Formulation of the Surface Ablation of a Silica-Nylon-Phenol Material

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Nomenclature

K	= permeability
K_0	= oxygen concentration
M	= mean molecular mass of pyrolysis gases
R	= ideal gas constant
T	= wall temperature
T_R	= fictional temperature corresponding to "embrittling" and "sublimation" activation energy
T_{ox}	= fictional temperature corresponding to oxidizing activation energy
a	= $6 \times d/l$
d	= height out of coke beam
p	= porosity
h, K, K', n	= coupling coefficients of various erosion factors
l	= thickness out of coke beam
$\dot{m}$	= gaseous mass flow (or equivalent)
p	= pressure
t	= time
x	= abscissa
α	= enthalpy transfer coefficient
β_1	= Munson formula coefficients
γ	= coke fiber and wall angle
η	= pressure gradient coefficient
ρ	= density
σ	= spallation stress
τ	= aerodynamic shear
ψ	= blocking factor

Subscripts

c, g, r	= thermochemical, pyrolysis, and thermomechanical mass flow
e	= external edge or boundary layer
0	= nonblocking condition
w	= at wall

Introduction

THIS Note presents a phenomenological expression of the mechanical erosion appearing concomitantly with thermochemical erosion in mass and energy transfer expressions at interface of boundary layer and of material being ablated. In the case of nylon-silica-phenol material (Orthostralon) this expression has been quantatively tested on Aerospatiale's (Sud Aviation) facilities (France). The results make it possible to determine the dimensions of a re-entry heat shield made of this material.

These temperature distribution calculations derive from an ablation computation model, which, at the material/boundary-layer interface, uses conditions of continuity with respect to the total mass flow of the solid constituent which has been transformed into the gaseous state or mechanically, eroded and conservation of energy at the wall, which gives the equation for the convection flux entering the material. The total mass flow comprises mass flows corresponding to three forms of decay of the solid: 1) $\dot{m}_g$ from pyrolytic decomposition and depthwise cracking, calculated as a function of the derivative of the fraction gasified depthwise

$$\dot{m}_g = \int_0^x (d\rho/dt)dx \qquad (1)$$

2) $\dot{m}_r$ from mechanical surface erosion, and 3) $\dot{m}_c$ from thermochemical surface erosion. This Note is concerned with the different ways at writing $\dot{m}_r$ and $\dot{m}_c$ adopted, by order of increasing complexity, for the ablation computation models used in France.

Previous research works conducted in USA have established the dependence of ablation rate not only in relation with the thermal flux or convection coefficient but also with environmental conditions such as pressure (Schneider's, Swann's Scala's work) and aerodynamic shear (Mathieu's, Bishop's, Schneider's work). However, no attempt was thoroughly conducted for an analytic expression of mechanical erosion in relation with these two parameters, mainly because of the discrete and cyclic features of mechanical erosion. In the case of our materials, the fibers revealed that small scales were torn off by mechanical erosion. The mechanical erosion phenomenon may be considered as continuous and resulting in an analytic expression assuming its rate is proportional to spallation stress.

Simplified Model for a Silica-Rich Material

This model deals with Stefan's problem by assuming that the wall temperature during ablation is a constant; it gives good results for materials very rich in silica (Orthostrasil). Some authors[1] have related this phenomenon of relatively constant temperature to the fact that since the vapor pressure is a very steep function of the temperature, the wall temperature is very close to the temperature corresponding to the saturation vapor pressure. In fact, since it would appear that there is very little vaporization of the melted silica which our films show streaming over the surface, this is more likely to be a temperature imposed by the silica-carbon reactions as a whole, which it is proposed to schematize as follows for the temperature and pressure conditions at the material's surface:

$$SiO_2 + C \rightarrow SiO \nearrow + CO \nearrow \qquad (2)$$
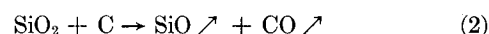
The SiO_2 and C equilibrium with a gaseous phase studied by Poch and Dietzel[2] shows that partial pressures of SiO and CO of the order of 1 atm correspond to equilibrium temperatures of 2250°K, close to those actually noted. This remains approximately true over a pressure range from 0.1 to 10 atm.

