Int. J. Heat Mass Transfer. Vol. 20, pp. 661–668. Pergamon Press 1977. Printed in Great Britain

AN ANALYTICAL MODEL OF THE TRANSIENT ABLATION OF POLYTETRAFLUOROETHYLENE LAYERS*

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(*Received* 28 *July* 1976)

Abstract—Pyrolysis experiments with polytetrafluoroethylene (PTFE) in a closed volume, which investigate the mechanism of depolymerization, the influences of sample size and of different gas atmospheres as well as the composition of the reaction products, are analysed with respect to unilaterally heated PTFE-layers. On the basis of this investigation of the high-temperature behaviour of PTFE an analytical model for the transient one-dimensional ablation of PTFE-layers has been developed. The crystalline–amorphous phase transition, the thermal expansion and the formation of higher-molecular products at the surface are taken into account. Comparisons of computed temperature profiles with measured values in plasma-arc jet facilities confirm the model for transient ablation and the limiting case of quasi-steady ablation.

NOMENCLATURE

a,	$\lambda/\rho c$, thermal diffusivity;
B,	$\dot{m}(h_s - h_w)/q_0$, blowing parameter;
c,	ρ_P/ρ_2, mass fraction of the polymer;
c_{gr},	limiting value of the mass fraction at the surface;
c_n,	specific heat of phase n;
E_A,	activation energy;
h,	enthalpy;
h_η,	heat of transition;
k_0,	frequency factor;
k',	coefficient of heat transmission;
$\dot{m}$,	ablation rate (ablating mass flux);
P,	polymer molecule;
q_{0c},	heat flux to a cool non-ablating wall;
q_0,	heat flux to a non-ablating wall of the same temperature as the ablating one;
q_ξ,	heat flux to the surface of the ablation layer;
R,	part of a polymer chain;
R_m,	part of a polymer chain with m CF_2-units;
T,	temperature;
T_η,	melting point;
t,	time;
w_n,	velocity due to thermal expansion in phase n;
x,	coordinate normal to the surface;
x_0,	initial thickness of the layer;
y_1,	$(x-\zeta)/(\eta-\zeta)$, transformed coordinate;
y_2,	$(x-\eta)/(\xi-\eta)$, transformed coordinate.

Greek symbols

δ_{hs},	thickness of the heat sink;
Δh_D,	heat of depolymerization;
ζ,	penetration bound, defined by equation (27);
η,	coordinate of the phase interface (melting plane);
λ_n,	thermal conductivity of phase n;
ξ,	coordinate of the surface;
ρ_n,	density of phase n;
ρ_P,	partial density of the decomposing polymer.

Subscripts

hs,	heat sink;
k,	coolant;
s,	stagnation point;
w,	wall, surface;
η,	phase interface;
ξ,	surface;
1, 2,	in phase 1, 2.

1. INTRODUCTION

ABLATION cooling is applied when it is necessary to protect a surface from severe heat fluxes and to limit the temperature of a material. During the process coatings are consumed by heat addition, i.e. they ablate. Ablating heat shields have successfully protected many hypersonic vehicles during atmospheric re-entry. Ablative thermal protection is employed also in rocket propulsion systems because of the severity of the heat flux conditions combined with a high-pressure environment. In chemical engineering ablation layers are used for protection of chemical reactors and other parts of apparatus. There are different mechanisms of ablation as sublimation, melting, pyrolysis or heterogeneous reaction with an environmental gas. The virgin material turns from the solid state to the liquid or gaseous state under absorption of heat, which is transferred to the environment with the liquid or gas.

The ablation layer is heated predominantly by convection or radiation from a gas flow. The ablation products are blown out into the gas flow. This thickens the boundary layer and reduces the convective heat-transfer rate to the surface. So there are two effects reducing heat addition to the surface: the heat absorption within the ablation layer by phase transition or reaction and the extension of the boundary-layer thickness.

Detailed knowledge of the characteristics of the various ablation materials and of the interaction mechanisms between materials and high-temperature environments is necessary. For calculating the heat and mass transfer within the ablation layer the materials are classified and special models are made.

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*Part of the Ph.D. thesis [1] of the author at the Institut für Thermo- und Fluiddynamik, Ruhr-Universität Bochum, BRD.

A suitable ablative material is polytetrafluoroethylene (PTFE), most referred to by one of its trademarks as Teflon (DuPont).

The transient, one-dimensional ablation of a PTFE-layer, which melts and depolymerizes when subjected to a severe heat flux, is considered in this investigation. An analytical model is made and compared with measurements in arc jet facilities. The model describes the heat and mass transfer within the ablation layer and at its surface without consideration of the gas flow.

