OBITUARY

EFFECT OF INTERNAL AND SURFACE PROCESSES OF HEAT ABSORPTION ON THE HEATING AND DESTRUCTION OF A MATERIAL

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The main factors of heat absorption causing the destruction of the surface of a material are considered. Conditions are investigated under which the maximal energy capacities of the internal and surface processes are achieved.

The interaction of a heated gas with a heat-shielding coating is accompanied by numerous interrelated processes. The flow of heat, delivered externally to the surface of the material is absorbed and dissipated through the heating of the inner layers, radiation from the surface, thermal effects inherent in the phase and physicochemical transformations, and through the effect of injection.

The equation of energy balance on the durface being destroyed, incorporating the above factors of heat absorption, is of the form

$$(\alpha/c_p)_0 (I_e - I_w) = \varepsilon\sigma T_w^4 + \Gamma G_\Sigma \Delta Q_w + \Gamma G_\Sigma \gamma (I_e - I_w) + q_\lambda. \tag{1}$$

Each of these factors depend to a greater or lesser degree on the properties of the material and also on the parameters of the injected gaseous flow. The determination of these factors is a complex independent problem. For example, the heat flow emanating from the internal layers q_λ depends on the temperature field of the coating and on the heat transfer coefficient of the material:

$$q_\lambda = -\lambda \left.\frac{\partial T}{\partial y}\right|_w . \tag{2}$$

In order to determine it, one has to use the equation of conservation of energy in a condensed phase (heat-transfer equation), in which all the processes inside the heat-shielding coating related to absorption or evolution of heat should be considered [1].

When determining the total heat effect of physicochemical transformations ΔQ_w, one should consider numerous chemical reactions on the damaged surface of the material. Only in certain cases can one succeed in obtaining simple analytic formulas for calculating the composition of the gas and, accordingly, solve the problem of the determination of ΔQ_w. No lesser difficulties arise also in calculating the degree of realization of ΔQ_w, which is determined by the gasification coefficient Γ.

One can see from Eq. (1) that if the surface is destroyed, then, as a rule, all the components of the heat balance are realized. However, the fraction of a specific component of heat absorption depends significantly on the parameters of the gas flow and can vary practically from 0 to its maximal value. Basically, in the study of new materials, one does not study the effect of each component of the thermal balance on the process of destruction, but determines the total energy characteristic, which is called the effective enthalpy of destruction [1]. At the same time, the results obtained in [2-8] show that a significant reduction in labor is possible in calculating both quasistationary and nonstationary processes of heating and destruction of the material by introducing a number of constants and estimating the range of the predominant influence of certain factors of heat absorption.

In the present work, we pose the problem of determining the conditions for achieving the maximal energy capacity of the basic processes of heat absorption and estimation of their influence on the rate of destruction of the material in the different ranges of enthalpy of a stagnation flow.

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For this purpose all the processes of absorption and dissipation of heat entering into Eq. (1) are divided into three groups: internal, surface, and external (heat effect of injection and radiation from the surface). The internal processes depend on thermophysical properties, include all effects related to the evolution and absorption of heat inside the material, and, ultimately, determine its enthalpy. In this case, the energy capacity should be understood as the enthalpy of the material in a layer of fixed thickness, equal to a quasistationary value of the depth of heating. For a given surface temperature it depends on the temperature profile inside the material and achieves its maximal value at the moment when the quasistationary temperature profile is established.

A principal difference in the mechanism of absorption of heat due to internal processes from that due to surface processes is that, in the first case, heat is accumulated in a certain volume, and in the second case, heat is absorbed in the surface layer of the damaged material. The time of the nonstationary period of accumulation of heat due to the processes inside the material τ_δ exceeds by almost an order of magnitude the time of the establishment of the quasistationary regime of heat absorption in the surface layer, which corresponds to the time when the quasistationary rate of mass ablation τ_V is attained [1]. Since the enthalpy of the material at the surface temperature $H(T_W)$ is realized in the surface layer, it, just as the total thermal effect of the physicochemical transformations, should be related to the surface processes of heat absorption. Then the energy capacity of the surface processes is determined by the thermodynamic enthalpy of the material and depends on the temperature of the surface and the degree of realization of the total thermal effect of the physicochemical transformations on the surface.

