of a numerical solution of the equations constructed for a frozen boundary layer on the surface of a carbon material, with allowance for the complete thermochemical model of the entrainment of its mass, are presented. The results obtained are compared with the data that correspond to the use of the analogy between the processes of heat and mass transfer in a boundary layer and of the simplified model of the mass entrainment of the materials of the class considered. The results of comparison between experimental and calculated-theoretical data on the rate of destruction of the ATJ-grade graphite are also presented.

Keywords: graphite, oxidation, sublimation, evaporation, condensation, diffusion, mass entrainment, boundary layer.

Introduction. Heat shielding by mass entrainment has for a long time been the main kind of protection for elements of rocket-space technology constructions and of other high-energy facilities from the action of high-velocity and high-temperature gas flows on them. The most widespread and promising class of heat-shielding materials of such a kind are carbon-carbon structure materials that possess high physicomechanical characteristics, with their chemical composition practically not differing from the chemical composition of graphite.

The generally accepted opinion on the mechanism of destruction of purely carbon materials (they will be called graphite in what follows) is given in Fig. 1 in which regimes 1 and 3 of kinetic oxidation of carbon and 2 and 4 of diffusional oxidation of carbon to carbon dioxide and carbon oxide, respectively, are singled out, as well as regime 5 of its sublimation. It should be noted in this connection that in such a view on the mechanism of graphite destruction no allowance is made for the possibility of the mutual influence of the processes of kinetic oxidation and sublimation of carbon. For the first time, this fact has attracted attention in work [1] in which it is shown, in particular, that account for this factor may lead to substantial deformation undergone by the dependence of the mass rates of the progress of the indicated processes on the temperature of the outer surface of the material immersed in an incoming gas flow (in what follows we will use the term "wall" for this surface). In the present work, we have made an attempt at developing and deepening these investigations.

Physicomathematical Statement of the Problem. The self-similar equations that describe the flow of a multicomponent nonionized gas mixture in a laminar frozen boundary layer in the vicinity of the critical point on a sphere in Lees–Dorodnitsyn variables are given in the following generally accepted form [2, 3]:

$$\left(\frac{\rho \mu}{\rho_e \mu_e} f_{\eta\eta} \right)_{\eta} = -ff_{\eta\eta} + 0.5 \left(f_{\eta}^2 - \frac{\rho_e}{\rho} \right), \tag{1}$$

$$\left(\frac{\rho \lambda}{\rho_e \mu_e} T_{\eta} \right)_{\eta} = -fc_p T_{\eta} + \Psi T_{\eta} \sum_{i=1}^n c_{pi} J_i, \tag{2}$$

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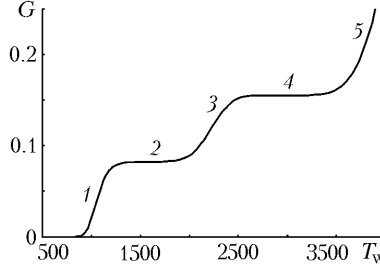


Fig. 1. Mass rate of graphite gasification vs. the "wall" temperature. T_w , K.

$$\Psi J_{i\eta} = f C_{i\eta} \quad (i = \overline{1, n-1}), \quad (3)$$

$$\kappa_{i\eta} = \frac{\Psi \rho_e \mu_e M}{\rho^2} \sum_{j=1}^n \left(\frac{\kappa_j J_j}{M_j D_{ij}} - \frac{\kappa_j J_i}{M_i D_{ij}} \right) \quad (i = \overline{1, n-1}), \quad (4)$$

$$\sum_{i=1}^n \kappa_i = 1, \quad \sum_{i=1}^n J_i = 0, \quad (5)$$

$$f(0) = -\Psi G_{\text{gas}} A, \quad f_\eta(0) = 0, \quad T(0) = T_w, \quad \kappa_i(0) = \kappa_{iw} \quad (i = \overline{1, n}), \quad (6)$$

$$f_\eta(\eta_e) = 1, \quad T(\eta_e) = T_e, \quad \kappa_i(\eta_e) = \kappa_{ie} \quad (i = \overline{1, n}). \quad (7)$$

The chemical composition of the gas mixture will be limited to the components O, O₂, N, N₂, NO, C, C₂, C₃, CO, CO₂, CN, and Ar for the calculation of the transfer properties of which we will use the Lennard-Jones potential function and the present-day data on viscosity that are generalized in [4]. In turn, to calculate the transfer properties of a gas mixture on the whole we will apply one of the most qualitative approaches based on the use of Hirschfelder's formulas [5].