2. HIGH-TEMPERATURE BEHAVIOUR OF POLYTETRAFLUOROETHYLENE

PTFE is a white, partially crystalline (up to 80%) material at room temperature. The polymer chains are linear. At 293 and 303 K changes of chain configuration occur, but the involved heats of transition are negligible. The polymer undergoes a sharp, reversible transition at 600 K changing from the white, translucent or opaque substance to a transparent, amorphous material, accompanied by a heat of transition of $h_\eta = 14\,\mathrm{cal/g}$. This phase transition is commonly called "melting point", but it should be pointed out, that molten PTFE is not particularly fluid, as the viscosity remains very high.

As the temperature of PTFE is raised above 620–670 K, pyrolysis occur. The polymer decomposes into gaseous products without charring or liquid layer formation. Though this decomposition is often called "sublimation", it is not a phase transition at a constant temperature, but a chemical reaction, namely the depolymerization of the polymer chains.

The mechanism of depolymerization of PTFE is simple as compared to other polymers because of the homogeneous and linear polymer chains. There are three parts of the depolymerization: the initiation, the depropagation and the termination [2–6].

In the initiation a random C–C split occurs to form a pair of free radicals (random initiation)

$$P \rightarrow R-\mathrm{CF_2}\text{–}\mathrm{CF_2}\text{–}\mathrm{CF_2}. + R-\mathrm{CF_2}.. \qquad (1)$$

The P represents any size polymer, R is a part of a polymer chain. The radicals remain in the vicinity of the site where they formed and depropagate by stepwise ejection of monomer molecules from the radical ends (depropagation)

$$R-\mathrm{CF_2}\text{–}\mathrm{CF_2}\text{–}\mathrm{CF_2}. \rightarrow R-\mathrm{CF_2}. + \mathrm{CF_2} = \mathrm{CF_2}. \qquad (2)$$

The monomer rapidly diffuses away from the reaction site. The *termination* is possible in several ways: by direct evaporation

$$R_m-\mathrm{CF_2}. \rightarrow \text{evaporation}, \qquad (3)$$

by disproportionation

$$R-\mathrm{CF_2}\text{–}\mathrm{CF_2}. + R-\mathrm{CF_2}\text{–}\mathrm{CF_2}. \rightarrow R-\mathrm{CF_2}\text{–}\mathrm{CF_3} + R-\mathrm{CF}=\mathrm{CF_2} \qquad (4)$$

or by radical combination

$$R-\mathrm{CF_2}. + R-\mathrm{CF_2}. \rightarrow P. \qquad (5)$$

R_m is a chain of about 70 carbon atoms. The mechanism then is one in which a bond breaks at random position of the chain forming radicals that unravel into monomer and terminate by one or more of the processes listed.

The depolymerization of PTFE is a first-order reaction. The kinetics of the reaction can be described by the equation

$$\frac{\partial \rho_P}{\partial t} = -k_0 \exp\left(-\frac{E_A}{RT}\right)\rho_P. \qquad (6)$$

Herein is E_A the activation energy, k_0 the frequency factor and ρ_P the partial density of the decomposing polymer. These quantities and the heat of depolymerization Δh_D were evaluated from a selection of measured values [1]: $E_A = 75.6 \pm 5.7\,\mathrm{kcal\,mol^{-1}}$, $k_0 = 3.1 \times 10^{19} \pm 3.7 \times 10^{19}\,\mathrm{s^{-1}}$, $\Delta h_D = 370\,\mathrm{cal\,g^{-1}}$.

During the pyrolysis of thick samples in a closed volume the phenomena were observed to be diffusion controlled [7] because of the high monomer concentration in the sample. In ablation layers diffusion control does not occur, for the reaction takes place in a very thin layer under the surface and the produced monomer is transferred immediately to the surface.

The measured reaction rates during the pyrolysis of samples in a closed volume in the presence of various gases were quite different [2, 3, 7]. For instance, the reaction rate is in an atmosphere of O_2 higher than in an atmosphere of N_2. O_2-molecules diffuse into the polymer sample and react with the produced monomer gas. This exothermic reaction accelerates the depolymerization. Some gases have a catalytic, others an inhibitory effect on the thermal decomposition of PTFE. In ablation layers, however, the ablation velocity (velocity of the surface) is higher than the diffusion rate of the molecules. So reactions of the monomer molecules with molecules of environmental gas occur only outside the ablation layer.

Mass spectrometric analyses of the volatile products from degradation in vacuum in the temperature range 773–1473 K show, that the monomer C_2F_4 is the major decomposition product throughout the whole temperature range [8]. The relative proportion of the monomer falls as the temperature increases. At a temperature of 1070 K the proportion of the monomer amounts to 90 mole%. Lewis and Naylor [9] observed a strong dependence of the product proportions upon pressure. With increasing pressure the proportion of the monomer decreases from 97% (5 torr) to 15.9% (760 torr). They suggested that the monomer was the primary product but that it reacted to an increasing extent at higher pressures to give higher-molecular-weight compounds. According to the investigation of [9] one can assume that in ablative PTFE-layers the decomposition product is pure monomer. Formation of higher-molecular-weight compounds by secondary reactions occur only outside the ablation layer, e.g. in the boundary layer of the environmental flow.