The calculations performed in [1] shows that ΔQ_W of quartz glass changes relatively little and at the boiling point achieves its maximal value of ~12,000 kJ/kg. According to the JANAF thermodynamic tables the change in ΔQ_W of sublimation of carbon in the range of temperatures 2500-5000°K does not exceed 8%, and $(\Delta Q_W)_{\max} \sim 28{,}000$ kJ/kg. For composite materials of the type of glass-fiber-reinforced plastic, ΔQ_W changes over a wide range and can even assume negative values. However, with increase in the rate of destruction, the contribution of the exothermal reactions of combustion decreases, and ΔQ_W achieves its maximal value relatively quickly.

For high values of the enthalpy of stagnation, the gasification coefficient approaches unity, the temperature of the surface approaches the boiling point of the material, and the total heat effect ΔQ_W, as a rule, achieves its maximal value. As a result, the thermodynamic enthalpy is realized completely, and the maximal energy capacity of the surface processes of heat absorption is established. In the given case

$$I_T = H(T_{\text{к}}) + (\Delta Q_w)_{\max}. \tag{3}$$

It is seen from the above that in order to characterize the energy capacity of the internal and surface processes, three thermal parameters should be considered: $H(\bar{T})$, $H(T_W)$ and ΔQ_W ($\bar{T}$ is the integrated temperature of a heated layer). In [5], it is shown that for quartz glass

$$(\Delta Q_w)_{\max} \approx 3.4 H(T_{\text{к}}), \tag{4}$$

this is also true for the heat of evaporation of a great number of ordinary substances. Therefore, when the maximal energy capacity of the surface processes is achieved, the following relation holds:

$$\frac{H(T_{\text{к}})}{(\Delta Q_w)_{\max}} \approx 0.3. \tag{5}$$

For the determination of the ratio of the enthalpy of a heater layer $H(\bar{T})$ to $H(T_W)$, we use the solution of the problem of heat transfer in a semiinfinite body whose surface is destroyed at a constant temperature [1]. In this case, the quasistationary profile of the temperatures, which is established at time τ_δ, is of the form

$$\tilde{\Theta} = \frac{\tilde{T} - T_0}{T_w - T_0} = \exp\left(-\frac{\bar{V}_\infty}{a}\, y\right). \tag{6}$$

At the same instant of time, according to [8], the ratio of the total thickness of the heated and entrained layers to the heated layer is approximately equal to 2, i.e., at time τ_δ, an approximate equality in thicknesses is established: $\delta_T \approx S(\tau_\delta)$. After considering the quantity of heat absorbed in the layers of the material δ_T and $S(\tau_\delta)$ owing to the heat capacity, for constant thermophysical properties we obtain

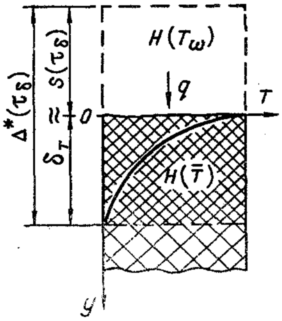

Fig. 1. Relationship between the enthalpies and thicknesses of the heated and entrained layers of the material when a quasistationary heating regime is established.

$$\frac{H(\bar T)}{H(T_w)} = \frac{\rho c \dfrac{1}{\delta_T} \int\limits_0^{\delta_T} (\bar T - T_0)\, dy}{\rho c (T_w - T_0)} = \frac{1}{\delta_T} \int\limits_0^{\delta_T} \frac{\tilde T - T_0}{T_w - T_0}\, dy. \tag{7}$$

The time τ_v is almost an order of magnitude less than τ_δ; therefore, by ignoring the entrainment of mass in the nonstationary period of destruction and taking into account the calculation of [6] for τ_δ,

$$\tau_\delta = \frac{K^2 a}{4 \bar V_\infty^2},$$

we write

$$\delta_T \approx S(\tau_\delta) \approx \bar V_\infty \tau_\delta = \frac{K^2 a}{4 \bar V_\infty}. \tag{8}$$

Solving (6) and (8) simultaneously and transforming (7) to the form

$$\frac{H(\bar T)}{H(T_w)} \approx \frac{1}{\delta_T} \int\limits_0^{\delta_T} \exp\left(-\frac{K^2}{4\delta_T} y\right) dy,$$

we find after integration

$$\frac{H(\bar T)}{H(T_w)} \approx \frac{4}{K^2}\left[1 - \exp\left(-\frac{K^2}{4}\right)\right]. \tag{9}$$

