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Transient Thermal Protection of Film Covering Circular Aperture by Sublimation and Weak Decomposition

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Abstract

Unwanted heating of sensitive surfaces in harsh thermal environments can be prevented by precise application of sacrificial materials such as sublimation layers and pyrolyzing films. The use of sublimation for the protection of circular polyimide membranes subjected to brief (~100 msec) heating by infrared radiation and hot (6000 K) inert gas convection is analyzed. Selection of sublimation material and sublimation layer and membrane thickness is considered with emphasis on providing sufficient thermal protection yet negligible unwanted material remaining at the end of a specified heating period. Though the analysis here is general, the motivation is protection of the polyimide films covering the laser entrance holes on IFE (inertial fusion energy) hohlraums being injected into the hot gas (xenon) protecting IFE reactor chambers. Both one and two dimensional thermal models are used to develop a robust thermal concept. Sensitivity analyses (SA) methods are exercised to show where the design may be vulnerable and which input parameters have the greatest effect on performance and likelihood of success. For the design and conditions considered, methane sublimating layers are probably preferred over xenon or pentane.

Keywords: Sublimation; Heat Transfer; Sensitivity Analysis; Variance Decomposition; Latin Hypercube

1. Introduction

Unwanted heating of sensitive surfaces in harsh thermal environments is observed at the ends of high power lasers, on the front of planetary probes on reentry, on the interior of viewports in plasma coating vessels and in numerous other applications. In an IFE application, polyimide membrane is used for the laser entrance hole (LEH) window positioned at the leading and trailing surfaces of an inertial fusion confinement target shown in Figure 1 [1]. The target is designed to be injected into a fusion chamber containing hot, low pressure xenon gas (6000K, 23 torr). In addition to the convective heating from the gas, there is an additional radiative heat load from the 900 K fusion chamber wall. The target is filled with helium gas at a density of about 1 mg/cc and at a temperature of about 18 K which cools the inner surface of the polyimide membrane. Successful fusion implosion requires that the DT in the capsule at the center of the target remain in solid form and that, in fact, the temperature of this solid remain within about 0.1

K of the design temperature. It is therefore critical that the LEH window remain intact and not permit hot gases to contact the inner capsule. For this and other applications, transient one-time use or transient periodic protection techniques are sometimes preferable. Forced convection cooling and abbreviated operation can be the transient thermal protection system at high power laser windows. Pyrolysis, blowing into the boundary layer and charring of the substrate is often the protection mode for the extreme surface heating on earth reentry. In other systems no protection method may be used and viewports or other hardware may be periodically discarded and replaced. Alternatively, precise knowledge of heating conditions and duration can permit precise application of sacrificial materials such as sublimation layers and pyrolyzing materials for transient applications in some technologies.

Figure 1. The sketch of an inertial fusion confinement target

Analysis of earth reentry dating to the 1950's includes many of the relevant phenomena for a consideration of protection of optical and other films built into terrestrial applications such as laser windows and viewports. Milos *et. al.* [2] have reviewed surface heating, ablation, pyrolysis and charring effects as applied to space applications. Additional work on pyrolysis and on the breakdown of polyimide and other membranes is applicable to both space and terrestrial systems requiring transient protection [3-6]. Sublimation is a special case within surface chemical effects with the capability of protecting a wide range of surfaces with minimal impact on other aspects

of device performance. Sublimation of carbon [7] and several other materials [8,9] may be well understood under many conditions but the influence of non-sublimating and non-condensing cover gases on the sublimation rate of the protective sublimating layer is not clear [10-12]. In some cases cover gases can suppress sublimation and in others they can enhance it. Here, we analyze the use of sublimation for the protection of circular polyimide membranes subjected to brief (~100 msec) heating by infrared radiation and hot (6000 K) inert gas convection. Selection of sublimation material and sublimation layer and membrane thickness is considered with emphasis on providing sufficient thermal protection yet negligible unwanted material remaining at the end of a specified heating period.

