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OF A TEFLON MASS DURING ITS DEGRADATION
IN A HIGH TEMPERATURE GAS STREAM

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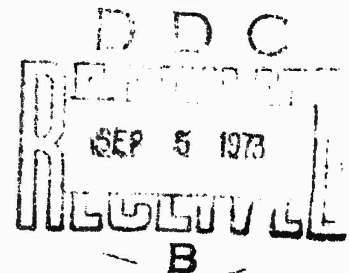
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A method of calculating the parameters for the entrainment of teflon mass in the neighborhood of the stagnation point of an axisymmetric blunt body as a function of the parameters of an incident high-temperature flow over a wide range of enthalpies and stagnation pressures is proposed.

Due to several properties of teflon (polytetrafluoroethylene), its investigation is of great interest in understanding the mechanism of mass entrainment. This is a typical homogeneous material, possessing high bond energy of its polymer chain and high heat capacity, with low thermal conductivity and so on. Its heat-physical properties were studied quite closely.

When teflon is degraded in a high-temperature flow, the formation of a liquid film and mechanical entrainment are absent, which permits a theoretical calculation of the degradation parameters with good accuracy and the comparison of these theoretical values with experimental values. The mechanism of the degradation of teflon in a high-temperature gas flow has been considered in several works [1-3, 6, 8-10].

Since the heated layer is very thin, its decomposition occurs in a very small volume at the surface of the layer. For this reason, thermal degradation is viewed as a one-dimensional problem. The rate of depolymerization is determined only by the heat flow to the degrading surface.

Adams [1] proposed a degradation scheme that is satisfactory for pressures close to atmospheric. At the degrading surface temperature $T_w = 750^\circ \text{K}$, teflon is depolymerized into the monomer C_2F_4 with a molecular mass of 100. Several other authors have supported a similar mechanism [1, 3, 8-10]. By the theory of radical depolymerization [7], teflon can be depolymerized only with the formation of a monomer. It was experimentally found [7] that in a vacuum teflon is depolymerized into a monomer.

The rate of depolymerization is described by an Arrhenius type equation

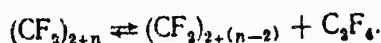
$$w = \rho B \exp\left(-\frac{E}{RT}\right), \quad (1)$$

where w is the rate of decomposition, $B = 3 \cdot 10^{19} \text{ sec}^{-1}$, $E = 347.8$ kilojoules/kg, and ρ = density.

In the case of decomposition under pressure, the following compounds were found in the reaction products [7]: C_3F_6 , C_4F_8 , and so on, with the general formula $C_2F_4 - (CF_2)_n$ or $(CF_2)_{n+1}$. These are none other than carbonyl fluorides. These compounds have molar thermodynamic functions which are linearly dependent on the order n [4]. For example, the approximate equality

$$C_p(CF_2)_{2+n} = C_p(C_2F_4) + \delta C_p n.$$

holds for heat capacity. It can be proposed that a gas injected into a boundary layer is in chemical equilibrium. Let us write the equilibrium equations for the reactions



Denoting by P_n the pressure of $(CF_2)_{2+n}$, by the law of active masses, we write

$$K_{P_n}(T) = \frac{P_{n-2} P_0}{P_n} \quad (2)$$

and for the reaction $2C_2F_6 \rightleftharpoons 3C_2F_4$

$$K'_p(T) = P_0^3 / P_1^3. \quad (2a)$$

The Gibbs potential for $(CF_2)_{2+n} \rightleftharpoons Z_k$ can be represented as:

$$Z_k = Z_0 + \delta Z_k.$$

Then

$$\ln K_{P_n} = -\frac{1}{RT} (Z_n - Z_{n-2} - Z_0) = -\frac{1}{RT} (Z_0 - 2\delta Z),$$

$$\ln K'_p = -\frac{1}{RT} (2Z_1 - 3Z_0) = -\frac{1}{RT} (Z_0 - 2\delta Z).$$

From this it is clear that the equilibrium constants are

$$K_{P_n}(T) = K'_p(T) = K_p(T).$$

The value of $K_p(T)$ calculated by the Van-Krevelen method [5] in 1000° K temperature range is close to 1 bar.

From equations (2) and (2a), we find

$$P_n = P_0 \left(\frac{P_0}{K_p} \right)^{\frac{n}{2}}. \quad (3)$$

Using Dalton's law and the formula $M_v P_v = \sum_{k=0}^{\infty} M_k P_k$,

we can get the formula

$$M_v = \delta M \left(2 + \frac{P_v}{2K_p} + \sqrt{\frac{P_v}{K_p} + \frac{P_v^2}{4K_p}} \right), \quad (4)$$

$\delta M = 50 \text{ g/mole,}$

where δM is the molecular mass of the CF_2 -group.