In the case of Orthostrasil, the char is almost stoichiometrically proportional to the silica in accordance with reaction (2), and is furthermore protected by a thick coat of melted silica against oxidation by the atmosphere. The process in which reaction (2) predominates is not affected, and surface temperature variations are reduced, the surface condition being $T_p = T_{abl}$.

Materials Less Rich in Silica: Orthostralon

In the case of Orthostralon, the layer of residual carbon is no longer protected by a thick coat of silica; furthermore, the coke produced has a certain natural strength depending on its mechanical properties, which means that its erosion does not depend solely on the progress of the silica-carbon reaction, hence on the kinetics of this reaction. Neglecting the mechanical erosion, Munson and Spindler[3] have nevertheless adopted the thermochemical erosion condition with the following semiempirical kinetics law:

$$\dot{m}_c = \beta_1 T \beta_2 e - \beta_3/T \qquad (3)$$

Dependency on three arbitrary coefficients (β_1, β_2, β_3) makes it possible to group together the kinetics of carbon attack by the silica and the environmental oxygen.

Now in the temperature zone under consideration, this oxidation by the atmosphere appears to be limited by the diffusion of the oxygen through the boundary layer rather than by the kinetics of this combustion. It seems therefore impossible to express a thermochemical recession law [analogous to Eq. (3)] without introducing the mission character-
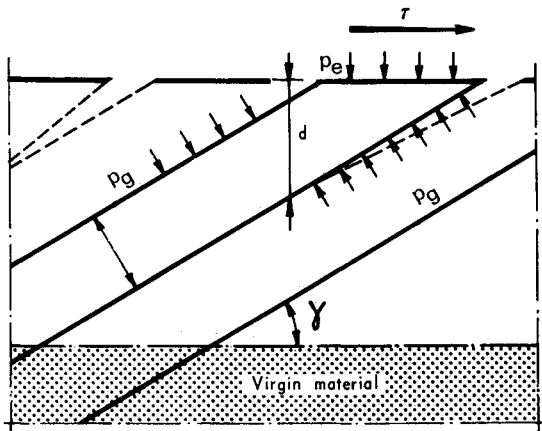
Fig. 1   Principal forces on fractured char (by Schneider, Dolton, and Reed[5]).

istics, if only by estimating the diffusion-oxygen input

$$\dot{m}_0 = \alpha_0 \quad \psi_0(K_{0e} - K_{0w}) \quad \alpha_0 = \alpha_0(t)$$

Though we may write a model in which the mass-energy coupling at the interface of the material and the environment is more elaborate, we are content at present with a rougher approximation. This pessimistic approximation consists in over-evaluating the thermochemical erosion: a) the silica-carbon reactions, limited by their kinetics, are discounted among the surface reactions, but are grouped with the kinetic reactions of pyrolysis and cracking and located depthwise to a slight extent; b) because the wall combustion reaction is really limited by the diffusion, there is no more oxygen at the wall; and c) the phenomena other than the silica-carbon reaction are transferred in full to the interface and the boundary layer, assumed to the frozen.

Taking into account the stoichiometry and the blocking factor ψ_0 and observing that a portion of the diffusing oxygen is absorbed by the pyrolysis gases combustion, one may write the approximate expression

$$\dot{m} = \dot{m}_r + \dot{m}_c = \dot{m}_r + (12/16)\alpha_0\psi_0 K_{0e} - \dot{m}gK_{0g} \quad (4)$$

where K_{0g} depends on the molar composition of the pyrolysis gases.

Determining the Mechanical Erosion Mass Flow $\dot{m}_r$

Mechanical erosion due to thermal stresses and aerodynamic shear seems to us to play an important and sometimes predominating role in the ablation of Orthostralon, as we found in particular with a number of experiments using small plates set at an angle to the plasma jet. The surplus carbon is eroded even underneath a viscous protecting silica material which, when it exists, could transmit the environmental stresses.

Thermal stresses cause limited fracturing, visible after heating on certain films, with a spontaneous return to equi-

librium. However this stable network of thermal fractures plays a part by offering a hold to the mechanical agents in the environment, pressure gradients and shear. Lacking at present sufficient data on the mechanical properties of cokes, we do not compute this network but nevertheless allow for embrittling of the material under heat, in a temperature-wise exponential form $e - T_R/T$, where $T_R = E_R/R$. The mass flow is assumed to bear a linear relationship ($\dot{m}_r = a\tau + b$, where a and b are constants), as shown by data in Ref. 4.

