Heat and Mass Transfer at a Vitroplastic Surface in a High-Temperature Air Stream

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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 $G_{z,\infty}$. 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 $G_{\Delta,\infty}$:

$$G_{z,\infty} = G_{\Delta,\infty}/\psi.$$  \(1\)

For comprehensiveness, we will limit our analysis to the case of "pure" sublimation ($G_{\Delta,\infty} = G_{\Delta, s}$), 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]

$$G_{\Delta, s} = \frac{P_{2,s}}{\sqrt{2\pi M_s R T_s}} G_{\Delta, s}.$$  \(2\)

The mass balance of elemental silicon at the heated surface is

$$(\beta + G_{\Delta, s}) C_{\text{Si,s}} = G_{z,\infty} \eta M_s/M_s.$$  \(3\)

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 $p_g \sim 1$ bar only and increases with decreasing pressure as $(p_g)^{-0.5}$. At the same time, a more complete dissociation of glass molecules (reduction to Si) becomes possible only at pressures $p_g < 10^{-8}$ 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 SiC 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:

$$\frac{p_{2,\text{CO}2}}{p_{2,\text{CO}2}} \approx 0.1 \frac{p_{2,\text{CO}2}}{p_2}.$$  \(4\)
\[ \frac{p_5}{p_3} > 10^5 \frac{p_1}{p_3} \]  

Since both stages of dissociation do not occur simultaneously,

\[ \frac{p_5}{p_2} > 10^6 \frac{p_1}{p_3} \]  

then it follows from (4) and (5) that the ingredients Si, SiO, SiO\(_2\), CO, and CO\(_2\) can exist above the surface of a vitreoplastic 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

\[ c_{o_2} \approx c_{o}, = 0.23 \]

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

\[ \text{SiO}_2, \text{SiO}, \text{CO}_2. \]  

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

\[ 1 < \frac{p_4}{p_3} < 10^4, \]

then

\[ \text{SiO}, \text{CO}_2, \text{CO} \]  

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:

\[ \text{SiO}, \text{CO}, \text{Si}. \]  

There is almost no reaction between carbon and nitrogen; acetylene C\(_2\)H\(_2\) 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

\[ \frac{p_5}{p_3} > 10^5 \frac{p_1}{p_3} \]  

\[ \frac{p_5}{p_2} > 10^6 \frac{p_1}{p_3} \]  

Fig. 1. Critical surface temperature (°K) as a function of the pressure in the boundary layer \( T(p_0) \) (1) and as a function of the heat transfer coefficient \( T_{(2)}(\alpha/c_{p}p_0) \) (2). Pressure \( p_0 \) (bars), heat transfer coefficient \( \alpha/c_{p} \) (kg/m\(^2\cdot\)sec).

Fig. 2. Typical curve of dimensionless decomposition rate as a function of the surface temperature (°K): \( p_0/(\alpha/c_{p}p_0) = 10^5 \) sec (1), \( 10^4 \) sec (2), \( 10^3 \) sec (3); dashed curve represents evaporation of silicon dioxide under vacuum.