2. Theory

Mass and energy balances applied to a sublimating and decomposing substrate were given in detail in Refs. 2, 13, and 14. For mass balance on a control volume of infinitesimal thickness with top edge coincident with a sublimating surface we have:

$$\dot{m}_{ab} + \dot{m}_{dec,top} = \dot{m}_{und} + \dot{m}_{dec,bot} . \quad (1)$$

Leaving the control volume on the fluid side are ablative (sublimative) and pyrolysis (decomposition) gas terms. Entering the control volume from the opposite side are the pyrolysis gas and solid material (which enters if the control volume is receding into the solid to stay centered on the sublimating surface).

Operative energy flows on a differential volume including the film covering the aperture and underlying sacrificial layer are shown in Figure 2.

Figure 2. Energy flows for control volume of infinitesimal thickness with top edge coincident with the sublimating surface

The steady state energy balance equation for the infinitesimal thickness volume at the top edge coincident with the sublimating surface can be written:

$$\dot{q}_{flcondn} + \dot{q}_{diff} + \dot{q}_{incradn} = \dot{q}_{solcondn} + \dot{q}_{refradn} + \dot{q}_{emitrdn} + \dot{q}_{pyrol} + \dot{q}_{ab} . \quad (2)$$

Terms on the left indicate heat input to the control volume from the fluid side. The first two terms, the heat conduction ($\dot{q}_{flcondn}$) and mass diffusion contributions ($\dot{q}_{diff}$), can be supplied by a computational fluid dynamics (CFD) solution. Here the coupling to a CFD solution is not done. We posit a pure stream of hot inert gas flowing past the assembly at high speed and a convective heat transfer correlation is applied. The third term on the left ($\dot{q}_{incradn}$) is the incident radiation from the fluid side. On the right hand side are terms for the heat conducted into the interior of the solid ($\dot{q}_{solcondn}$), reflected radiation ($\dot{q}_{refradn}$), emitted radiation ($\dot{q}_{emitrdn}$), the net flux of pyrolysis gas out of the control volume ($\dot{q}_{pyrol}$) and the enthalpy due to formation and ejection of ablated species ($\dot{q}_{ab}$). The pyrolysis gas term includes both the enthalpy of the material ejected to the flow field from the control volume and the enthalpy of the underside material moving into the control volume. In this work we consider applications where decomposition does not proceed as far as pyrolysis gas generation but we note its potentially significant cooling effects. For some applications we note that a small amount of pyrolysis is probably tolerable and beneficial and thus ignoring these effects here will be making the proposed protection analysis conservative or possessing more margin of safety than actually represented here. A net surface chemical reaction (sublimation) rate, r_q , then determines the ablative heating term, $\dot{q}_{ab}$:

$$\dot{q}_{ab} = \frac{1}{N_o} \sum_{s=1}^{nspec} M_s h_{f,s} \sum_{q=1}^Q D_{s,q} r_q \quad (3)$$

The net reaction rate for species r is r_q , N_o is Avogadro's number, M is molecular weight, h is enthalpy and $D_{s,q}$ is the stoichiometry matrix for the operative chemical kinetic mechanism.

For sublimation of, for example xenon, into a xenon gas stream the net reaction rate, r_q , will depend on the surface temperature and the local xenon gas stream pressure. For an external gas stream composed solely of the sublimating material, we expect the net reaction rate to be the difference between the sublimation rate and the condensation rate. In this work we present xenon sublimating into xenon as an example of this condition. We also consider two alkanes,

methane and pentane, sublimating into pure xenon. While ignoring cover gas effects, we expect there to be a negligible condensation rate and the net reaction rate to be the sublimation rate computed from the vapor pressure dictated by the solid surface temperature. For sublimation of methane into pure xenon, the net methane sublimation rate will depend on local surface temperature and the inert gas pressure for cases where we posit that the xenon “cover” gas will have some sublimation suppression effect despite the fact that it is not the same species as the sublimating layer. Sublimation without cover gas suppression is treated in a generalized version of the surface chemistry formulation given in Zhukhtov and Abe [15] that was derived in Ref. 16:

$$r_q = k_{fq} \prod_{w=1}^W [PX_{qw}]^{\nu_{qw}} \prod_{l=1}^L \theta_l^{\eta_{ql}} - k_{rq} \prod_{w=1}^W [PX_{qw}]^{\mu_{qw}} \prod_{l=1}^L \theta_l^{\lambda_{ql}} . \quad (4)$$

The two terms on the right give the rates that reaction q goes forward and backward, respectively. Just as with homogeneous chemical kinetics, the rate reactions run forward depends on stoichiometry and availability of reactants, and the rate reactions run backward depends on stoichiometry and availability of products. Here, there are two product terms for each of the right hand side terms because the fluid species and the surface species are tracked separately. The forward and backward reaction rate constants, k_{fq} and k_{rq} , are specified from a combination of theory and experiments.