The values of the quantities G_{gas} , T_w , and κ_{iw} entering into the boundary condition on the "wall" are determined by solving a system of nonlinear algebraic equations that are given in [1] and that describe the mechanism of thermomechanical destruction of graphite; the mechanism accounts for the complete thermochemical model of the graphite mass entrainment. This system of equations, which includes the Langmuir–Knudsen formula in the form given in [2] to calculate the rate of nonequilibrium sublimation of carbon, the formula to calculate the rate of kinetic oxidation of carbon in the form of the Arrhenius law, the heat and mass balances of chemical elements on the "wall," and the equations of equilibrium of chemical reactions, has the following form:

$$G_{\text{gas}} = G_{\text{ox}} + G_{\text{sub}}, \quad (8)$$

$$G_{\text{ox}} = \rho_w \left(C_{\text{O}_2 w} + C_{\text{O} w} r_{\text{O}} + C_{\text{NO} w} r_{\text{NO}} + C_{\text{CO}_2 w} r_{\text{CO}_2} \right) \frac{K_w}{A} \exp \left(-\frac{E_w}{R_{\text{un}} T_w} \right), \quad (9)$$

$$G_{\text{sub}} = \sum_{k=1}^3 \zeta_k \frac{P_{C_k w, s} - P_{C_k w}}{A \sqrt{2\pi R_{\text{un}} T_w} / (kM_C)}, \quad (10)$$

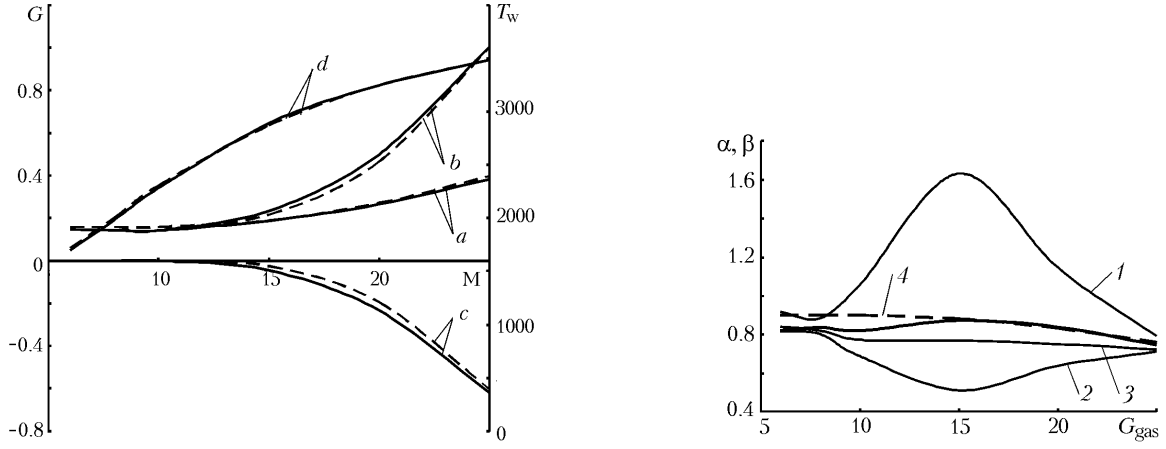


Fig. 2. Dependence of the wall temperature, rate of graphite gasification, and of its components on the Mach number with different approaches to calculation of the processes of heat and mass transfer in a boundary layer: a) G_{gas} ; b) G_{ox} ; c) G_{sub} ; d) T_w . T_w , K.

Fig. 3. Heat- and mass transfer coefficients of chemical elements vs. the velocity of injection of the material vapor into the boundary layer with different approaches to calculation of the processes of heat and mass transfer in a boundary layer: 1) β_{O} ; 2) β_{N} ; 3) β_{C} ; 4) α .

