HEAT AND MASS TRANSFER AT A VITROPLASTIC SURFACE IN A HIGH-TEMPERATURE AIR STREAM

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UDC 536.244:629.7.023.225

Analyzed are the basic laws which govern the decomposition of vitrographitic materials and the effect of superficial carbon burnout on the wear characteristics of such materials.

The material under consideration is heat resistant glass with an organic binder which at moderate temperatures decomposes into coke. As was done in [1], we assume that the surface layer of this material consists of silicon dioxide and carbon. Among the gaseous products formed by decomposition of the binder we will consider only molecular hydrogen and carbon monoxide.

When a material contains several ingredients, then the decomposition rate of each is interrelated with those of all others and with the total mass wear rate $G_{\Sigma,\infty}$ It will be assumed that the predominance of silicon dioxide within the total mass is sufficient to justify considering this ingredient to be the governing one in the process. Then, after the quasisteady stage of decomposition has been reached, and resultant mass wear rate can be expressed in terms of the decomposition rate of glass $G_{2,\infty}$:

$$G_{\Sigma,\infty} = G_{2,\infty}/\varphi. \tag{1}$$

For comprehensiveness, we will limit our analysis to the case of "pure" sublimation ($G_{\Sigma,\infty} = G_{\Sigma,s}$), assuming that the results can then be easily extended to the case of partially mechanical wear (in the form of melting of glass and solid carbon particles). We will also assume that the process of glass evaporation is described by the Hertz–Knudsen–Langmuir equation of nonequilibrium sublimation [2]

$$G_{2,s} = \eta \frac{p^*_{2,s} - p_{2\,s}}{\sqrt{2\pi R T_s/M_2}}. \tag{2}$$

The mass balance of elemental silicon at the heated surface is

$$(\beta + G_{\Sigma,s})\, C_{\mathrm{Si},s} = G_{\Sigma,s}\, \varphi M_4/M_2. \tag{3}$$

Here the mass concentration of elemental silicon combines that in all ingredients of the material containing it. The evaporation rate under thermodynamic conditions in the gaseous boundary layer favorable to chemical reaction between glass molecules and other molecules present cannot, therefore, be calculated according to Eqs. (2) and (3) unless the complete composition of the gas is known.

Thermodynamic Analysis for the 2000-3500°K Temperature Range. According to the data in [3], partial dissociation of silicon dioxide is appreciable within a wide temperature range already under a pressure $p_9 \sim 1$ bar only and increases with decreasing pressure as $(p_9)^{-0.5}$. At the same time, a more complete dissociation of glass molecules (reduction to Si) becomes possible only at pressures $p_9 < 10^{-8}$ bar. When the conditions above the heated surface are favorable to a formation of elemental silicon, then together with it there probably appear also other silicon compounds such as Si_2C and SiH foremost. Carbon and oxygen can combine into carbon monoxide and carbon dioxide, with the ratio of their partial pressures varying with the degree of dissociation of silicon dioxide molecules:

$$\frac{p_6}{p_5} \approx 0{,}1\, \frac{p_3}{p_2}; \tag{4}$$

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 24, No. 3, pp. 407-413, March, 1973. Original article submitted February 11, 1972.

$$\frac{p_6}{p_5} > 10^5 \frac{p_4}{p_3}. \qquad (5)$$

Since both stages of dissociation do not occur simultaneously,

$$\frac{p_3}{p_2} > 10^6 \frac{p_4}{p_3}, \qquad (6)$$

hence it follows from (4) and (5) that the ingredients Si, SiO, SiO_2, CO, and CO_2 can exist above the surface of a vitroplastic material not more than three at a time. Within the range of low decomposition rates, when the concentration of molecular oxygen is close to the concentration of free oxygen in the air stream

$$c_{9,s} \approx c_{O,e} = 0.23$$

and the degree of dissociation of silicon dioxide molecules is rather low, the following three of the six compounds just enumerated predominate:

$$SiO_2,\ SiO,\ CO_2. \qquad (7)$$

At medium decomposition rates, when the amount of oxygen in the material and in the air stream during partial dissociation of silicon dioxide is not sufficient for oxidizing all the carbon into carbon dioxide and when the ratio of partial pressures of CO and CO_2 remains within the range

$$1 < p_6/p_5 < 10^4,$$

then

$$SiO,\ CO_2,\ CO \qquad (8)$$

predominate.