Langmuir’s result [17] for the sublimation rate of metals fits into this formulation:

$$\dot{m}_{sub} = \frac{P_{vap}}{\sqrt{2\pi RT/M}} . \quad (5)$$

The vapor pressure (as a function of temperature) determines the forward reaction rate in equation (4) above and, when the cover gas is xenon, its pressure determines the backward reaction rate. For the three materials of interest here the dependence of vapor pressure on temperature is well fit by the Antoine equation (in the relevant temperature ranges):

$$\log_{10}(P_{vap}) = \left(C_1 - \frac{C_2}{T_w + C_3} \right) . \quad (6)$$

This form is implemented here both in the general chemical treatment (equation (4)) and in a simple subroutine with the sublimation rate multiplied by a suppression term dependent on cover gas pressure. The three materials are compared in Figure 3. Methane has the dual advantages of

higher sublimation rates for the low temperatures of interest and for the cover gas pressure of interest it has the lowest phase change temperature, Figure 4.

Figure 3. Comparison of sublimation pressures for the three materials of interest

Figure 4. Phase diagram for methane [18]

We have used the data in Davy and Somorhai [10] to construct a curve fit for the dependence of suppression on cover gas pressure:

$$SupprFn = D_1 P_{cov}^3 + D_2 P_{cov}^2 + D_3 P_{cov} + D_4 . \quad (7)$$

The cubic form facilitates imposing no suppression at vacuum (suppression function value of 1) and an asymptote for suppression at some selected cover gas pressure. We have not implemented a model for the dependence of suppression (or enhancement) of sublimation on cover gas temperature. Gas phase collisions between sublimated atoms and cover gas atoms would increase with temperature and lead to increased condensation of sublimated atoms but collisions between high temperature cover gas atoms and surface atoms may increase apparent sublimation rate by sputtering surface atoms into the gas stream.

Nominal parameters of interest are shown in Table 1. The volume, thickness and mass required columns were obtained by ignoring transient conduction and other effects and computing the material required for the latent heat of sublimation to equal the convective heating by the hot inert cover gas.

Chemical decomposition and degradation in strength of polyimide films after full loss of sublimating material can be a failure mode. Here we consider only the early phases of decomposition as a design choice to ensure survival. For substrate temperatures below about 850 K decomposition of polyimide is relatively slow and the fraction of mass reacted for the time scales of interest here is well below 10% [19,20]. Lua and Su [20] compared several analytical modeling methods and although none was exceptional over the full possible range of reacted fraction, the method of Coats and Redfern [21] only slightly over-predicted reacted mass out to 10% reacted. Hatori *et. al.* [19] and Burger *et. al.* [22] show that for this early phase of decomposition the products of decomposition are well approximated as half CO and half CO₂. The Coats and Redfern model with this CO/CO₂ product split is used here to represent polyimide performance in the transient protection assembly:

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[\left(\frac{AR}{\beta E} \right) \left(1 - \frac{2RT'}{E} \right) \right] - \frac{E}{RT} \quad (8)$$

where α is the mass conversion fraction, the activation energy E is 177 kJ/mol., the pre-exponential factor A is 4.38e+9 and n is 1.63. Here we use $\beta=10$ K/min and $T'=848$ K in the absence of more rapid sample heating data. This model assesses the degree of decomposition of all polyimide substrate elements in the computation. Degree of reaction for each discretized

portion of the film and substrate is computed as it heats so that degrees of reaction greater than 10% can be identified and the design revised.