It can be suggested that the concentration of the decomposition products is close to unity at the degrading surface. This means that $P_v = P_e$. The mean molecular weight of the gaseous products will be a function only of the stagnation pressure:

$$M_v = 50 \left(2 + \frac{P_e}{2} + \sqrt{\frac{P_e^2}{4} + P_e} \right),$$

where P_e is given in bars.

Fig. 1 shows the dependence of M_v on P_e as calculated by formula (4). It is clear that the mean molecular weight of the teflon depolymerization products when $P_e > 0$ is higher than 100 and increases with pressure. The data of Grassi [7], which differ from the calculated values by not more than 13 percent, are given for the rarefaction region.

Another important quantity is the enthalpy of decomposition H_p , the amount of heat expended in heating and decomposition per unit weight of the material:

$$H_p = H'_w - H_0,$$

where H'_w is the enthalpy of the decomposition product at the temperature of the degrading surface and H_0 is the enthalpy of the material at standard conditions.

Enthalpy H_p is determined not only by the surface temperature T_w , but also by the energy expended in breaking bonds in the polymer chain.

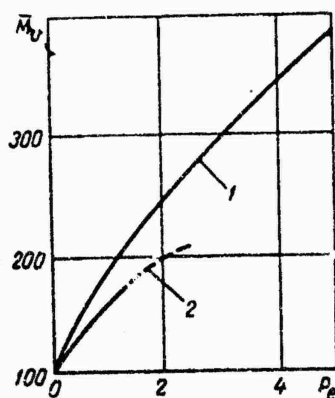


Fig. 1. Dependence of the mean molecular mass of the teflon degradation products on pressure P_e , bar:

- 1 -- theoretical curve
2 -- Grassi's data [7]

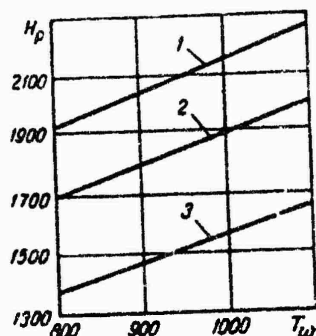


Fig. 2. Dependence of the enthalpy of the degradation of teflon on the surface temperature at different stagnation pressures:

- 1 -- 0.5 bar 2 -- 1 bar
3 -- 10 bar

To calculate H_p , let us use the method of methyl substitutions [5] and the approximate linear dependence of molar enthalpy on reaction order:

$$H_p = 858 + 418(T_w \cdot 10^{-3}) + 54(T_w \cdot 10^{-3})^2 + \\ + 74(T_w \cdot 10^{-3})^3 + \frac{75.6 + 6.75(T_w \cdot 10^{-3})^2 + 16.5(T_w \cdot 10^{-3})^3}{M_p} \text{ kilojoules/kg.}$$

When $T_w = 1000^\circ \text{K}$ and $M_v = 100 \text{ g}$ and $H_p = 2200 \text{ kilojoules/kg.}$ which agrees with the value of H_p in several studies in which H_p is assumed to be constant. The dependence of H_p on T_w when $P_e = 0.1, 1, \text{ and } 10 \text{ bar}$ is shown in Fig. 2.

Let us set up the equation of the energy balance at the glass-gas interface:

$$(\alpha/C_p)(H_p + 0.21H_{\text{top}} - H_w) = GH_p + \epsilon\sigma T_w^4. \quad (5)$$

The term $0.21 H_{\text{top}}$ takes account of the effect of an enthalpy rise at the outer boundary of the boundary layer as a result of the combustion of the

