A METHOD OF CALCULATING TEFLON MASS REMOVAL WHEN TEFLON IS BROKEN UP IN A HIGH TEMPERATURE GAS FLOW

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

Due to a number of its properties, teflon (polytetrafluorethylene) is of interest to investigate in order to understand the mechanism of mass removal. It is a typical homogeneous material with large binding energy in the polymer chains and large specific heat, but low thermal conductivity, etc. Its thermophysical properties are quite well known.

When teflon is broken up in a high temperature flow there is no formation of a liquid film or mechanical removal, so that the parameters of the break up can be calculated to a high degree of accuracy theoretically and compared with experimental data. The mechanism of teflon breakup in a high temperature gas flow has been discussed in a number of papers [1-3, 6, 8-10].

Since the heated layer is very thin, its decomposition occurs in a small volume at the surface of the layer. For this reason the thermal decomposition can be considered as a one-dimensional problem. The rate of depolymerization is defined only by the thermal flux to the decomposing surface.

Adams [1] proposed a decomposition scheme which is satisfactory for a pressure close to atmospheric. When the temperature of the decomposing surface is $T_W = 750°K$, the teflon depolymerizes into the monomer C_2F_4 with a molecular mass of 100. A similar mechanism has been maintained by a number of other authors [1, 3, 8-10]. According to the theory of radical depolymerization [7], teflon can depolymerize only to a monomer. It has been established experimentally [7] that in a vacuum teflon depolymerizes into a monomer.

The rate of depolymerization is described by the Arrhenius equation

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

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

When decomposition takes place under pressure, we observe the following compounds [7] among the products: C_3F_6; C_4F_8, etc., with general formula $C_2F_4-(CF_2)_n$ or $(CF_2)_{n+1}$. These are nothing else than unsaturated fluorocarbons.

These compounds have molar thermodynamic functions linearly dependent on n [4]. For example, for the specific heat we have the approximate equation

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

It can be assumed that the gas injected into the boundary layer is in chemical equilibrium. The equilibrium equation for the reaction is

$$(CF_2)_{2+n} \rightleftarrows (CF_2)_{2+(n-2)} + C_2F_4.$$

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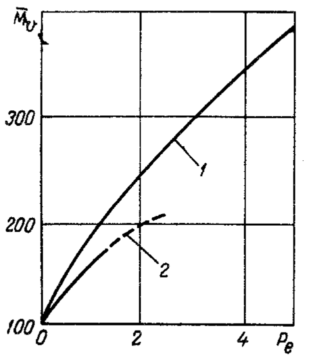

Fig. 1

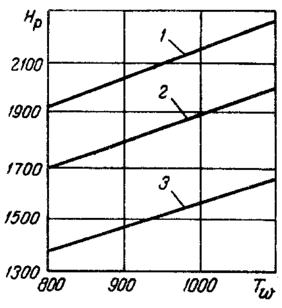

Fig. 2

Fig. 1. The mean molecular weight of the teflon decomposition products as a function of the pressure P_e, bar: 1) theoretical curve; 2) Grassi data [7].

Fig. 2. Teflon decomposition enthalpy as a function of the surface temperature at various stagnation pressures: 1) 0.1 bar; 2) 1 bar; 3) 10 bar.

Letting P_n denote the pressure of $(CF_2)_{2+n}$, from the law of mass action we can write

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

and for the reaction $2C_3F_6 \rightleftharpoons 3C_2F_4$ we have

$$K_p'(T) = P_0^3/P_1^2. \tag{2a}$$

The Gibbs potential for $(CF_2)_{2+n} - Z_k$ can be written as follows:

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

Then

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

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

Thus we see 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-Krevlen method [5], is close to 1 bar in the range of temperatures up to 100°K.

From (2) and (2a) we find that

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

Using Dalton's law and the equation

$$M_v P_v = \sum_{k=0}^{\infty} M_k P_k,$$

we can obtain the equation

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

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

where δM is the molecular mass of the CF_2 group.

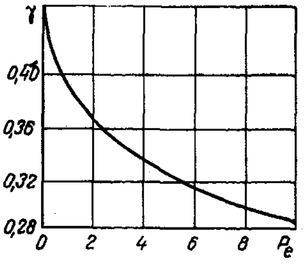

Fig. 3

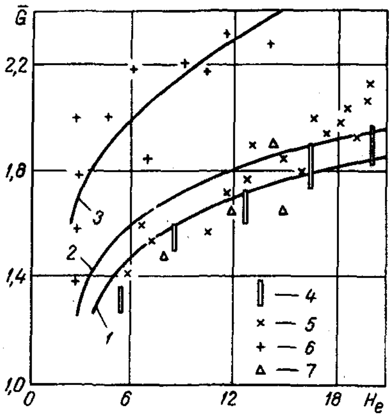

Fig. 4

Fig. 3. The injection coefficient as a function of the stagnation pressure.