For each time step of a thermal calculation using a surface chemical model, there is a system of ordinary differential equations to be solved for every sublimating facet. A fast and stable solver (DVODE [23]) is used to obtain the local reaction rates, which then give the local heat load to the solid. Thus at each time step, the conduction equation is repeatedly solved until the temperature dependent heat load converges. Rate systems similarly coupled are given in [15,16]. For a film environment composed of low pressure noble gas we expect sublimation to be the only significant surface reaction.

material (-)	molecular weight (kg/mol)	melting Temperature at 1. atm. (K)	boiling Temperature at 1. atm. (K)	thickness required (m)	sublimation or evaporation temperature (K)	vapor pressure at phase change temperature (Pa)	10^{C_1} in Antoine vapor pressure fit equation (pa)	C_2 in Antoine vapor pressure fit equation (K)	C_3 in Antoine vapor pressure fit equation (K)	enthalpy of sublimation (J/kg)
xenon	131.3	161	165	20.e-6	125	1800	6.41E+03	577.661	-13	1.14E+05
pentane	72	143	309	10.e-6	243	6560	9.75E+03	1070.617	-40.454	5.83E+05
methane	16	90	112	31.e-6	73	277	9.76E+03	443.028	-0.49	6.06E+05

Table 1. Key parameters for a sublimating surface protection layer

3. Boundary Conditions and Initial Conditions

Convective heating by a hot inert gas stream is approximated with a correlation for Nusselt number [24,25]:

$$Nu \propto Re^{0.5} Pr^{0.4} . \quad (9)$$

For xenon at 6000 K and 0.8 kg/m³ moving past the film at 250 m/s, we expect the convective heating coefficient to be as high as 55 W/(m²K). For convection on the cold side of the substrate we set h=5 W/(m²K). and T_∞ = 20 K. We also assume the cold side radiation is exchanged with a sink at 20 K while on the exterior the exchange is with a sink at 900 K. We assume the assembly is initially uniform in temperature at 20 K. Sinks are given emissivity 1.0 and the film and substrate assembly surfaces are given emissivity 0.3. For simplicity we specify that rather than accumulating in front of the film all sublimated material is rapidly convected downstream.

A sublimating layer of initially uniform thickness is analyzed here though appropriately non-uniform layers may be preferred, e.g. lower thickness near the outer film edges may be preferable because lower rates of sublimation may be experienced there. A liquid methane film might be applied to the surface at about 100 K as the target is cooled to about 20 K and rotated if

necessary for higher thickness uniformity. The wettability of the methane or other material to the polyimide should be investigated and surface treatments applied if necessary.

4. Aspects of the numerical analysis

The finite element method is convenient for coupling the chemical effects, solid conduction and the nonlinear boundary conditions. TOPAZ3D [26] has been modified to treat the chemistry while simultaneously receding the sublimating surface toward its interface with the underlying polyimide membrane. The surface recession is determined by the time step size, and density and mass flux of the sublimating material. Results shown below were obtained from surface recession computations done with either of two approaches. In the first approach, most of the mesh is stationary and only the sublimating surface recedes toward the substrate. As an individual finite element brick is consumed by sublimation, it is effectively removed from the calculation and then sublimation resumes at the outer surface of the underlying brick. Recession at finite element nodes which are included in more than one sublimating facet is determined by simple averaging. The second approach accommodating the moving sublimation surface is best explained with the transient one dimensional conduction equation:

$$\rho C_p \left[\frac{\partial T}{\partial t} + \frac{\zeta}{a-s} \frac{ds}{dt} \frac{\partial T}{\partial \zeta} \right] = \frac{1}{(a-s)^2} \frac{\partial}{\partial \zeta} \left(k \frac{\partial T}{\partial \zeta} \right). \quad (10)$$

The spatial coordinate has been transformed to move along with the sublimating surface (Blackwell [27]) and this gives rise to an advection like term on the left hand side and a multiplier term on the right hand side. Strictly speaking, these terms should be assembled in the finite element computation if the mesh within the sublimating material is to adjust time step by step as the surface recedes. Further, the behaviour as the magnitude of the recession (s), approaches the sublimating layer thickness (a), may be difficult numerically. In this work we ignore the mesh motion term on the left hand side of the governing equation because its magnitude is relatively small and we do not use the mesh motion approach results as the sublimating material is exhausted (as s goes to a). We use the first method results for calculations through the point where all material is sublimated and we compare the two methods for several cases as a method of assessing some errors. In the second approach, the motion of the mesh internal to the sublimating mass is relocated every time step by solving the elastic deformation equations [28]:

$$I\ddot{\mathbf{u}} + F^{int}(\mathbf{u}, \dot{\mathbf{u}}, T) = \Gamma(\mathbf{u}, b, t, T) \quad (11)$$

in which b , t , and T represent, respectively, the body force, time step, and temperature. Updates to nodal positions $\mathbf{u}$ are done with rubber like mechanical properties imposed on the sublimating material:

$$Y_{ij}u_j = g_i \quad (12)$$

with the boundary condition that the interface to the membrane is stationary and the sublimating surface moves the amount defined by mass transfer. This is simpler and less general than an arbitrary lagrangian-eulerian treatment but given the slow rates of surface recession the errors due to moving the mesh and correcting local temperatures are small.

