HEAT AND MASS TRANSFER AT THE SURFACE OF GLASS–GRAPHITE MATERIALS IN A HIGH-TEMPERATURE FLOW OF GAS

V. V. Gorskii and Yu. V. Polezhaev

The article discusses the mutual effect of vaporization and combustion processes during the breakdown of glass–graphite materials in a hypersonic flow of gas. It demonstrates the possibility of the appearance of a nonunique dependence of the vaporization rate on the temperature of the heated surface. The effect of the composition of a material on the principal characteristics of the process of its breakdown is established.

1. Principal Laws Governing the Breakdown of Glass–Graphite Materials

The statement of the problem and the principal special characteristics of the process of the breakdown of vitreous materials in a high-temperature flow of air are described in [1–3]. The present work constitutes a further development of the above-mentioned articles; above all, it considers the range of high breakdown rates, when the effect of the chemical composition of the material on the heat- and mass-transfer rates in the boundary layer becomes considerable. Here, we limit ourselves at the start to the case of the breakdown of nonfusing vitreous materials in a flow of air.

By analogy with [4] we assume that the heated surface layer of a composite material based on glass and an organic binder consists of the following components: silicon dioxide, free carbon, gaseous products of the decomposition of the binder (mainly carbon monoxide and molecular hydrogen). The content by weight of a chemical element or component in the starting material is denoted by \( \varphi_1 \). Both a molecule of the glass and the polymer chains of the binder contain oxygen. However, to isolate the role of vaporization of the glass in the overall mechanism of the breakdown, it is more convenient to separate its content in the glass and in the binder. We note that in many resins used as binders the oxygen content \( \varphi_0 \) is so small that it can be neglected. In particular, a glass plastic based on a phenol–formaldehyde binder has approximately the following composition by weight [5]:

\[
\varphi_{SiO_2} = 0.7, \quad \varphi_C = 0.23, \quad \varphi_H = 0.02, \quad \varphi_O = 0.05
\]

All the numerical examples in the present article will be based on precisely these numerical data.

During the process of the breakdown of a glass plastic, three types of gaseous components enter the boundary layer through the surface of the body: 1) volatile products of the thermal decomposition of the binder; 2) vaporized molecules of the glass; 3) products of the combustion of solid carbon, i.e., cokes, which are secondary products of the thermal decomposition of phenol–formaldehyde and certain other types of binders.

The reaction between the two latter types of gaseous components also determines the special characteristics of heat and mass transfer at the surface of glass–graphite materials.

It must be noted that the gaseous boundary layer above the surface which is breaking down may contain up to 50 different components. However, the effect of many of these, such as the thermal effect of...
physicochemical transformations, $\Delta Q_S$, or the rate of entrainment of mass, $G_w$, on the overall parameters of the breakdown turns out to be rather weak; therefore, a correct choice of the model of the process and of the calculating scheme is an extremely important undertaking.

When there are several components in the material, the rate of breakdown of each is interconnected with the rates of breakdown of the remaining components and with the overall rate of entrainment of mass $G_w$. Given the predominance by weight of silicon dioxide, we shall take this component as determining. Then, up to the attainment of quasisteady-state breakdown conditions, the overall rate of entrainment of mass, $G_w$, must be proportional to the rate of vaporization of the glass, $G_{SiO_2}$:

$$G_w = G_{SiO_2}/\rho_{SiO_2}$$

We shall assume that the process of vaporization of the glass can be described by the Hertz-Knudsen-Langmuir equation [6] for nonequilibrium sublimation

$$G_{SiO_2} = \frac{a \cdot \rho_{SiO_2} - \rho_{SiO}}{2\pi R T_w / M_{SiO_2}}$$

where $\rho_{SiO_2}$ and $\rho_{SiO}$ are the partial pressure and the pressure of the saturated vapors of silicon dioxide; $a$ is the coefficient of vaporization (accommodation), taking account also of the fraction of the surface occupied by the glass; $R$ is the universal gas constant; $T_w$ is the temperature of the surface; $M$ is the molecular mass.