Finally, at decomposition rates sufficiently high to require both oxygen atoms of the main glass ingredient for the oxidation of the carbon, then practically only the following ingredients exist above the surface:

$$SiO,\ CO,\ Si. \qquad (9)$$

There is almost no reaction between carbon and nitrogen: acetylene C_2H_2 is the most noteworthy here of all carbon compounds, as it may form in appreciable quantities under a sufficiently high pressure p_7 and pressure ratio p_4/p_3. The most stable compound of hydrogen and oxygen is water, with

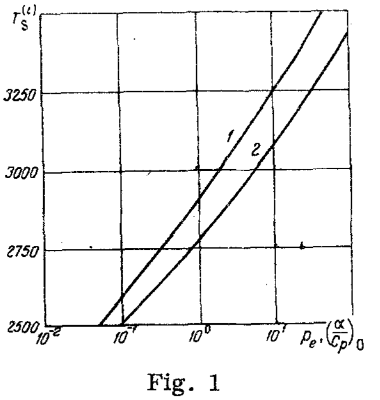

Fig. 1

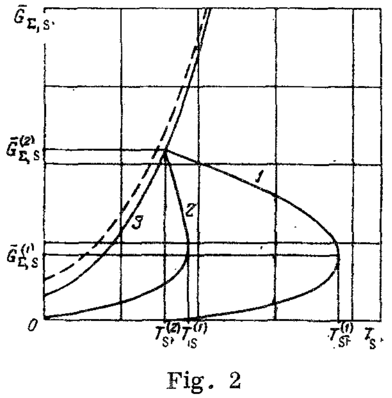

Fig. 2

Fig. 1. Critical surface temperature (°K) as a function of the pressure in the boundary layer $T_s^{(1)}(p_e)$(1) and as a function of the heat transfer coefficient $T_s^{(2)}(\alpha/c_p)_0$(2). Pressure p_e (bars), heat transfer coefficient α/c_p (kg/m$^2 \cdot$sec).

Fig. 2. Typical curve of dimensionless decomposition rate as a function of the surface temperature (°K): $p_e/(\alpha/c_p)_0 = 10^5$ sec (1), 10^4 sec (2), 10^3 sec (3); dashed curve represents evaporation of silicon dioxide under vacuum.

$$\frac{p_7}{p_8} \approx 0.1 \frac{p_8}{p_5} \tag{10}$$

and, to the first approximation, it may be assumed that up to the second decomposition stage (8) all the hydrogen is bonded in water (H_2O) while the amount of water at the end of this decomposition stage becomes negligible.

Critical Decomposition Rates. In materials of the given class there is usually not sufficient free oxygen available during partial dissociation of glass molecules, not even for the lowest level of carbon oxidation (to CO). It is possible, therefore, to establish the maximum decomposition rate $G^{(1)}_{\Sigma,s}$ beyond which the air stream cannot cover the deficit of oxygen needed for the oxidation of carbon and hydrogen into carbon dioxide and water respectively, even when $c_{9,s} \ll c_{O,e}$.

Indeed, the mass balance of oxygen yields

$$\beta C_{O,e} + G^{(1)}_{\Sigma,s} \left[\varphi \frac{M_{10}}{M_2} + (1-\varphi) \nu_{O,1} \right] = G^{(1)}_{\Sigma,s} (1-\varphi) \left(\nu_{C,1} \frac{M_9}{M_{11}} + \nu_{H,1} \frac{M_{10}}{M_7} \right). \tag{11}$$

Taking $\beta = (\alpha/c_p)_O - \gamma G_{\Sigma,s}$, we have from Eq. (11)

$$\overline{G}^{(1)}_{\Sigma,s} = C_{O,e} \left[\gamma C_{O,e} + (1-\varphi) \left(\nu_{C,1} \frac{M_9}{M_{11}} + \nu_{H,1} \frac{M_{10}}{M_7} - \nu_{O,1} \right) - \varphi \frac{M_{10}}{M_2} \right]^{-1}. \tag{12}$$