5. Results

For no sublimation or phase change during exposure to a nominally severe environment external to the assembly the surface temperature rises rapidly until radiation loss terms become large enough to balance the convective heating (Figure 2). A simple estimate of the heating reduction due to phase change (ignoring sublimation and surface recession) models the material applied to the polyimide window as able to absorb a defined amount of latent heat before heating toward the same convective to radiative balance. This result is shown as the red line in Figure 5.

Figure 5. Comparison of temperature histories for substrate and surface protection

The fully sublimating and receding simulation is computationally much more intensive but largely similar to the simple phase change case. Here the thickness of the initial sublimating layer was arbitrarily selected for a ~40 millisecond thermal exposure time.

Figure 6 contrasts the two methods for computing the transient temperature and solid surface position during sublimation. In the purple curve most of the mesh is fixed in space from time step to time step and only the surface nodes recede as material sublimates. This method, described above and referred to here as the fixed mesh method, periodically does this mesh definition revision based on a user defined minimum brick thickness. The difference between the remesh result, green curve, and the fixed mesh result is small compared to the margin to failure based on the decomposition behavior we impose to define survival. Figure 7 contrasts sublimating materials.

Figure 6. Comparison of temperature histories for remesh and fixed mesh computational method

Figure 7. Comparison of temperature histories for the three materials of interest

As expected from the phase diagrams for these materials, pentane sublimates at the highest temperature and methane the lowest. Methane is preferable from the standpoint of lowest heat transfer through the assembly toward the interior (while sublimating) but other factors such as ease of manufacture and unwanted residual effects may also be influential. Lowest sublimating temperature is also preferred because it provides the lowest starting point for the temperature rise which begins after all material has been sublimated.

Figure 8 compares the transient responses for three initial thicknesses of methane applied to the polyimide substrate. Rates of temperature rise after removal of all methane are similar for the three cases. Thicker layers last longer for two reasons; they have more latent heat to give up and they have more solid phase thermal inertia – material mass which slows the rise to temperatures at which sublimation becomes appreciable.

Figure 8. Comparison of temperature histories for three methane initial thicknesses

Figure 9. Comparison of temperature histories for five levels of sublimation suppression by cover gas

Figure 9 contrasts levels of cover gas suppression of sublimation. The five curves correspond to no suppression and the four different levels of suppression selected arbitrarily. As expected, the curves show modest and high levels of suppression of methane sublimation by xenon cover gas, but test data and/or molecular rate modeling is required to inform this area.

Figure 10 shows the finite element mesh for a cylindrically symmetric model of a film and substrate with a retaining shell on the perimeter.

Figure 10. Two dimensional finite element mesh of substate, sublimator and portion of mounting framework

The model only requires a small portion of the body holding the polyimide film because the film and methane have such lower thermal inertia than the body. For the model shown here there are 14 sublimating surfaces, five of which reside over the exterior shell. Of the nine inner sublimating surfaces, the most inboard begins at 74 % of the full assembly radius and the retaining shell begins at 91 % of the full assembly radius. Here our main concern will be non-uniformity of the sublimation and surface recession for the 8th to 12th radial positions of these 14 sublimating surfaces. In the work shown below the bricks under surfaces eleven, twelve, and thirteen will be successively removed in the simulations to show the effect of reduced thermal “sinking” between the polyimide and the retaining shell. Removal of this material results in adequate methane sublimation over the full assembly diameter. Figure 11 shows the transient vertical position history for five methane surface nodes across the top.