More precisely, the procedure is based on the generalized calculation for an inserted coke beam given by Schneider and Dolton,[5] who write it as a function of the angle γ of the coke fiber to the aerodynamic flow of p_e the external environmental pressure and of p_g the mean pressure of the pyrolysis gases on the faces of a beam of thickness l left clear over a height d (Fig. 1).

The strength calculations give an extraction stress σ_r as a function of the fiber's dimensionless parameter $a_0 = \sigma d/l$ and the porosity $f =$

$$\sigma_r = (a_0/\sin\gamma)[\tau(fp_g - p_e)/\tan\gamma] + \tau/\tan\gamma - p_e \quad (5)$$

We carry the calculations farther than Schneider by writing the mean pressure $p_g(p_g \neq p_e)$ at half-depth $d/2$, according to Darcy's law, as a function of the permeability K

$$p_g = p_e + \frac{d}{2} \cdot \frac{dp_g}{dx} \neq p_e + \frac{d}{2} \cdot \frac{1}{p_e} \cdot \frac{R\bar{T}}{\bar{M}K}\dot{m}g \quad (6)$$

Whence

$$\sigma_r = \tau\frac{1}{\sin\gamma}(a_0 + \cos\gamma) + p_e\left[\frac{a_0\cos\gamma}{\sin^2\gamma}(1 - f) - 1\right] - \frac{1}{p_e}\left(f\frac{a_0\cos\gamma}{\sin^2\gamma}\frac{d}{2}\frac{R\bar{T}}{\bar{M}K}\dot{m}_g\right) \quad (7)$$

We may estimate that $\dot{m}_r$ remains proportional to σ_r, and we shall make allowance for the role, on a melted silica surface, of the longitudinal pressure gradient dp/ds by taking[6] into account $\tau' = \tau + \eta\ dp/ds$.

We may then proceed to a theoretical approximation of $\dot{m}_r$ by introducing $e - T_R/T$ as a multiplying factor:

$$\dot{m}_r = he^{-T_R/T}[\eta dp/ds + \tau(1 + l\tau + ..) + Kp_e(1 + K'p_e + ..) - n\dot{m}_g/p_e] \quad (8)$$

Although the expansions in terms of τ and p_e go beyond the theoretical formulation established previously, they enable us to set up a phenomenological representation with the help of the tests performed with plasmajets. Indeed all the preceding theoretical demonstrations have been given for indicative purposes only, and the correlations between $\dot{m}_r$ T, τ, p_e are the result of the experiments enabling us to determine the necessary parameters h, η, l, K, K', n.

Theoretical Approach to the Surface Law

Before the results of the coupled schematic[7,8] can be used, we must content ourselves with a phenomenological law of the

Table 1   Experimental data for 14 plasmajet tests at 1500 kw and comparison of measured and calculated [from Eq. (12)] $\dot{m}$

Atmosphere	Air	Air	Air	Air	Air	Air	Air	Air	Air	N_2	N_2	N_2	Air	Air
Geometry[a]	T	T	T	T	P	P	P	P	T	T	T	T	S	S
p_e, g/cm²	700	900	1170	3700	1800	800	2100	1900	1480	850	1800	1150	5000	5000
α, g/m²-sec	440	590	570	510	1220	1060	1270	1920	630	520	1300	710	2130	1780
													0	0
τ, 10^{-2}g/cm²	530	900	965	220	970	1840	1615	1965	955	600	1040	750	Stagnation	
Φe, 10^3w/m²	1560	4000	4750	3600	4400	6600	9900	8700	4150	940	2260	1350	8150	10000
T, °K	1900	2150	2275	2300	1900	1850	2400	2325	2325	1680	1850	1770	2250	2350
$\dot{m}_{exp}$, g/m²-sec	50	95	135	175	95	73	550	450	265	0	0	0	400	600
$\dot{m}_{calc}$, g/m²-sec	49	97	139	175	101	55	549	387	197	≪1	≪1	≪1	384	476
Error, %	−2	2	3	0	7	−25	−0.2	−14	−26	—	—	—	−4	−21

[a] P = plate, T = square tube, S = blunt body (stagnation point).