The available measured values of the thermal conductivity, the density and the specific heat of PTFE (see [1]) were for the numeric computation correlated by polynomials (index 1 = crystalline state, index 2 = amorphous state)

$$\lambda_1 = [1.2+1.467\times10^{-2}\,\mathrm{T/K}]\times10^{-4}\,\mathrm{cal\,cm^{-1}\,s^{-1}\,K^{-1}}$$
$$\lambda_2 = [21.04-3.34\times10^{-2}\,\mathrm{T/K}+1.39\times10^{-5}\,\mathrm{T^2/K^2}]\;10^{-4}\,\mathrm{cal\,cm^{-1}\,s^{-1}\,K^{-1}}$$
$$\rho_1 = [2.119+7.92\times10^{-4}\,\mathrm{T/K}-2.105\times10^{-6}\,\mathrm{T^2/K^2}]\,\mathrm{g\,cm^{-3}}$$
$$\rho_2 = [2.07-7\times10^{-4}\,\mathrm{T/K}]\,\mathrm{g\,cm^{-3}}$$
$$c_1 = [0.123+0.3733\times10^{-3}\,\mathrm{T/K}]\,\mathrm{cal\,g^{-1}\,K^{-1}}$$
$$c_2 = [0.216+0.156\times10^{-3}\,\mathrm{T/K}]\,\mathrm{cal\,g^{-1}\,K^{-1}}.$$

3. PREVIOUS WORKS

With simplifying assumptions it is possible to calculate the heat and mass transfer in ablative PTFE-layers without numerical work. This is valid for the so-called quasi-steady ablation. The limiting case of quasi-steady ablation is reached after a transient process in the beginning on the condition that the heat flux to the surface is constant and the initial thickness of the layer is large enough. In this case the ablation velocity and the mass flux of ablation products are constant.

In the quasi-steady ablation the energy balance across the layer is given by

$$q_\xi = \dot{m}\left(\int_{T_k}^{T_\eta} c_1\,\mathrm{d}T + \int_{T_\eta}^{T_\xi} c_2\,\mathrm{d}T + h_\eta + \Delta h_D\right), \qquad (7)$$

q_ξ represents the heat flux to the surface, $\dot{m}$ is the mass flux of ablation products, T_k the initial temperature of the layer, T_η the melting point and T_ξ the surface temperature. If a mean value for the surface temperature T_ξ is assumed equation (7) yields directly the mass flux $\dot{m}$ to a known heat flux q_ξ [10–12]. Authors of later works [11, 13–17] deduce a relation between the surface temperature T_ξ and the mass flux $\dot{m}$ from the heat-conduction equation and an expression for the reaction kinetics. This relation and equation (7) yield the required mass flux. Several authors take the melting point [15] or the deformation of the temperature profile by the depolymerization [16, 17] into account.

The transient ablation of PTFE layers was calculated up to now only numerically by difference methods [7, 18, 19]. Numerical methods become very complex due to the nonlinear boundary condition for heat flux at the phase interface and the surface and due to the depolymerization reaction. In [18] it is assumed that the material depolymerizes only at the surface and the surface temperature is determined by an expression that is valid only for quasi-steady ablation. In all previous works for simplification the depolymerization is treated as zero-order reaction although pyrolysis experiments show that the depolymerization is a first-order reaction. Moreover the thermal expansion is neglected in spite of the strong temperature dependence of the density and the formation of higher-molecular-weight compounds at the surface is not taken into consideration. The purpose of this paper is to present an analytical model which takes into account the depolymerization as a first-order reaction, the thermal expansion and the formation of higher-molecular-weight compounds.

4. PHYSICAL MODEL AND MATHEMATICAL FORMULATION

Consider a PTFE-layer, which is situated before a plane wall and is heated by the heat flux q_ξ as shown in Fig. 1(a). The wall is convectivèly cooled on the backside with a coefficient of heat transmission k'. The layer is assumed to have initially the thickness x_0 and the temperature T_k of the coolant which lies under the melting point: $T_k < T_\eta = 600\,\mathrm{K}$. Therefore the polymer is in the crystalline state.

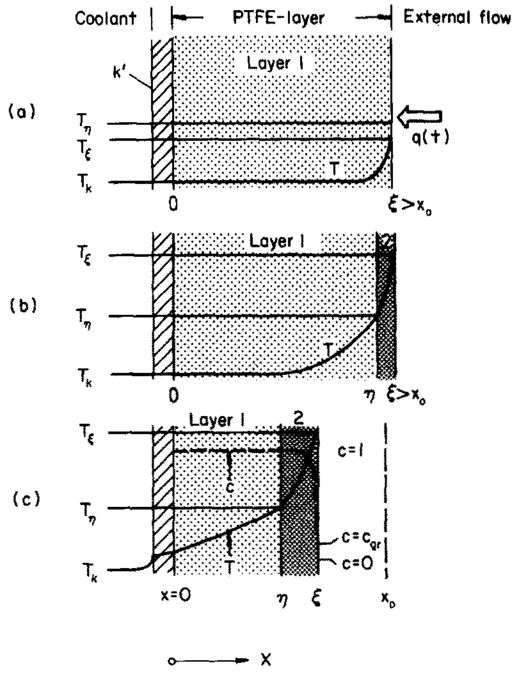

FIG. 1. Schematic representation.