Figure 11. Transient position histories for nodes on top (sublimating) surface

For these studies the whole part starts with a 10 micron film of methane and the more inner surface nodes (positions 1 through 8 nearly equally) sublime the most and thus recede toward the zero position. The more outer radial nodes (positions 9 to 12) recede less and thus have a larger thickness of methane remaining at the end of the calculation. The residual methane may be a problem depending on the performance requirements for the assembly at the end of the transient heating pulse.

Many design changes could positively revise the residual methane distribution shown in Figure 11. Perhaps the simplest is to remove shell material at the inner radius of the shell-polyimide interface. The surface position time histories for the same five key nodes in this configuration are shown in Figure 12.

Figure 12. Transient position histories for nodes on top (sublimating) surface where a single underlying brick has been removed

Residual methane on the substrate perimeter is reduced but not fully eliminated. Figure 13 shows similar results but for three of these subsurface bricks removed from the calculation. Since only position 12 has significant residual methane, it is more likely that this design is practical. Similar measures or other design options can further improve on this result.

Figure 13. Transient position histories for nodes on top (sublimating) surface where three underlying bricks have been removed

6. Sensitivity Analysis

Sensitivity analysis (SA) as applied here studies the relative importance of various model inputs of varying uncertainty. Due to the complexity of the physics involving building the computational model, SA often can be used to examine the fidelity of the computational model.

Let the computational model response Y be a deterministic real-valued function of the d -dimensional variable $X = (x_1, x_2, \dots, x_d) \in \mathbb{R}^d$. Mathematically, this global sensitivity analysis is based on the following identity [29]: $V[Y] = E[V[Y|X]] + V[E[Y|X]]$. The term $V[E[Y|X]]$ is called the variance of the conditional expectation (VCE) which is a suitable measurement of the importance of X since it relates to how well $E[Y|X = x]$ mimics Y . The $E[V[Y|X]]$ term describes the error or residual term measuring the remaining variation in Y . In essence, one can apportion the variance of output Y to different sources of input uncertainties. As a consequence, one can quantify and rank the importance of input parameters [29-31] using first-order, second-order, and total sensitivity indices, by applying variance decomposition techniques on the results from forward uncertainty propagation.

One derives the decomposed total variance of output (V) as:

$$V = \sum_{i=1,2,\dots,n} V_i + \sum_{1 \leq i \leq j \leq n} V_{ij} + \sum_{1 \leq i \leq j \leq k \leq n} V_{ijk} + \dots \quad (13)$$

where $V_i = V[E[V|x_i]]$, $V_{ij} = V[E[V|x_i, x_j]]$. The sensitivity measures, defined by $S_{ijk\dots} = V_{ijk\dots}/V$, represent the percentage of total variance that can be explained with the combination of parameters, $x_i, x_j, x_k, \dots$. Therefore, S_i is the first order sensitivity index of parameter x_i . The second order sensitivity index, S_{ij} , quantifies the strength of interaction between parameters x_i and x_j . While the first order indices quantify the parameter sensitivity, one can also explore the curves of conditional expectation, $[Y|x_i]$, the so-called main effect plots, which can be treated as the first order partial derivative of Y with respect to x_i . To present the main effect plots of all parameters in a single figure, we scaled the parameters, $x = (x_1, x_2, \dots, x_d)$, to be ranged between $[-0.5, 0.5]$ and response Y so it has a zero mean and standard deviation of one.

Table 2. List of parameters and ranges

parameter	symbol	range
methane heat capacity	C_{P1}	[0.70,1.30]
methane thermal conductivity	K_1	[0.80,1.20]
polyimide heat capacity	C_{P2}	[0.80,1.20]

methane density	ρ	[0.90,1.10]
internal fluid heat transfer coefficient	h_{int}	[0.50,1.50]
internal fluid temperature	T_{int}	[0.50,1.50]
sublimation enthalpy	h_{sub}	[0.90,1.10]
Antoine constant 1	C_1	[0.80,1.20]
Antoine constant 2	C_2	[0.80,1.20]
Antoine constant 3	C_3	[0.80,1.20]

The 10 input parameters were varied in 1000 calculations using the maximin Latin Hypercube [32] design. We then compute the VCE, using these 1000 calculations, and then rank the importance of parameters.

Figure 14. Pie charts of first order indices (left) and main effect plots (right) of temperature of the polyimide exterior surface.