following form for the surface recession:

$$\dot{m} = a.\alpha_0.f(D)[1 - \beta(\dot{m}_g + \dot{m}_c)/\alpha_0] - \dot{m}_g K_{0g} +$$
$$he^{-T_R/T}[\eta dp/ds + \psi_1 \tau(1 + l\psi_2 \tau + ..) +$$
$$Kp_e(1 + K'p_e + ..) - n\dot{m}_g/p_e] \quad (9)$$

For the sets of measurements concerning relatively low wall temperature, where combustion is limited by the kinetic reaction rather than by the diffusion reaction, these sets agree with the other provided that values assumed for the following parameter are appropriate:

D = kinetic recession rate/diffusion recession rate =

$$\tfrac{4}{3}K_v p_e^{1/2} e^{-T_{ox}/T} K_{0e}^{1/2}/\alpha_0 \psi K_{0e}$$

or

$$D = K_1(p_e^{1/2}/\alpha_0)e^{-T_{ox}/T} \quad (10)$$

and we introduce in Eq. (8) following Scala[9] and Medford[4]

$$f(D) = (D/2)[(D^2 + 4)^{1/2} - D] \quad (11)$$

and ψ_1 as a blocking factor for τ.

The test runs enabling the various parameters of Eq. (8) to be determined—a phenomenological determination being alone possible—were under way at Aerospatiale Oct. 15, 1970. The initial results are submitted in the following paragraph.

Experimental Results

We have so far conducted simulations in a 1500-kw plasma-jet facility. They provided sets of values to τ, p_e, α, that stem directly from experimental measurements, except for τ, which is calculated.

These initial experimental results are compared, in Table 1, with theoretical results obtained with a simplified form of Eq. (9) as follows:

$$\dot{m}_{calc} = \rho s = a\,\alpha\,(D/2)[(D^2 + 4)^{1/2} - D] +$$
$$he^{-T_R/T}(\tau + Kp_e) \quad (12)$$

Relation (12) is deduced from Eq. (9) by assuming $\eta = 0$, $l = 0$, $n = 0$, and $K_{0g} = 0$. We next determine by a least-squares method

$$a = 0.1516, \; h = 9.318\ 10^{11}\ (1/sec), \; K = 5.461\ 10^{-3}$$

$$T_R = 60000°K, \; T_{ox} = 27500°K; \; K_1 = 4500$$

The differences of $\dot{m}_{calc}$ from the measured $\dot{m}_{exp}$ are satisfactorily small. As a matter of fact, the mean error is $\sim 10\%$, and it may be considered that calculation of ablation rate to within 20% is satisfactory.

In conclusion, for over-all erosion rate calculation (mechanical + thermochemical), good results, in relation with local environmental conditions, are obtained from a simple phenomenological expression. In this expression, the thermochemical coupling with the boundary layer is a close approximation, but can be entirely calculated in diffusion state, thereby allowing a direct determination of mechanical erosion. The results are already satisfactory and can be easily improved, especially if the pressure longitudinal gradient is taken into account.

References

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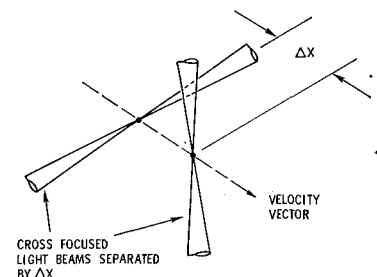# Optical Technique for the Measurement of Local Velocities in Single- and Two-Phase Flowfields

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IN dense two-phase flowfields, neither Pitot-tube nor hot-wire probes work with any degree of success. For local particle velocity measurements, streak and high-speed-framing photography have been used, but the data reduction is laborious and often subject to reading errors. This Note presents a crossed-beam optical technique that has been used to measure local gas velocities in a gaseous N_2 freejet and local droplet velocities in a dense gas/liquid sprayfield. For the latter, a gas/liquid rocket-motor injector element was used with water and N_2 as nonreactive propellant simulants. Local liquid/gas mass flow ratios up to ~ 10 and droplet number densities up to $\sim 10^9/ft^3$ were employed.

Approach and Apparatus

Two reference points in the flowfield are provided by two focused beams spaced ΔX (~ 0.1 in.) apart (Fig. 1). The intensity fluctuations of the focused light beams are monitored by two photodetectors (Fig. 2), and local values of velocity

Fig. 1 Perspective drawing of crossed focused beams.