In [2, 3], it is proved experimentally that the total thickness of the heated and entrained layers Δ^* in the heating time interval $\tau_T < \tau < \tau_\delta$ is described by the expression

$$\Delta^* = K \sqrt{a} \left(\sqrt{\tau} - \sqrt{\tau_\xi}\right), \tag{10}$$

where for $\Theta^* < 0.2$, from the coefficient K is found from the dependence

$$\Theta^* = \frac{T^* - T_0}{T_w - T_0} = \operatorname{erfc} \frac{K}{2}, \tag{11}$$

and for $\Theta^* > 0.2$, from the formula

$$K = -\frac{1}{K_{T_p}} \Theta^* + \frac{K_{T_p}^2}{1 - K_{T_p}}. \tag{12}$$

From expression (10), it is seen that Δ^* is directly proportional to the square root of the heating time: therefore, when the injected heat flow is constant, an analogous dependence for it on the square root of the quantity of the absorbed heat should be valid. Indeed, calculations from (9) for the depth isotherms (when Θ^* varies from 0.005 to 0.1) show that the relation established in [8] for the thicknesses $\Delta^*(\tau_\delta)/\delta_T \approx 2$ (see Fig. 1) with accuracy up to 15% is equal to the ratio of the enthalpies

$$\frac{\Delta^*(\tau_\delta)}{\delta_T} = \frac{\delta_T + S(\tau_\delta)}{\delta_T} \approx \left[\frac{H(\bar T) + H(T_w)}{H(\bar T)}\right]^{0,5}. \tag{13}$$

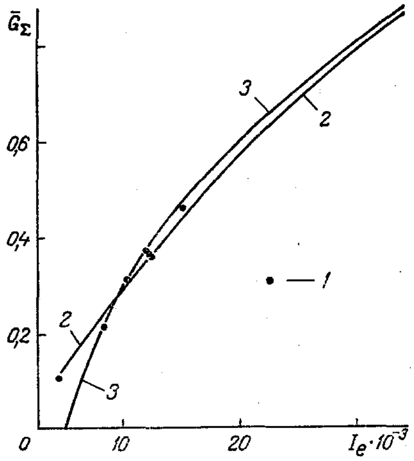

Fig. 2. Dimensionless ablation rate vs stagnation flow enthalpy for alloyed quartz ceramics: 1) experiment; 2, 3) calculation from Eqs. (1) and (19), respectively. I_e, kJ/kg.

At the same time, the heat balance at the instant of time τ_δ, if we neglect the change in the heat flow during time τ_T, is of the form

$$(q_0 - \varepsilon\sigma T_w^4)\,\tau_\delta = \rho\,\{\delta_T H(\bar{T}) + S(\tau_\delta) H(T_w) + \Gamma S(\tau_\delta)\,[\Delta Q_w + \gamma (I_e - I_w)]\}, \tag{14}$$

where

$$q_0 = q_к \frac{I_e - I_w}{I_e - I_c}.$$

Consequently, there is a contradiction: on the one hand, $\Delta^*(\tau_\delta)$ includes the linear entrainment of the material and should depend on all the terms in the heat balance equation (14), including the gasification coefficient, and, on the other hand, according to data in [1, 8], the relation $\Delta^*(\tau_\delta)/\delta_T \approx 2$ does not depend on the thermal efficiency of the material, which is supported by expression (13).

From Eq. (14) it follows that relation (13) is valid either when there is no evaporation of the entrained material, i.e., when $\Gamma = 0$, or when there is, at least, a weak dependence of the ablation rate of the material on the fraction of its evaporation. The fulfillment of the last condition means that practically any value of the gasification coefficient satisfying the equation of heat balance (14) should correspond to the same mass ablation rate. Numerical calculations [1] and experiments [4] show that the main change in the gasification coefficient and the surface temperature occurs in a comparatively small interval of the stagnation enthalpy. For example, for quartz glass this range is 4000-20,000 kJ/kg. In the given interval of the enthalpy of a stagnation flow, the gasification coefficient varies from 0.1 to 0.9, and the surface temperature varies by approximately 300-400°K. Such a change in T_w affects only slightly the enthalpy; however, it covers practically the entire range of destruction rates for materials based on quartz glass.