At the time $t = 0$ the layer is exposed to the heat flux q_ξ, which is transferred to surface in general by convection and radiation and is here assumed to have a known value. In the following there are three periods of time. In period I the temperature distribution results only from transient heat conduction. Surface temperature and penetration depth increase with time. Also does the thickness of the layer by thermal expansion.

When the surface temperature T_ξ reaches the melting point $T_\eta = 600\,\mathrm{K}$ an amorphous phase (phase 2) is formed at the surface beside the original crystalline phase (phase 1) as shown in Fig. 1(b) (period II). The two phases are separated by the phase interface η, which is characterized by the absorption of the heat of transition and the discontinuities of physical properties. In the phase 2 the virgin material decomposes with increasing temperature. The mass fraction c of the polymer which is defined as the density of the decomposing polymer divided by the density of the undecomposed polymer decreases towards the surface and with time.

If the mass fraction c reaches a limiting value c_{gr} period III begins. Henceforth the coordinate ξ of the surface is not determined by the thermal expansion as in period I and II, but is defined by the condition $c(x = \xi) = c_{gr}$. Figure 1(c) shows the distribution of temperature T and of mass fraction c of the polymer. The thickness of the crystalline phase decreases till the phase interface reaches the wall.

4.1. *Mathematical formulation*

Between the periods I and II the number of phases, in which various equations are valid, increases from one to two because of the formation of the amorphous phase. In the three periods various systems of equations have to be solved. In the following first the equations for period III are represented and then those for period I and II.

In the crystalline phase (see Fig. 1c) transient heat conduction and thermal expansion are described by the conservation equations for energy and mass

$$\rho_1 c_1\left(\frac{\partial T}{\partial t} + w_1\frac{\partial T}{\partial x}\right) = \frac{\partial}{\partial x}\left(\lambda_1\frac{\partial T}{\partial x}\right) \tag{8}$$

$$\frac{\partial \rho_1}{\partial t} = -\frac{\partial(\rho_1 w_1)}{\partial x}. \tag{9}$$

The symbols are: t for the time, λ_1, ρ_1 and c_1 for the thermal conductivity, the density and the specific heat in phase 1 and w_1 for the velocity in phase 1. Equations (8) and (9) must be solved with the boundary conditions of finite heat transfer and of vanishing velocity at the wall

$$x = 0{:}\ \lambda_1\frac{\partial T}{\partial x} = k'(T - T_k) \tag{10}$$

$$x = 0{:}\ w_1 = 0 \tag{11}$$

and with the boundary condition of a constant temperature due to the melting point at the phase interface η

$$x = \eta{:}\ T = T_\eta. \tag{12}$$

The melting produces at the phase interphase a heat flux discontinuity

$$h_\eta \rho_{1\eta}\left(\frac{d\eta}{dt} - w_{1\eta}\right) = \lambda_{1\eta}\left.\frac{\partial T}{\partial x}\right|_1 - \lambda_{2\eta}\left.\frac{\partial T}{\partial x}\right|_2, \tag{13}$$

but the mass fluxes on both sides of the phase interface have to be equal

$$\rho_{1\eta}\left(\frac{d\eta}{dt} - w_{1\eta}\right) = \rho_{2\eta}\left(\frac{d\eta}{dt} - w_{2\eta}\right). \tag{14}$$

As previously noticed the molten PTFE in the amorphous phase 2 can be treated as a solid material. Clark [19] has shown that the lateral velocity is several orders of magnitude (perhaps 9) less than the ablation velocity. The conservation equations for energy, mass and mass polymer

$$\rho_2 c_2\left(\frac{\partial T}{\partial t} + w_2\frac{\partial T}{\partial x}\right) = \frac{\partial}{\partial x}\left(\lambda_2\frac{\partial T}{\partial x}\right) - \rho_2 \Delta h_D k_0 \exp\left(-\frac{E_A}{RT}\right)c \tag{15}$$

$$\frac{\partial \rho_2}{\partial t} = -\frac{\partial(\rho_2 w_2)}{\partial x} \tag{16}$$

$$\frac{\partial c}{\partial t} + w_2\frac{\partial c}{\partial x} = -k_0 \exp\left(-\frac{E_A}{RT}\right)c \tag{17}$$

take the depolymerization into account. Diffusion is neglected in the energy balance because the diffusion heat flux is negligible compared with the conduction heat flux. The quantities λ_2, ρ_2, c_2 for the decomposing material are evaluated from the properties of the undecomposed material which are functions of temperature only. Equations (15) and (17) are solved with the boundary conditions of constant temperature due to the melting point and constant mass fraction at the phase interphase η

$$x = \eta{:}\ T = T_\eta \tag{18}$$

$$x = \eta{:}\ c = 1 \tag{19}$$

and with the boundary condition of a known heat flux at the surface ξ

$$x = \xi{:}\ \lambda_{2\xi}\frac{\partial T}{\partial x} = q_\xi(t). \tag{20}$$

Equation (14) serves as boundary condition for equation (16).