The pressure of the saturated vapors, $\rho_{SiO_2}^*$, is a known thermodynamic function of the temperature of the surface $T_w$ while the partial pressure $\rho_{SiO}$ depends on the whole set of physicochemical processes in the boundary layer, i.e., on the rate of diffusion (mass transfer) across the boundary layer, on the presence of silicon- and oxygen-containing components, on the rate of vaporization, etc. These interrelationships are rather complex even for homogeneous quartz glass [2], and, at the surface of carbon-containing glass plastics, they can occasion many unexpected phenomena, for example, a nonunique dependence of the rate of vaporization on the temperature.

Denoting the mass-transfer coefficient by $\beta$, we write the balance for the mass of the element silicon at the surface which is breaking down:

$$(\beta + G_w) G_{Si} = G_{d\rho_{SiO},M_{Si}} / M_{SiO_2}$$

Here the weight concentration of the element silicon takes account of the whole variety of components which contain this element, i.e., silicon dioxide and monoxide, silicon, various of its carbides and nitrides, etc. Therefore, if the thermodynamic conditions in the gaseous boundary layer are favorable to a chemical reaction between molecules of the glass and the components in it, calculation of the rate of vaporization using relationships (1.2) and (1.3) demands a knowledge of the whole composition of the gas.

**Thermodynamic Analysis.** We shall consider the principal reactions and shall determine the possibility that they will take place during the breakdown of materials of the class under consideration. The thermodynamic data necessary for this purpose are given in Fig. 1 [7], on which $K_{p,i}$ denotes the following equilibrium constants of the chemical reactions:

$$k_{p,1} = p_{SiO}^3 p_{CO}^2 p_{SiO}^{-2} (p_{C} = p_{O}^0), \quad k_{p,2} = p_{SiO}^4 p_{O}^{-4} p_{SiO}^{-1}$$
$$k_{p,3} = p_{Si}^4 p_{CO}^2 p_{SiO}^{-4} p_{Si}^{-1}, \quad k_{p,4} = p_{Si}^4 p_{SiO}^{-1} p_{H_2}$$
$$k_{p,5} = p_{SiO} p_{CO} p_{SiO}^2 p_{CO}^{-1}, \quad k_{p,6} = p_{SiO}^{-1} p_{CO} p_{CO}^{-1}$$
$$k_{p,7} = p_{SiO}^2 p_{CO}^2 p_{SiO}^{-1} p_{CO}^{-1}, \quad k_{p,8} = p_{SiO}^2 p_{SiO}^{-1} p_{CO}^2$$
$$k_{p,9} = p_{SiO}^3 p_{SiO}^2 p_{C}^{-4} p_{SiO}^{-1}, \quad k_{p,10} = p_{SiO}^{-2} p_{SiO}^{-1} p_{SiO}^{-1}$$
$$k_{p,11} = p_{SiO}^2 p_{SiO}^{-1} p_{SiO}^{-1}, \quad k_{p,12} = p_{SiO} p_{CO} p_{CO}^{-1}$$
$$k_{p,13} = p_{SiO}^2 p_{SiO}^2 p_{SiO}^{-2}, \quad k_{p,14} = p_{OH} p_{H_2} p_{SiO}^{-1}, \quad k_{p,15} = p_{SiO}^{-1}$$
$$k_{p,16} = p_{SiO} p_{SiO}^{-1} p_{SiO}^{-1}, \quad k_{p,17} = p_{H_2} p_{SiO} p_{CO}^{-1}$$
$$k_{p,18} = p_{SiO} p_{CO}^{-1} p_{H_2} p_{SiO}^{-1} p_{SiO}^{-1}, \quad k_{p,19} = p_{H_2} p_{SiO}^{-1} p_{CO}^{-1} p_{SiO}^{-1} p_{SiO}^{-1}$$

Here and in what follows, $k_p$ is measured in bars and $T$ in °K; the number of the curve corresponds to the number of the equilibrium constant.