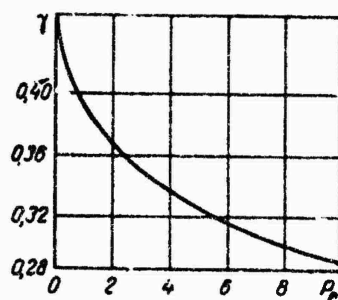


Fig. 3. Dependence of the injection coefficient on the stagnation pressure

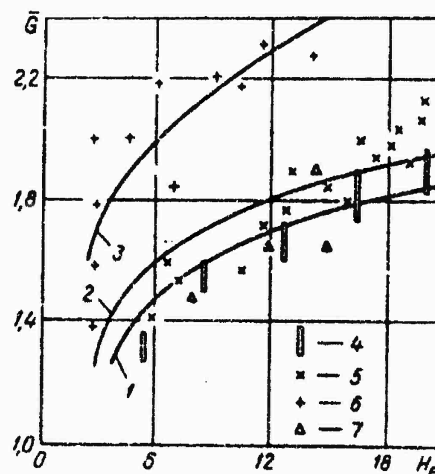


Fig. 4. Dimensionless rate of entrainment of teflon mass in an air flow as a function of stagnation enthalpy and pressure:
1, 2, 3 -- theoretical curves for $P_e = 0.1, 1.0, \text{ and } 6.0 \text{ bar}$, respectively
4, 5, 6, 7 -- experimental results
(4 -- $P = 0.1 \text{ bar}$; 5 -- $P = 1 \text{ bar}$ [10]; 6 -- $P_e = 6 \text{ bar}$ bar [2]; 7 -- $P_e = 1 \text{ bar}$ [6])

teflon decomposition products with the formation of COF_2 , $H_{\text{top}} = 22,300$ kilojoules/kg (on the basis of 1 kg oxygen). The degree of blackness of the teflon surface $\varepsilon = 0.1 - 0.2$ [9]. Analysis [3] shows that the variation in the temperature at the surface and the teflon surface amounting to 100° changes the rate of entrainment by tenfold. In actual conditions, the entrainment rate of the mass varies only mildly. Therefore the temperature of the surface varies slightly or remains practically constant.

Variation in the molecular mass of the depolymerization products injected into the boundary layer leads to a change in the heat transfer coefficient at the degrading surface. This is taken into account by the injection factor.

Values of the injection factor calculated by the formula in the study [11], without allowing for the enthalpy factor, is shown in Fig. 3 as a function of the stagnation pressure.

Calculations show that the use of the injection factor as a constant ($\gamma = 0.49$) for different degradation conditions is inapplicable and can lead to erroneous results.

The heat transfer coefficient calculated with allowance for the injection effect can be calculated from the following expression:

$$(\alpha/C_p) = (\alpha/C_p)_0 - 0.6 \left(\frac{M_c}{M_w} \right)^{0.24} \left(\frac{H_c}{H_w} \right)^{0.03} G.$$

In equation (5) the two unknowns are G and T_w . So to close the system of equations, let us use the equation of the kinetics of the degradation of a teflon coating [3]

$$G = \sqrt{\frac{B \exp\left(-\frac{E}{RT_w}\right) RT_w^2 (\rho_T \lambda)_w}{H_p^0 E}}. \quad (6)$$

where H_p^0 is the enthalpy of degradation of teflon with the formation of a monomer; λ is the thermal conductivity of teflon:

$$\lambda = (12.1 + 4.85 \cdot 10^{-3} T_w) \cdot 10^{-2} \text{ watts/m} \cdot \text{deg};$$

and ρ_T is the density of teflon.

Equation (5) can be given the form of an expression of the dimensionless entrainment rate of the mass:

$$\bar{G} = \frac{G}{(\alpha/C_p)_0} = \frac{1}{\frac{H_p + \frac{eG T_w^4}{G}}{H_c + 0.21 H_p - H_w} + 0.6 \left(\frac{M_c}{M_w} \right)^{0.24} \left(\frac{H_c}{H_w} \right)^{0.03}}.$$

The heat transfer coefficient for an impermeable surface $(\alpha/C_p)_0$ is determined by the Fay-Ridell formula [12]

$$(\alpha/C_p)_0 = 0.92 (\rho_\infty \mu_\infty)^{0.4} (\rho_w \mu_w)^{0.1} \left[1 + 0.19 \frac{H_c}{H_\infty} \right] \sqrt{\frac{1}{R}} \sqrt{\frac{2(P_\infty - P_w)}{\rho_\infty}}.$$

The calculated functions $G = f(H_e)$ for $P_e = 0.1, 1, \text{ and } 6 \text{ bar}$, corresponding to the stagnation pressures obtained experimentally in several studies [2,6,9,10] are shown in Fig. 4. From the figure it follows that the calculated values of G obtained by the proposed method agree quite satisfactorily with the experimental data of several authors for different pressures and stagnation enthalpies.

Symbols

- M_v = mean molecular mass of injected products
- (α/C_p) = heat transfer coefficient
- $\bar{G}$ = dimensionless rate of entrainment of mass
- G = rate of entrainment of mass
- e = index of conditions at the stagnation point
- w = index of conditions at the body surface
- P_v = pressure of the decomposition products
- ρ, μ = density and viscosity of air
- H_0 = enthalpy of dissociation of unit mass of air
- δM = molecular mass of the (CF_2) -group
- R = radius of blunt body.

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