The position of the surface ξ results from the mass fraction distribution of the polymer by the definition

$$x = \xi{:}\ c = c_{gr}. \tag{21}$$

At the surface higher-molecular-weight products are formed by the termination reactions (3)–(5). At stronger heat fluxes, i.e. at higher surface temperatures molecules of longer chain length are ejected from the surface because of their higher thermal energy. In the model this is taken into consideration by the assumption of a rest mass fraction $c_{gr}(T_\xi)$ of the polymer at the surface, which increases with surface temperature. The function $c_{gr}(T_\xi)$ was according to the reaction kinetic expression correlated by

$$c_{gr} = 35.6\exp\left(-\frac{5000\,\mathrm{K}}{T_\xi}\right) - 0.089 \quad \text{for } T_\xi \geqslant 850\,\mathrm{K} \tag{22}$$

$$c_{gr} = 0.01 \quad \text{for } T_\xi < 850\,\mathrm{K}.$$

The constants were determined by comparison with measurements of the ablation rate in quasi-steady ablation.

Equations (8)–(22) are valid in the period III. In the period I only the equations (8)–(11) with the boundary condition

$$x = \xi{:}\ \lambda_{1\xi}\frac{\partial T}{\partial x} = q_\xi(t) \tag{23}$$

must be solved. The phase interface η does not exist. The position of the surface ξ is only determined by thermal expansion

$$\frac{d\xi}{dt} = w_{1\xi}. \tag{24}$$

In period II the same equations as in period III are valid with the exception of (21), which is replaced by

$$\frac{d\xi}{dt} = w_{2\xi}. \tag{25}$$

If the initial thickness of the layer is large enough and the heat flux to the surface is constant, the ablation velocity $d\xi/dt$, the surface temperature T_ξ and the thickness of the amorphous layer $\xi - \eta$ reach asymptotic limiting values. This limiting case of quasi-steady ablation can be directly computed without consideration of the transient ablation by the assumption of a layer of infinite thickness. The boundary condition (10) is replaced by the relation

$$x \to \infty: \frac{\partial T}{\partial x} = 0 \tag{26}$$

and a penetration depth $\xi - \zeta$ is introduced by the definition

$$x = \zeta: \ T = T_k + 0.01(T_\eta - T_k). \tag{27}$$

Transformation to the coordinates $y_1 = (x-\zeta)/(\eta-\zeta)$, $y_2 = (x-\eta)/(\xi-\eta)$ and introduction of the following two stationary conditions into the equations (8)–(22) yield the system of equations for quasi-steady ablation: the velocities of the surface ξ, the phase interphase η and the penetration bound ζ are equal and all derivatives with respect to time at constant y_1 or y_2 vanish.

5. NUMERICAL SOLUTION

The system of equations for the transient ablation consists of two partial differential equations in the crystalline phase, three partial differential equations in the amorphous phase, an ordinary differential equation for determining the position of the phase interface and the corresponding boundary conditions. These equations are nonlinear because of moving boundaries, the temperature dependence of the properties and the chemical reaction. After transformation to constant boundaries and to dimensionless variables the system of equations is solved by an implicit finite difference method with the exception of the two conservation equations for mass, which are converted into an integral form and solved by numerical integration.

The introduction of finite differences yields a system of nonlinear algebraic equations which is solved by the nonlinear successive overrelaxation [20]. At the beginning of period II there are numerical difficulties by the formation of the amorphous phase. Therefore the equations are divided into groups with different overrelaxation factors. When the amorphous layer is very thin, these overrelaxation factors are altered as function of the thickness of the layer.

6. COMPARISON WITH MEASURED VALUES

6.1. *Transient ablation*

Clark [19] made PTFE-ablation tests in a plasma-arc jet facility. He measured the temperature distribution in a thin PTFE-layer during the transient process at the beginning of ablation. Since quasi-steady ablation is realized very quickly for PTFE, very short testing times were necessary. The manufacture of the sample was conceived as a sandwich construction where layers of PTFE are stacked up with three or four thermocouples located between the layers. The layers were cut from PTFE tape and were molded together under high temperature and moderate pressure. The total diameter of the sample, 6.25 cm, was more than sufficient to insure one-dimensional heat transfer. A stainless-steel heat sink was cemented to the sample back.