Naturally, carbon monoxide may appear in appreciable quantities already at lower decomposition rates but, to the first approximation, that rate $G_{\Sigma,s}$ may be regarded as the limit for the first mode of mass wear. Formula (12) can be extended to any value of the parameter ξ:

$$\overline{G}^{(1)}_{\Sigma,s}(\xi) = C_{O,e} \left[\gamma C_{O,e} + (1-\varphi) \left(\frac{2+\xi}{1+\xi} \nu_{C,1} \frac{M_{10}}{M_{11}} + \nu_{H,1} \frac{M_{10}}{M_7} - \nu_{O,1} \right) - \varphi \frac{M_{10}}{M_2} \right]^{-1}. \tag{13}$$

Here $\overline{G}^{(1)}_{\Sigma,s}(\xi = 1)$ is an upper estimate of the lower limit for the second mode of mass wear, while relation (12) represents a special case of formula (13) at $\xi = 0$. The second decomposition stage is characterized by moderate rates $\overline{G}_{\Sigma,s}$ and the existence of the three ingredients (8) in the products. This stage ends when the oxidation of carbon precipitated on the surface requires already more than one oxygen atom from the glass molecule. We denote by $G^{(2)}_{\Sigma,s}$ the mass wear rate at which the relative silicon content p_4/p_3 is of the order of 10^{-2}. According to relations (5) and (6), there are no silicon dioxide and carbon dioxide molecules present in the decomposition products at the surface and compounds of the Si_2C class appear still in very small quantities. As a consequence, $G^{(2)}_{\Sigma,s}$ satisfies the conditions of both the second and the third mode of mass wear and may be regarded as the boundary value between them. The mass balance of oxygen yields, as before, this critical decomposition rate according to the expression

$$\overline{G}^{(2)}_{\Sigma,s} = C_{O,e} \left[\gamma C_{O,e} + (1-\varphi) \left(\nu_{C,1} \frac{M_{10}}{M_{11}} - \nu_{O,1} \right) - \varphi \frac{M_{10}}{M_2} \right]^{-1} \tag{14}$$

Furthermore, it follows from this mass balance that complete dissociation of glass molecules can occur only in this case if

$$\frac{1-\varphi}{\varphi} \left(\nu_{C,1} - \nu_{O,1} M_{11}/M_{10} \right) > 0.2.$$

Condition for the Existence of a Bivalent Range in the Relation between Evaporation Rate and Surface Temperature. In the first two modes of mass wear the number of silicon compounds is limited to silicon oxide and silicon dioxide. Therefore,

$$G_{\Sigma,s} = \frac{\eta p^*_{2,s}}{\varphi \sqrt{2\pi R T_s / M_2} + \frac{M_{\Sigma,s}}{M_2} \cdot \frac{\eta \varphi p_e}{(\beta + G_{\Sigma,s})(1 + p_{3,s}/p_{2,s})}} \tag{15}$$

In the first mode the value of ratio $p_{3,s}/p_{2,s}$ is usually not higher than 10 and the second term in the denominator of (15) is much larger than the first term. When $G_{\Sigma,s} = G^{(2)}_{\Sigma,s}$, on the contrary, the value of that ratio is higher than 10^4 and it is already permissible to disregard the second term. For a standard-grade vitroplastic on a phenolic resin base with $\gamma = 0.6$, $\nu_{C,1} = 0.77$, $\nu_{O,1} = 0.17$, $\nu_{H,1} = 0.06$, and $\varphi = 0.7$, we have the following formulas for the surface temperatures corresponding to the critical decomposition rates (12) and (14):