In Table 1, we present the results of the determination of the ablation rate for specimens of alloyed quartz glassceramic, examined in the jet of an electric arc heater and a gas generator operating on kerosine—oxygen fuel. The technique for conducting the experiments and calculations is described in [4]. From Table 1, it is seen that approximately equal integrated heat flows provide equal ablation rates, in spite of the fact that the gasification coefficients differ approximately eightfold. In both cases, the experimental data agree well with calculations from the heat-balance equation (1).

Hence, in the range of the enthalpy of the stagnation flow corresponding to the main change in T_w and Γ, the rate of heat absorption owing to the heat capacity of the material, specified by the rate of heating and by the thermophysical properties, has a decisive affect on the rate of destruction of the surface. The fraction of the remaining factors of heat absorption in the total balance is determined by the vlaue of the heat flow in the quasistationary heating regime; it increases with an increase in the stagnation enthalpy, but in the range of the main change in T_w and Γ it has a weak effect on the mass ablation rate. In this

TABLE 1. Rate of Destruction of an Alloyed Quartz Glassceramic, 0.5% Cr_2O_3; $\rho \approx 2000$ kg/m³ [I) experiment, II) calculation from Eq. (1)]

q_K, kW/m²	I_e, kJ/kg	$P_e \cdot 10^{-5}$, Pa	T_w, K	q', kW/m²	q'_0, kW/m²	Γ	G_Σ, kg/(m²·sec)	
							I	II
11500	12300	1,0	2800	9250	5550	0,82	0,36	0,34
14700	4700	3,5	2610	8540	1530	0,1	0,36	0,38

case, the maximal energy capacity of the internal processes is achieved when the thicknesses of the heated and entrained layers become equal.

It is of interest to note that at the instant when the maximal energy capacity of the surface processes is attained, a relation analogous to (13) also holds. Taking into consideration (5), one can write

$$\left[\frac{H(T_K) + (\Delta Q_w)_{\max}}{H(T_K)}\right]^{0,5} \approx 2. \tag{15}$$

An analysis of the experimental and calculated values of the dimensionless rates of entrainment for materials of different classes [7], covering practically the entire range of the rates of destruction of the heat-shielding coatings, shows that the quasistationary mass ablation rate in the absence of burning at the surface varies directly with the square root of the heat delivered

$$\bar{G}'_\Sigma = \sqrt{\frac{I_e - I_w}{H}} - 0{,}3, \tag{16}$$

where

$$\bar{G}'_\Sigma = \bar{G}_\Sigma \frac{I_e - I_w}{I_e - I_c}.$$

In order to determine the entire heat of destruction of the material H, in [7] an expression is obtained which taking into account (5), can be rewritten in the simplified form

$$H \approx \left\{\frac{[H(T_K) + (\Delta Q_w)_{\max}]\sqrt{I_e - I_w}}{\bar{q}_{BH} + 1{,}3H(T_K)}\right\}^2, \tag{17}$$

where $\bar{q}_{BH} = (1 - \gamma\bar{G}'_\Sigma)(I_e - I_w) - \bar{\varepsilon}\sigma T_w^4$; $\bar{\varepsilon}\sigma T_w^4 = \varepsilon\sigma T_w^4/(\alpha/c_p)_0$, kJ/kg, is the reduced energy of radiation.

Calculations from formula (17) for quartz glass in the pressure range 10^4 to 10^6 Pa using the surface temperatures calculated in [1] show that in the interval $I_e = (1-5)\cdot 10^4$ kJ/kg the difference between H and $2(\Delta Q_w)_{\max}$ does not exceed ±5%. This is supported by the experimental data of [7] and by the relationship [6]

$$H = \frac{(K_{T_p}^2 + 1)\sqrt{\pi}}{K_{T_p}^3} H(T_K) = 6.79H(T_K). \tag{18}$$

From expressions (18) and (4) it is also seen that H is approximately equal to twice the value of $(\Delta Q_w)_{\max}$. Then, taking into consideration that the empirical constant in (16) is equal to the relation $H(T_K)/(\Delta Q_w)_{\max}$, we write

$$\bar{G}'_\Sigma = \sqrt{\frac{I_e - I_w}{2(\Delta Q_w)_{\max}}} - \frac{H(T_K)}{(\Delta Q_w)_{\max}}. \tag{19}$$