$$\left(\beta_{\text{O}} + G_{\text{gas}}\right) \sum_{i=1}^n C_{iw} v_{Oi} = \beta_{\text{O}} \sum_{i=1}^n C_{ie} v_{Oi}, \quad (11)$$

$$\left(\beta_{\text{N}} + G_{\text{gas}}\right) \sum_{i=1}^n C_{iw} v_{Ni} = \beta_{\text{N}} \sum_{i=1}^n C_{ie} v_{Ni}, \quad (12)$$

$$\left(\beta_{\text{C}} + G_{\text{gas}}\right) \sum_{i=1}^n C_{iw} v_{Ci} = G_{\text{gas}}, \quad (13)$$

$$\frac{p_{\text{Ow}}^2}{p_{\text{O}_2\text{w}}} = k_{\text{eqO}_2}, \quad \frac{p_{\text{Nw}}^2}{p_{\text{N}_2\text{w}}} = k_{\text{eqN}_2}, \quad \frac{p_{\text{Ow}} p_{\text{Nw}}}{p_{\text{NOw}}} = k_{\text{eqNO}}, \quad \frac{p_{\text{Cw}}^2}{p_{\text{C}_2\text{w}}} = k_{\text{eqC}_2},$$

$$\frac{p_{\text{Cw}}^3}{p_{\text{C}_3\text{w}}} = k_{\text{eqC}_3}, \quad \frac{p_{\text{Ow}} p_{\text{Cw}}}{p_{\text{COw}}} = k_{\text{eqCO}}, \quad \frac{p_{\text{Ow}} p_{\text{Cw}}}{p_{\text{CO}_2\text{w}}} = k_{\text{eqCO}_2}, \quad \frac{p_{\text{Nw}} p_{\text{Cw}}}{p_{\text{CNw}}} = k_{\text{eqCN}}, \quad (14)$$

$$\alpha_{\text{h}} (h_{00} - h_w) - \sum_{i=1}^n \gamma_i (C_{iw} - C_{ie}) h_{iw} - \frac{\varepsilon_w \sigma T_w^4}{A} = G_{\text{gas}} \left(h_{\text{C con}} \frac{P_{\text{er}}}{1 - P_{\text{er}}} + h_w - h_{\infty} \right). \quad (15)$$

Results of Investigations. In Figs. 2 and 3 the solid lines present a number of data calculated within the framework of the outlined physicomathematical statement of the problem for a sphere of radius equal to 0.1 m at a pressure in a boundary layer equal to 101,325 Pa. Presented in the figures for comparison are also the results of the

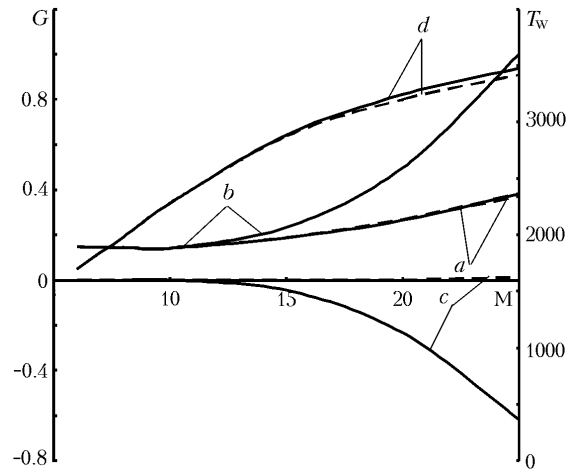


Fig. 4. Dependence of the wall temperature, rate of graphite gasification, and of its components on the Mach number in different approaches to the account for the chemical activity of purely carbon substances: a) G_{gas} ; b) G_{ox} ; c) G_{sub} ; d) T_w . T_w , K.

investigations (dashed lines) carried out using the analogy between the processes of heat and mass transfer, within the framework of which $\beta_{\text{O}} = \beta_{\text{N}} = \beta_{\text{C}} = \alpha$ and the function of the weakening of a heat flux by gas injection into a boundary layer [6].

In carrying out these calculations, the same values of the accommodation coefficients as in [2] were used: $\zeta_{\text{C}} = 0.3$, $\zeta_{\text{C}_2} = 0.5$, and $\zeta_{\text{C}_3} = 0.1$; the kinetic constants were equal to $K_w = 4.5 \cdot 10^{10}$ m/sec and $E_w = 1.72 \cdot 10^8$ J/kmole, which, according to the terminology of work [1], signifies the application of the "fast" kinetics of oxidation of carbon; no distinction was made between the rates of oxidation of carbon by various oxidants, i.e., $r_{\text{O}} = r_{\text{NO}} = r_{\text{CO}_2} = 1$.