For SA applied to the one dimensional model of the sublimating layer (initial sublimating film thickness 32 microns), the output attribute (or quantity of interest) is the temperature (Kelvin) of the polyimide exterior surface at a specific time (0.075 second). From the first order (left diagram in Figure 14) indices, we find that methane density (ρ), sublimation enthalpy (h_{sub}), Antoine coefficient C_2 (equation (6)), and methane heat capacity (C_{p1}) are the leading parameters affecting the temperature.

Figure 14 also shows the main effect plots, which provides directional information regarding the parameter effect. The increase of methane density, heat capacity, and sublimation enthalpy will increase the thermal energy required to sublime, and hence the peak polyimide temperature

will decrease. The Antoine coefficient C_1 , in equation (6), promotes sublimation and hence the polyimide temperature increases when C_1 increases. On the other hand, Antoine coefficient C_2 suppresses sublimation. Notice that the VCE quantifies the variance of these curves over the parameter ranges. Therefore, the larger variation of the main effect curve ($E[Y|x_i]$), the larger the variance and hence larger the sensitivity index will be.

Using the one dimension model, we can predict the likelihood the polyimide temperature will rise above a specific temperature. Figure 15 shows the distribution of polyimide temperatures at time = 0.075 second. If we set the temperature threshold at 786 K, the likelihood of failure, at which the temperature rises above 786 K, is 15%.

Figure 15. Histogram of polyimide tempeature at time = 0.075 seconds

For the two dimensional model (initial sublimating film thickness 10 microns), the key output attribute is defined as the remaining methane thickness at the edge of the assembly at 0.0186 seconds. Figure 16 shows the first order indices for edge thickness at a specific time. Based on these, we conclude that methane density (ρ) and sublimation enthalpy (h_{sub}) are the two leading parameters affecting the edge methane thickness. This is consistent with results from the single dimension case. The methane heat capacity (C_{P1}) becomes the 4th influential parameter in the two dimension case. Parameter C_2 , becomes the third influential parameter.

Figure 16. Pie chart of first order (left) indices and main effect plots (right) of the edge thickness at specific time.

In a second scenario using the two dimensional model, we study the non-uniformity with the methane sublimation rate. We considered the edge methane thickness when the center methane thickness had been reduced to a threshold of 3% of original thickness. This leads to two output attributes: center methane sublimation time, with SA results shown in Figure 17, and edge methane sublimation thickness, with SA results shown in Figure 18. A strong correlation exists between the SA results of center methane sublimation temperature (Figure 17) and edge methane thickness at a specific timing (Figure 16) from the previous analysis.

Figure 17. Pie charts of first order indices (left) and main effect plots (right) of center sublimation timing

Figure 18. Pie charts of first order indices (left) and main effect plots (right) of edge thickness

Based on the main effect plot of edge thickness (shown on the right diagram of Figure 18) methane heat capacity will slow down the edge methane thickness reduction since a large heat capacity will help methane absorb more heat and hence suppress sublimation. Thermal conductivity increases the heat transfer from center to edge and hence enhances the edge methane sublimation.

7. Conclusions

Transient thermal protection can be accomplished with sublimating films. Thermal modeling can be used to specify design particulars, compare designs and to probe the sensitivity of various designs to uncertain material properties, use conditions or tolerance in fabricated parts. For single cycle use of initially cold parts being subjected to very harsh conditions, sublimation of methane, xenon or pentane layers may provide a highly reliable and low cost protection mechanism for films covering simple circular geometries.

Nomenclature

A	constant in decomposition expression
a	transformed frame item
b	body force
C	specific heat (joule/kgK)

C_1 to C_3	constants in Antoine equation
D	stoichiometry matrix (-)
D_1 to D_4	constants in suppression function
E	constant in decomposition expression
F	force term
g	load vector
h	enthalpy (joule/kg)
I	inertia matrix
k	reaction rate constant ($\#/m^2\text{sec}$)
L	number of surface species (-)
l	surface species index (-)
m	mass (kg)
$\dot{m}$	mass flux ($\text{kg}/m^2\text{sec}$)
M	molecular weight (kg/kmol)
Nu	nusselt number
N_o	avogadro's number ($\#/kmol$)
P	pressure (N/m^2)
Pr	Prandtl number
Q	number of surface reactions (-)
$\dot{q}$	heat flux ($\text{joule}/m^2\text{sec}$)
q	chemical species index (-)
Re	Reynolds number
R	universal gas constant ($\text{joule}/\text{kmolK}$) or ($\text{joule}/\text{gmolK}$)
r	net forward reaction rate ($\#/m^2\text{sec}$)
s	species index
s	surface recession
T	temperature (K)
u	displacement vector
W	number of gaseous species (-)
w	gaseous species index (-)
X	mole fraction of gaseous species (-)