In Fig. 2, the experimental rates of destruction of the alloyed quartz glassceramics from [4, 9] are compared with the calculated values from Eqs. (1) and (19). In determining $\bar{G}_\Sigma$ from (1), we used the calculated values T_w and ΔQ_w from [1] and the experimental gasification coefficients from [4]. The enthalpy $H(T_w)$ was taken from [10], and the degree of blackness, from [11]. As is seen from Fig. 2, starting even from $I_e \sim 8000$ kJ/kg, calculation from (19) agrees well with the experimental data and practically coincides with the calculation from the heat-balance equation (1). The applicability of (19) to materials of other classes was shown in [7].

Hence, the introduction of the dimensionless ablation rate $\bar{G}'_\Sigma$ instead of $\bar{G}_\Sigma$ makes it possible to calculate its value taking into consideration the complete realization of the thermodynamic enthalpy of the material (3), while the maximal energy capacity of the surface processes is established at the instant when $(\Delta Q_w)_{max}$ is equal to the sum of all the other factors of heat absorption entering (1).

The analogy between the internal and surface processes of heat absorption is not exhausted by dependences (13) and (15). Expressions (10) and (16) contain a lot in common. If Δ^* is in direct proportion to the square root of the quantity of heat absorbed due to the heat capacity of the material, then for $\overline{G}'_\Sigma$, an analogous relation is characteristic for the dependence of the square root on the heat delivered. The results obtained in [2, 3, 8] indicate that $\sqrt{\tau_\xi}$ in (10) can be taken equal to $\sqrt{I_c}$ with good accuracy. Hence, dependences (10) and (16) have "foci." Finally, the tangents of the angles of inclination of the linear dependences (10) and (16), i.e., the coefficients K and $1/\sqrt{H}$, are energy coefficients from the variable parameters characterizing the given processes. However, the temperature coefficient K does not depend on the parameters entering into it, and the heat of destruction of the material H does not depend on the external conditions [3, 7].

Thus, the maximal energy capacity of the internal processes is achieved at the instant when the thicknesses of the heated and entrained layers are equal, and the maximal energy capacity of the surface processes is achieved when the maximal total heat effect of physicochemical transformations is equal to the sum of all the other factors of heat absorption; in this case, the parameters characterizing internal and surface processes are related through the constant of destruction.

It should be noted that the given conclusions are made by neglecting burning and radiative flows inside and on the surface of the material.

NOTATION

I_e, P_e, stagnation enthalpy and stagnation pressure; T_w, T_o, temperatures of the heated surfaces and the unheated material, respectively; T^*, temperature of the isotherm under consideration; T, instantaneous value of the temperature inside the material; I_w, I_c, gas enthalpies at the temperature of the surface of the material and of the temperature of the calorimeter; $(\alpha/c_p)_o$, heat transfer coefficient; q_k, calorimetric heat flow; q_o, q'_o, heat flow to the hot surface neglecting and considering radiation losses; q'_{int}, integrated heat flow; q_λ, heat flow for heating inner layers; $\overline{V}_\infty$, G_Σ, linear and mass ablation rates; $\overline{G}_\Sigma$, $\overline{G}'_\Sigma$, dimensionless ablation rates; Γ, gasification coefficient; ΔQ_e, heat of evaporation; ΔQ_w, $(\Delta Q_w)_{max}$, total thermal effect of physicochemical changes on the surface and its maximal value; $H(T_w)$, $H(T_k)$, heat content of the material at the surface and boiling points; $H(\overline{T})$, heat content of the hot layer; I_T, thermodynamic enthalpy of the material; H, total heat of destruction of the material; ε, degree of blackness; σ, Stefan–Boltzmann constant; γ, injection parameter; λ, thermal conductivity coefficient; a, thermal diffusivity coefficient; ρ, density; τ, heating time; τ_T, τ_v, τ_δ, time of the establishment of quasistationary values of the surface temperature, ablation rate, and heating depth, respectively; δ_T, $S(\tau_\delta)$, heating depth and linear entrainment at the instant τ_δ; Δ^*, total thickness of the heated and entrained layers; K, temperature coefficient; K_{Tp}, constant of destruction of the material.

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