As it follows from the analysis of the data presented, at high Mach numbers there actually appears a third kinetic branch of carbon oxidation induced by the dissociation of carbon oxide; the existence of this branch was first noted in [1]. The dissociation of carbon oxide also leads to an excess of the partial pressure of free carbon over the pressure of its saturated vapor causing carbon condensation on the "wall." Thus, allowance for the complete thermochemical scheme of carbon mass entrainment leads to a qualitative change in the physics of the phenomenon considered (as compared to its classical representation): the diffusional regime of carbon oxidation is replaced by a kinetic one, whereas its sublimation proceeds not in the regime of evaporation, but rather in the regime of condensation.

Important is also the fact that the use of engineering methods of solution based on the analogy between the processes of heat and mass transfer allows one to qualitatively correctly describe the principal laws governing the progress by the phenomenon considered. Besides, from the quantitative point of view, the error of engineering calculation of the rate of destruction of material that does not exceed $\sim 10\%$ may be considered admissible for the majority of practical applications. At the same time, attention should be paid to the fact that within the framework of the engineering approach the quality of description of mass transfer processes proceeding in a boundary layer is extremely low.

A comparison of the results of numerical solution of the boundary layer equations (solid lines) with similar data obtained assuming the absence of carbon sublimation products in chemical reactions on the "wall" (dashed lines) is presented in Fig. 4. With the latter assumption, it turns out that the incipience of the regime of carbon condensation is impossible in principle, which, as can be easily seen from the data presented, exerts a noticeable influence on the intensity of an increase in the rate of its oxidation with a rising Mach number. However, the difference in the total characteristics of the material mass entrainment G_{gas} and T_w that corresponds to the use of numerical solutions of the boundary-layer equations with different formulas to calculate the carbon sublimation rate appears so insignificant that it can be neglected.

Figure 5 compares the results of the numerical solution of the boundary-layer equations obtained within the framework of the complete thermochemical model of the graphite mass entrainment with different models of carbon

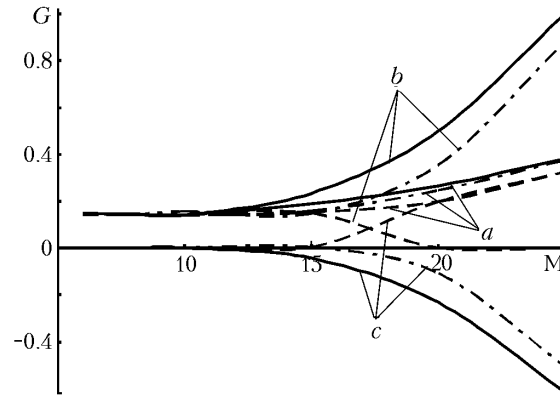


Fig. 5. Dependence of the rate of graphite gasification and of its components on the Mach number for various models of kinetic oxidation of carbon: a) G_{gas} ; b) G_{ox} ; c) G_{sub} .

oxidation. According to the terminology of [1], the oxidation models 1 and 2 will be called the models of the "fast" and "slow" kinetics. Just as above, for the former it is assumed that $K_w = 4.5 \cdot 10^{10}$ m/sec, $E_w = 1.72 \cdot 10^8$ J/kmole, $r_{\text{O}} = r_{\text{NO}} = r_{\text{CO}_2} = 1$, with model 2 differing from model 1 only by the value of the constant $K_w = 4.5 \cdot 10^6$ m/sec. In turn, model 3 differing from model 1 only by the value of the constant $r_{\text{CO}_2} = 0.0001$ and being intended for the analysis of the influence that may be exerted on the mechanism of material mass entrainment by the difference in the kinetic constants of individual heterogeneous chemical reactions of its oxidation will be called the model of the "intermediate" kinetics. The calculation results obtained within the framework of oxidation models 1, 2, and 3 are represented in Fig. 5 by solid, dash, and dash-dotted lines, respectively.

As is seen, at high Mach numbers the transition from the "fast" kinetics of carbon oxidation to a "slow" one is accompanied by a cardinal change in the mechanism of material mass entrainment. With an increase in the Mach number the rate of carbon oxidation no longer increases but decreases, attaining the zero level, whereas the process of carbon sublimation passes from a condensation phase into an evaporative one. Thus, when the model of the "slow" kinetics is used, the traditional mechanism of the graphite mass entrainment is implemented, within the framework of which the process of carbon evaporation occurs against the background of its diffusional oxidation. In view of this, it seems important that the total rates of the destruction of the material in oxidation models 1 and 2 differ substantially. In the given series of calculations this difference attains already a factor of 1.5 and may be still higher in transition to a faster kinetics of carbon oxidation. Thus, we note the substantial influence exerted by the kinetics of oxidation of carbon on the sum characteristics of thermochemical destruction of carbon.