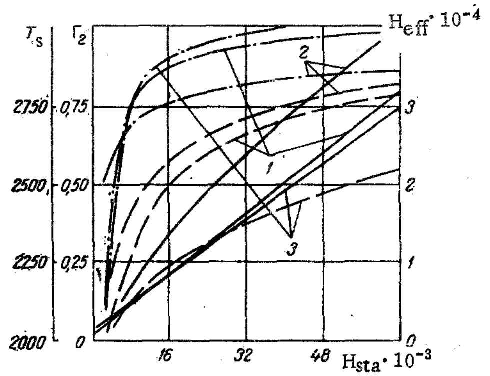

Fig. 3

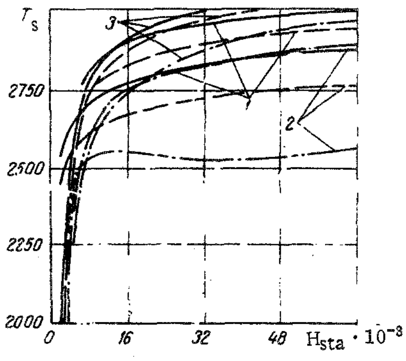

Fig. 4

Fig. 3. Basic characteristics of mass wear of the material, as functions of the stagnation enthalpy of the air stream H_{sta} (kJ/kg): mechanical wear of carbon mass (1), superficial carbon burnout (2), homogeneous quartz glass (3) (solid line for r = 0.007 m, dashed line for r = 0.05 m, dashed-dotted line for r = 1.0 m).

Fig. 4. Surface temperature T_s (°K) as a function of the stagnation enthalpy H_{sta} (kJ/kg) and of the surface bluntness radius r (m): mechanical wear of carbon mass (1), superficial carbon burnout (2), homogeneous quartz glass (3) (solid line for r = 0.007 m, dashed line for r = 0.05 m, dashed-dotted line for r = 1.0 m).

$$T_s^{(1)} = 86480/(30.13 - 3.45 \lg p_e),\ p_e,\ \text{bar}, \tag{16}$$

$$T_s^{(2)} = 61700/\left[22.3 - 2.3 \lg\left(\frac{\alpha}{c_p}\right)_0\right],\ \frac{\alpha}{c_p},\ \frac{\text{kg}}{\text{m}^2\cdot\text{sec}};\ T_s,\ ^\circ\text{K}. \tag{17}$$

It is to be noted that temperature $T_s^{(1)}$ is a function only of the pressure in the boundary layer, while temperature $T_s^{(2)}$ is completely determined by the heat transfer coefficient. In view of this, with the relations between both fully determinate, $T_s^{(2)}$ will be lower than $T_s^{(1)}$ (Fig. 1), i.e., the relation $\bar{G}_{\Sigma,s}(T_s)$ will pass through a bivalent range (Fig. 2). For a material of the given composition, this relation ceases to be univalent at

$$\frac{p_e}{(\alpha/c_p)_0} > 0.5\cdot 10^4\ \text{sec}.$$

Thermal Effect of Surface Reaction. As has been shown, a change in the decomposition rate leads to a qualitative distortion of the chemical reaction pattern in the boundary layer above the decomposing surface. At low decomposition rates the heat of SiO_2 dissociation is almost lost and the burnout of carbon makes the thermal effect much smaller than during evaporation of homogeneous glass. As $G_{\Sigma,s}$ increases further, however, this difference $\Delta Q_{\Sigma,s}$ fades due to a higher dissociation rate of glass molecules as a result of carbon burnout. Also, as has been mentioned already, at a higher $G_{\Sigma,s}$ rate the degree of carbon and hydrogen oxidation becomes lower.