For taking the heat sink into account the boundary condition (10) is replaced by the equation

$$x = 0: \ \rho_{hs} c_{hs} \delta_{hs} \frac{\partial T}{\partial t} = \lambda_1 \frac{\partial T}{\partial x}. \tag{28}$$

The symbols ρ_{hs}, c_{hs} and δ_{hs} represent the density, the specific heat and the thickness of the heat sink. Clark measured the heat flux using a water-cooled copper calorimeter. From this heat flux q_{0c} to a cool wall the heat flux q_0 to a non-ablating wall of the same temperature as the PTFE-surface is calculated by the relation $q_0/q_{0c} = [h_s - h_w(T_\xi)]/[h_s - h_w(T_{\text{cal}})]$. The symbols are: h_s, $h_w(T_\xi)$ and $h_w(T_{\text{cal}})$ for the enthalpy of the gas (N_2) at the stagnation point, at a wall with the surface temperature T_ξ and at a wall with the temperature T_{cal} of the calorimeter. The reduction of heat transfer by blowing out the ablation products into the boundary layer is calculated by a correlation of PTFE-ablation measurements in inert gases. Several correlations are shown in Fig. 2. The blowing parameter B is less than 1.3 in the experiments of Clark. Therefore the simple correlation of Nomura [23] $q_\xi/q_0 = 1 - 0.52B$ is used for determining the heat flux q_ξ to the ablating wall.

Thirteen tests of Clark have been computed using the described model. The results for four tests with

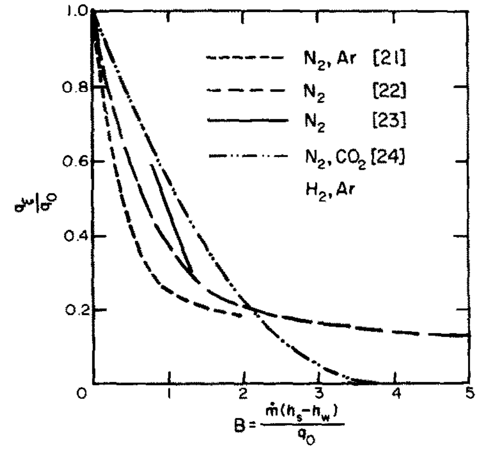

FIG. 2. Influence of the ablation rate $\dot{m}$ on the heat flux q_ξ (PTFE-ablation at the stagnation point, flow of inert gases).

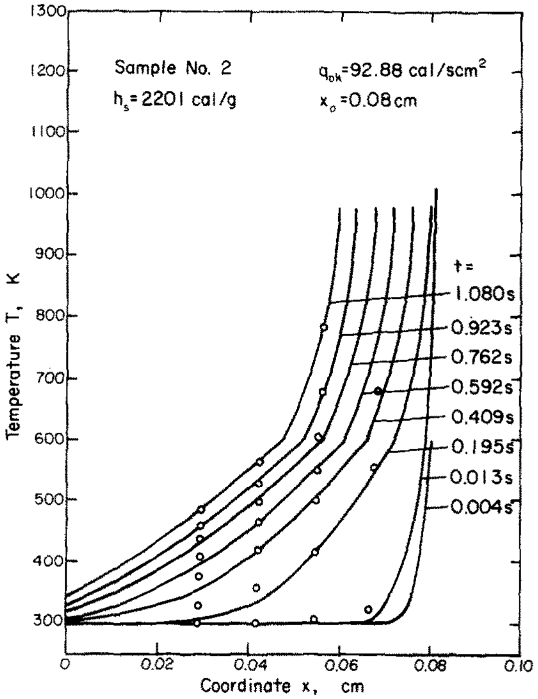

FIG. 3. Comparison of calculated transient temperature profiles with measured values of Clark [19].

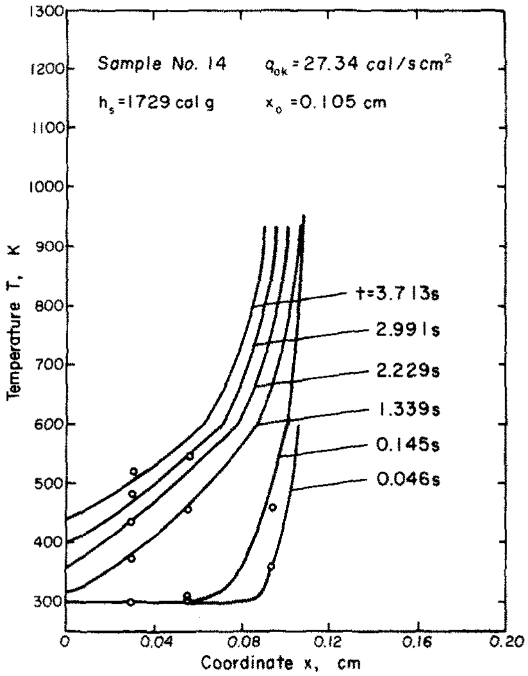

FIG. 5. Comparison of calculated transient temperature profiles with measured values of Clark [19].