An analysis of the chemical composition of a gas on the "wall" shows that at high Mach numbers the partial pressure of carbon dioxide substantially exceeds that of free oxygen if $r_{\text{O}} = r_{\text{CO}_2}$. Thus, on the third kinetic branch of carbon oxidation the rate of the process is determined by carbon dioxide. At the same time it is known that the intensity of the process of carbon oxidation in the vapors of carbon dioxide is much lower than in an air medium. Therefore it is of considerable interest to carry out investigations with different rates of carbon oxidation by free oxygen and carbon dioxide, precisely which was done within the framework of oxidation model 3.

As is seen, the change of the oxidizing components in transition from oxidation model 1 to oxidation model 3 does not lead to a noticeable change in the main results of calculation. At the same time, within the framework of model 3 one has the possibility of accounting for the difference in the rates of carbon oxidation by carbon dioxide and free oxygen.

Figure 6 presents the results of computational-theoretical investigations and experimental data on the dependence of the dimensionless rate of the destruction of ATJ-type carbon on the "wall" temperature [1] (the data were obtained on the basis of the primary results of experimental investigations from [7]). Here, the results of calculations were obtained within the framework of the above-described "intermediate" model of carbon oxidation (i.e., at $r_{\text{O}} = 1$ and $r_{\text{CO}_2} = 0.0001$) by varying the Mach number and preserving the value $p_{00} = 101,325$ Pa (they relate to the vicinity of the critical point on the blunt body of revolution). Curves 1 and 2, in turn, correspond to the case of equality

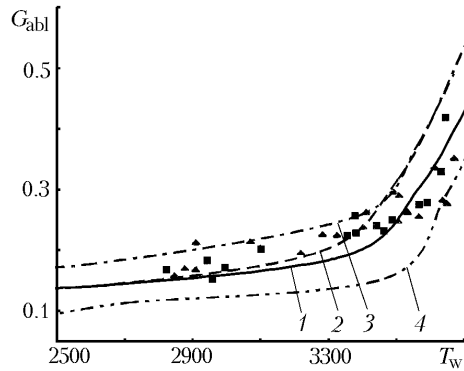


Fig. 6. Comparison between computational-theoretical and experimental data on the dependence of the mass velocity of ATJ-type graphite destruction on the wall temperature (different symbols relate to different shapes of samples).

of the mass velocities of gasification and destruction of the material when the values of the kinetic constant $K_w = 10^{10}$ m/sec and $3 \cdot 10^{10}$ m/sec were used in calculations. The experimental data presented here and designated by different symbols correspond to the same stagnation level. To ensure the adequacy of the average of predicted and experimental values of the heat transfer coefficient on an impermeable "wall," the value of the body bluntness radius was adopted equal to 0.026 m. It is seen that the use of the above-indicated data on the kinetics of carbon oxidation in calculations allows one in principle to satisfactorily describe the entire range of experimental data. However, attention should be paid to the stable excess of the experimental values of the rate of graphite destruction over the corresponding computational-theoretical data in the regime of diffusional oxidation of material.

In the carrying out of the present investigation use was made of both rigorous methods of calculation of diffusion in a multicomponent boundary layer and the present-day data on the transfer properties of gas mixtures. This allows us to state that in a diffusional regime of material destruction a certain portion of carbon is entrained mechanically. A similar conclusion on the necessity of accounting for the mechanical entrainment of the carbon mass in the analyzed series of experimental investigations was also made in [7]. The reason for the given phenomenon seems to be associated with the inhomogeneity of the material whose components possess a different chemical activity relative to the heterogeneous chemical interaction with oxidizing components [8]. As a result, some of the carbon grains on the "wall" can be "stripped" and subsequently entrained by the incoming gas flow.

Curve 3 in Fig. 6 presents the results of calculations obtained with the use of the fraction of mechanically entrained mass in the total rate of material destruction equal to 0.2. It is seen that virtually the entire experimentally fixed scatter of the rate of material destruction lie on the region bounded by curves 1 and 3 and corresponding to the value of the kinetic constant $K_w = 10^{10}$ m/sec.