A Study Concerning the Effect of Carbon Burnout on the Basic Parameters of Material Decomposition. The results of calculations shown in Fig. 3 illustrate the differences between the basic wear characteristics of the vitrographitic material and those of fused quartz. The calculations were made for specimens in a supersonic air stream, the specimen surfaces blunted with a 0.007 m radius. The flow in the boundary layer was assumed laminar. The rate of SiO_2 mass wear in the liquid phase was calculated by the method in [4]. As has been shown earlier, the basic effects of carbon burnout are an increase in the decomposition rate at a given surface temperature and a decrease in the difference $\Delta Q_{\Sigma,s}$, the first effect becoming stronger and the second effect becoming weaker with a higher $G_{\Sigma\infty}$ rate. As a result, the effect of carbon burnout on the effective enthalpy of the material and on the temperature of the heated surface becomes bivalent. At a low stagnation enthalpy of the stream, when the $\bar{G}_{\Sigma,\infty}$ rate is also low, a reduction in the difference $\Delta Q_{\Sigma,s}$ is foremost and, as a result, temperature T_s rises while the effective enthalpy H_{eff} drops. The difference between the decomposition parameter values of fused quartz and of the vitrographitic material at $\Gamma_{11} = 0$ is in this mode insignificant. At high values of $\bar{G}_{\Sigma,\infty}$, when air injection contributes essentially to the heat balance and when the surface temperature of the material stabilizes at a level which ensures the required gasification rate, the relation $\overline{G}_{\Sigma,\infty}(T_s)$ becomes most important. Moreover, the surface temperature drops even during mechanical wear of the carbon mass, owing to the injection of gaseous products of decomposition of the organic binder, which in turn makes the evaporation rate lower than what it is in the case of fused quartz glass. A sharp increase in the gasification rate, which occurs during this stage of decomposition with carbon burnout, has the effect of lowering the temperature T_s appreciably and raising the gasification rate Γ_2 as well as the effective enthalpy H_{eff}.

The results of calculations shown in Fig. 4 illustrate qualitatively how carbon burnout affects the relation $T_s(H_{sta})$. As is well known, in a laminar boundary layer

$$\frac{p_e}{(\alpha/c_p)_0} \sim r^{0.25},$$

and, as a consequence, with a large enough bluntness radius the relation $\overline{G}_{\Sigma,\infty}(T_s)$ may cease to be univalent, i.e., within some range of decomposition rates an increase $\overline{G}_{\Sigma,\infty}$ is accompanied by a drop in the surface temperature. In this case a univalent increase in the decomposition rate, which usually occurs with an increase in H_{eff}, produces a hump in the $T_s(H_{sta})$ curve. Furthermore, one also notes appreciably different effects of the parameter $p_e/(\alpha/c_p)_0$ on the surface temperature as determined under different assumptions.

NOTATION

T	is the temperature;
G	is the velocity of mass in the direction of the surface;
p	is the pressure;
M	is the molecular mass;
φ	is the mass content of glass in the original material;
Γ	is the gasification rate;
R	is the universal gas constant;
r	is the bluntness radius;
α/c_p	is the heat transfer coefficient;
β	is the mass transfer coefficient;
c	is the mass concentration;
γ	is the injection coefficient;
η	is the acommodation coefficient accounting for the fraction of surface covered with glass;
$\Delta Q_{\Sigma,s}$	is the thermal effect of surface reaction;
$\xi = p_6/p_5$	
$\overline{G} = G/(\alpha/c_p)_0$	
$\overline{G}^{(1)}_{\Sigma,s}$, $G^{(2)}_{\Sigma,s}$	are the critical decomposition rates (13) and (14) respectively;
$T^{(1)}_s$, $T^{(2)}_s$	are the critical surface temperatures (16) and (17) respectively;
$\nu_{j,i}$	is the mass content of the j-th chemical element in the i-th ingredient of the material;
H_{sta}	is the stagnation enthalpy of the air stream;
H_{eff}	is the effective enthalpy of the material.

Subscripts

e	refers to outer edge of boundary layer;
s	refers to heated surface;
∞	refers to unheated material;
o	refers to impermeable surface;
*	refers to saturated vapor;
1	refers to resin;
2	refers to silicon dioxide (SiO_2);
3	refers to silicon oxide (SiO);
4	refers to silicon (Si);
5	refers to carbon dioxide (CO_2);
6	refers to carbon oxide (CO);

7	refers to hydrogen (H_2);
8	refers to water (H_2O);
9	refers to oxygen (O_2);
10	refers to oxygen (O);
11	refers to carbon (C);
sta	refers to stagnation enthalpy (of air stream);
eff	refers to effective enthalpy (of material).

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