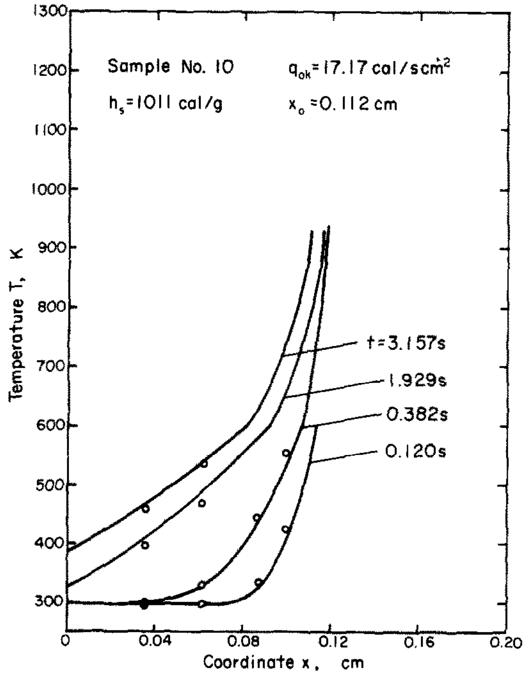

FIG. 4. Comparison of calculated transient temperature profiles with measured values of Clark [19].

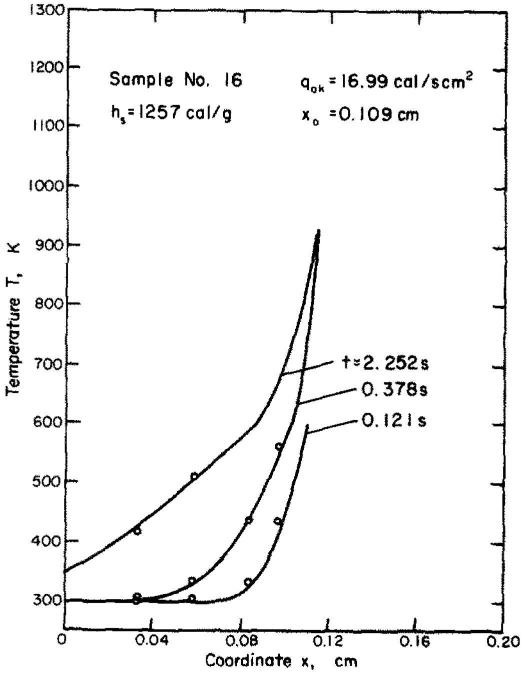

FIG. 6. Comparison of calculated transient temperature profiles with measured values of Clark [19].

different heat fluxes are shown in the Figs. 3–6. The curves represent the computed temperature profiles at different times, the symbols the measured values of Clark (interpolated). The distance L_0 of the thermocouples from the sample back given for the cool PTFE-layer are converted for the heated layer using the relation

$$L = \int_0^{L_0} \{\rho_0/\rho[T(x)]\}^{1/3}\,dx. \tag{29}$$

The index 0 denotes the cool state, the temperature distribution is assumed to be linear between the field points. The "kinks" in the temperature distributions at the phase transition plane ($T_\eta = 600\,K$) are produced by the heat absorption and the discontinuity of the thermal conductivity. The number of field points associated with each curve decreases with time if the surface approaches a thermocouple. Nevertheless the field points extend in Fig. 3 into the amorphous phase and confirm in each of the thirteen tests the computed temperature profiles.

6.2. *Quasi-steady ablation*

For measurements of the quasi-steady ablation usually cylindrical samples are used with a plane front side which is exposed to the plasma-arc jet. The length of the cylinder is great enough to ensure quasi-steady ablation. With the exception of the edge the heat and mass transfer can be assumed to be one-dimensional.

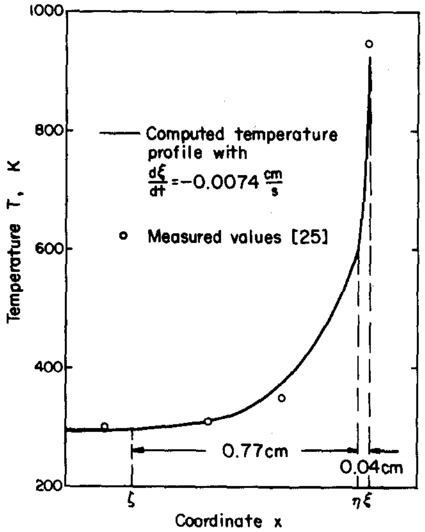

FIG. 7. Temperature profile and thickness of the two layers at quasi-steady ablation (the computation was performed with a heat flux q_ξ that yields the same ablation velocity as in the experiment).

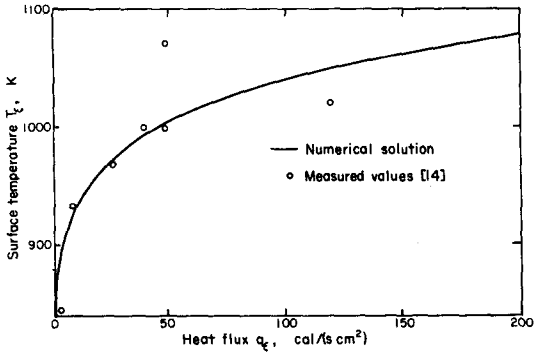

FIG. 8. Dependence of the surface temperature on the heat flux: comparison of the computation with measured values ($T_k = 293\,K$).