The results of calculations performed at $K_w = 10^6$ m/sec and in the absence of the mechanical entrainment of the mass of the carbon are shown by curve 4 in Fig. 6. They illustrate the possibility of application of the traditional mechanism of graphite mass entrainment within the framework of which the process of carbon evaporation occurs against the background of its diffusional oxidation. As is seen, the computational data obtained within the framework of such an approach do not allow one to satisfactorily describe the considered range of experimental data without introduction of the mechanical entrainment of the carbon mass. But if we introduce the nonzero value of P_{er} into calculation, it should be much higher than 0.2.

CONCLUSIONS

1. A numerical solution of self-similar equations of a frozen laminar boundary layer in the vicinity of the critical point of a sphere on the surface of a carbon material with account for the entire thermochemical model of its destruction has been obtained.

2. The use of the complete thermochemical scheme of entrainment of the mass of carbon materials leads to a qualitative change in the physics of the progress of this phenomenon: to the appearance of the third kinetic branch in

the region of high temperatures in the zone of carbon oxidation and of the associated condensation regime of carbon sublimation.

3. The application, for the solution of the given problem, of the engineering approach based on the use of the analogy between the processes of heat- and mass transfer allows one to qualitatively correctly describe all basic trends in the phenomenon considered and ensure a satisfactory accuracy of computation for the majority of practical applications.

4. At high temperatures of the "wall" the replacement of the diffusional model of carbon oxidation by the kinetic one may lead to a substantial increase in the rate of material destruction.

5. The exclusion of the products of carbon sublimation from the chemical reactions proceeding on the "wall" does not lead to a noticeable change in the total characteristics of mass entrainment despite the qualitative distortion of the physics of the progress of the phenomenon considered.

6. The results of experimental investigation of the destruction of the ATJ-type graphite show that approximately 20% of its mass are entrained mechanically.

7. A satisfactory agreement between calculated and experimental data on the dependence of the rate of destruction of ATJ graphite on the "wall" temperature has been obtained.

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NOTATION

A , coefficient of convective heat transfer on an impermeable wall, $\text{kg}/(\text{m}^2\cdot\text{sec})$; C , mass concentration; c , heat capacity, $\text{J}/(\text{kg}\cdot\text{K})$; D , coefficient of binary diffusion, m^2/sec ; E_w , activation energy, J/kmole ; f , dimensionless stream function; G , mass velocity in fractions of the coefficient of convective heat transfer on an impermeable wall; h , enthalpy, J/kg ; J , diffusional mass flux, $\text{kg}/(\text{m}^2\cdot\text{sec})$; K_w , kinetic constant, m/sec ; k_{eq} , constant of the equilibrium of the chemical reaction of formation of a substance from atoms, Pa^a ($a = 1, 2$); M , Mach number in the incoming flow; M , mole mass, J/kmole ; n , number of components in a mixture; P , fraction in the total rate of destruction; p , pressure, Pa ; R , gas constant, $\text{J}/(\text{kmole}\cdot\text{K})$; r , ratio of the rate of oxidation of carbon by the substance to the rate of its oxidation by molecular oxygen; T , temperature, K ; u , longitudinal component of velocity vector, m/sec ; α , coefficient of convective heat transfer in fractions of its value on an impermeable wall; β , γ , coefficients of mass transfer of a chemical element and substance in fractions of the coefficient of convective heat transfer on an impermeable wall; ε , emissivity; η , self-similar Lees–Dorodnitsyn coordinate; κ , mole concentration; λ , thermal conductivity, $\text{W}/(\text{m}\cdot\text{K})$; μ , coefficient of dynamic viscosity, $\text{kg}/(\text{m}\cdot\text{sec})$; v , mass fraction of the chemical element in the substance; ρ , density, kg/m^3 ; σ , Stefan–Boltzmann constant, $\text{W}/(\text{m}^2\cdot\text{K}^4)$; Ψ , $1/\sqrt{2\rho_e\mu_e u_{ex}}$, $\text{m}^2\cdot\text{sec}/\text{kg}$; ζ , accommodation coefficient. Subscripts: 00, stagnation; ∞ , unheated material; con, condensed phase; e, external edge of the boundary layer; en, mechanical entrainment; eq, equilibrium; gas, material gasification; h, component owing its origin to heat conduction; i, j , numbers of components; k , number of atoms in a purely carbon substance; ox, oxidation; s, saturated vapor; sub, sublimation; x , derivative over the longitudinal coordinate; un, universal; w, "wall;" η , derivative over the coordinate η .

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