Fig. 4. The nondimensional rate of teflon mass removal in an air flow as a function of the enthalpy and stagnation pressure:

It can be assumed that the concentration of the decomposition products is close to unity at the decomposing surface of the polymer. This implies that $P_v = P_e$. The average molecular weight of the gaseous products is 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 the bars.

Figure 1 shows M_v as a function of P_e, using Eq. (4). We see that the mean molecular weight of the teflon depolymerization products is greater than 100 when $P_e > 0$ and it increases as the pressure increases. Grassi's data [7] are given in the region of rarefaction; they differ from the calculated values by no more than 13 per cent.

Another important quantity is the decomposition enthalpy H_p, the heat content going towards heating and decomposition of unit mass of the material:

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

where H'_w is the enthalpy of the decomposition products at the temperature of the decomposing surface; H_0 is the material enthalpy at standard conditions.

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

To calculate H_p we use the method of methyl substitutions [5] and an approximate linear equation between the molar enthalpy and the order:

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

For $T_w = 1000$°K and $M_v = 100$ g, $H_p = 2200$ kJ/kg, which coincides with the value of H_p in a number of papers in which H_p was assumed to be constant. Figure 2 shows H_p as a function of T_w for $P_e = 0.1$, 1, 10 bar.

The energy balance equation at the boundary between the wall and the gas is

$$(\alpha/C_p)(H_e + 0.21H_{\text{comb}} - H_w) = GH_p + \varepsilon\sigma T_w^4. \tag{5}$$

The term $0.21\ H_{\text{comb}}$ takes into account the effect of an increase in the enthalpy at the outer edge of the boundary layer as a result of the combustion of the teflon decomposition products with the formation of

COF_2; $H_{comb} = 22300$ kJ/kg (per kilogram of oxygen). The degree of blackness of the teflon surface was $\varepsilon = 0.1-0.2$ [9]. Analysis [3] shows that a change in the teflon surface temperature of 100° changes the rate of removal by an order of magnitude. In actual conditions the rate of mass removal does not vary strongly.

Hence the surface temperature changes insignificantly, or remains practically constant.

A change in the molecular mass of the decomposition products injected into the boundary layer leads to a change in the heat transfer coefficient at the decomposing surface. This is taken into account through the injection coefficient.

Figure 3 shows the injection coefficient computed from an equation of [11], ignoring the enthalpy factor as a function of stagnation pressure.

Calculations showed that using an injection coefficient which is assumed to be constant ($\gamma = 0.49$) leads to erroneous results for various decomposition conditions.

Taking account of injection, the heat transfer coefficient can be calculated from the following expression:

$$(\alpha/C_p) = (\alpha/C_p)_0 - 0.6\left(\frac{M_e}{M_v}\right)^{0.24}\left(\frac{H_e}{H_w}\right)^{0.03} G.$$

Equation (5) contains two unknowns, G and T_w. Hence to complete the system of equations we use the equations for the kinetics of the teflon covering decomposition [3]

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

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

$$\lambda = (12.1 + 4.85\cdot 10^{-2} T_w)\cdot 10^{-2}\ \frac{\mathrm{W}}{\mathrm{m.\ deg}};$$

and ρ_T is the teflon density.

Equation (5) can be given the form of an expression for the nondimensional rate of mass removal:

$$\bar{G} = \frac{G}{(\alpha/C_p)_0} = \frac{1}{\dfrac{H_p + \dfrac{\varepsilon\sigma T_w^4}{G}}{H_e + 0.21H_{comb} - H_w} + 0.6\left(\dfrac{M_e}{M_w}\right)^{0.24}\left(\dfrac{H_e}{H_w}\right)^{0.03}}.$$

The heat transfer coefficient for the impermeable surface $(\alpha/C_p)_0$ was determined from the Fey–Riddle equation [12]

$$(\alpha/C_p)_0 = 0{,}92\,(\rho_e\mu_e)^{0,4}\,(\rho_w\mu_w)^{0,1}\left[1 + 0{,}19\,\frac{H_0}{H_e}\right]\sqrt{\frac{1}{R}\sqrt{\frac{2(P_e - P_\infty)}{\rho_e}}}.$$

We evaluated the equation $G = f(H_e)$ for $P_e = 0.1$, 1, and 6 bar, which corresponds to the stagnation pressure obtained experimentally in a number of papers [2, 6, 9, 10], the results being shown in Fig. 4. It follows from Fig. 4 that the values of G computed by the proposed method agree quite well with the experimental data from a number of authors for various stagnation pressures and enthalpies.

NOTATION

M_v	is the mean molecular mass of injected products;
(α/C_p)	is the heat transfer coefficient;
$\bar{G}$	is the nondimensional rate of mass removal;
G	is the mass removal rate;
e	is the subscript denoting conditions at the stagnation point;

w	is the subscript denoting conditions at the body surface;
P_V	is the pressure of decomposition products;
ρ, μ	are the density and viscosity of air;
H_0	is the enthalpy of dissociation of unit mass of air;
δM	is the molecular mass of (CF_2) group;
R	is the radius of blunt body.

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