Kindler [25] made four bore holes near the axis of the cylinder normal to the front side in which thermocouples were located in different distances from the surface. The symbols in Fig. 7 show measured temperatures in the moment when the surface reached the first thermocouple. The curve representing the temperature distribution is computed for a heat flux q_ξ to the surface that yields the same ablation velocity as in the experiment. The initial temperature of the sample is in the test and in the calculation 293 K. The difference between measured and calculated surface temperature amounts to 6%.

In quasi-steady ablation the surface temperature and all other variables only depend on the initial temperature of the layer and on the heat flux to the surface. In Fig. 8 the surface temperature is plotted as a function of the heat flux q_ξ for an initial temperature $T_k = 293\,K$. The calculated curve is in good agreement with the measured values quoted by Newman [14]. A comparison of the heat of ablation $q_0/\dot{m}$ with measured values has been represented in [26].

7. SUMMARY

Investigations of the high-temperature behaviour of PTFE were taken as a basis for an analytical model of the transient ablation of PTFE-layers. The resulting system of differential equations was numerically solved. The results of computations were compared with ablation measurements in arc-jet facilities for transient ablation and the limiting case of quasi-steady ablation. Computed temperature profiles showed good agreement with measured distributions.

Consequently a set of equations is at disposal, which makes the calculation of ablative PTFE-layers possible. It can be solved also simultaneously with boundary-layer equations because of the interaction between the ablation layer and the high-temperature environment.

Acknowledgement—The author would like to express his appreciation and gratitude to Prof. Dr.-Ing. K. Stephan for his support and encouragement.

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UN MODELE ANALYTIQUE DE L'ABLATION TRANSITOIRE DE COUCHES DE POLYTETRAFLUORETHYLENE

Résumé—On analyse des expériences de pyrolyse avec le polytétrafluoréthylène (PTFE) dans un volume clos, avec des couches de PTFE chauffées unilatéralement, pour étudier le mécanisme de dépolymérisation, les influences de la taille de l'éprouvette et des atmosphères gazeuses aussi bien que la composition des produits de la réaction. A partir de ces recherches sur le comportement du PTFE à haute température, on développe un modèle analytique pour l'ablation transitoire et monodimensionnelle. On tient compte de la transition de phase cristalline–amorphe, de la dilatation thermique et de la formation des produits à grosse molécule sur la surface. Des comparaisons entre les profils de température calculés et les valeurs mesurées dans un jet de plasma confirment le modèle pour l'ablation transitoire et le cas limite de l'ablation quasi-stationnaire.

EIN ANALYTISCHES MODELL DER INSTATIONÄREN ABLATION VON POLYTETRAFLUORÄTHYLEN-SCHICHTEN

Zusammenfassung—Auswertungen von Pyrolyseversuchen mit Polytetrafluoräthylen (PTFE) in einem geschlossenen Volum, die den Depolymerisationsmechanismus, den Einfluß von Probendicke und unterschiedlicher Gasatmosphäre und die Zusammensetzung der Ablationsprodukte untersuchen, werden auf einseitig beheizte PTFE-Schichten übertragen. Aufgrund dieses Verhaltens bei hohen Temperaturen wird ein analytisches Modell für die instationäre eindimensionale Ablation von PTFE-Schichten entworfen. Es berücksichtigt den kristallin–amorphen Phasenübergang, die thermische Ausdehnung und die Bildung höhermolekularer Produkte an der Oberfläche. Ein Vergleich berechneter Temperaturprofile mit Meßwerten aus Ablationsversuchen im Plasmakanal bestätigt das Modell bei instationärer Ablation und im Grenzfall quasistationärer Ablation.

АНАЛИТИЧЕСКАЯ МОДЕЛЬ НЕСТАЦИОНАРНОГО ПРОЦЕССА АБЛЯЦИИ СЛОЕВ ФТОРОПЛАСТА

Аннотация — Выполнен анализ результатов экспериментального исследования пиролиза фторопласта в замкнутом объёме, проведенного с целью изучения механизма деполимеризации, влияния размера образца и различных газовых сред, а также состава продуктов реакции при одностороннем нагреве слоев фторопласта. На основании этих исследований при высоких температурах предложена одномерная аналитическая модель нестационарного процесса абляции слоев фторопласта. В модели учитываются переход кристаллической фазы в аморфную, тепловое расширение и образование высокомолекулярных продуктов на поверхности. Сравнение рассчитанных температурных профилей с измеренными в плазмоструйных генераторах подтвердило справедливость модели нестационарного и предельного случая квазистационарного процесса абляции.