Y	stiffness matrix
α	fraction reacted in decomposition expression
Γ	forcing functions
ρ	density
β	constant in decomposition expression
μ	stoichiometric coefficient of gaseous products (-)
ν	stoichiometric coefficient of gaseous reactants (-)
λ	stoichiometric coefficient of surface products (-)
η	stoichiometric coefficient of surface reactants (-)
κ	thermal conductivity
ζ	spatial coordinate in transformed frame
θ	surface species population fraction (-)
ε	emissivity (-)
ε	parameter in surface species reaction constant (-)

Subscripts

ab	ablation
bot	bottom side
cov	cover gas
dec	decomposition
diff	diffusion
emitradn	emitted radiation
f	forward
f	formation
flcondn	fluid conduction
incradn	incident radiation
n	constant in decomposition expression
nspec	number of species
p	pressure
pyrol	pyrolysis

q	reaction index
refradn	reflected radiation
s	species index
solcondn	solid conduction
sub	sublimation
top	top side
T	temperature
und	underside
vap	vapor
w	wall

Superscripts

o	formation
dot	rate

Acknowledgements

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References

1. Miles, R., Chang, A., Fornasiero, F., Havstad, M., Kucheyev, S., Leblanc, M., Rosso, P., Schebler, G., "Thermal and Structural Issues of Target Injection into a Laser-Driven Inertial Fusion Energy Chamber", *Fusion Science and Technology*, 66 (2014) 343-348.
2. Milos, F.S. and Rassky, D.J., "Review of Numerical Procedures for Computational Surface Thermochemistry," *Journal of Thermophysics and Heat Transfer*, Vol. 8, No. 1, 1994, pp. 24-34.
3. Sazanov, Y.N. and Shibaev, L.A., "High temperature degradation of compounds modeling polyimide fragments," *Thermochemica Acta*, Vol. 15, pp. 43-54, (1976).
4. Heltzel, S. and Semprimoshnig, O.,A., "A detailed study on the thermal endurance of Kapton HN and Upilex S," *High Performance Polymers*, Vol. 16, pp 235-248, (2004).
5. Heltzel, S., Semprimoshnig, O.A. and van Eesbeek, M.R.J.; "Investigation of the degradation of thermal control materials by thermal analysis," *High Performance Polymers*, Vol. 20, pp. 492-511, (2008).
6. Moser, M., Heltzel, S., Semprimoshnig, O.,A. and Martin, G.G., "Screening of the thermal endurance of spacecraft materials by kinetic modeling," *Material Research Society Symp. Proc.*, Vol. 851, (2005).
7. Baker, R.L., McDonough, Herr, K.C., Klingberg, R.A., Coffey, J.C., Covington, M.A., Carbon vaporization condensation effects," *NASA TM 87430*, July 1984.
8. Maahs, H.G., "Ablation performance of glasslike carbons pyrolytic graphite, and artificial graphite in the stagnation pressure range 0.035 to 15 atmospheres," *NASA TN D-7005*, March 1972.
9. Lundell, J.H. and Dickey, R.R., "Ablation of ATJ graphite at high temperature," *AIAA Journal*, Vol. 11, No. 2, 1973, pp. 216-222.
10. Davy, J.G. and Somorjai, G.A., "Studies of the vaporization mechanism of ice single crystals," *The Journal of Chemical Physics*, Vol. 55, No. 3624, pp. 3624-3636, (1971).
11. Waller, D., Stokes, D.J., and Donald, A.M., "investigating sublimation and the effect of an imaging gas in a VPSEM," *Eur. Phys. J. Appl.*, Vol. 51, 10901 (2010)
12. Bryson, C.E., Cazcarra, V. and Levenson, L.L., "Condensation coefficient measurements of H₂O, N₂O and CO₂," *Journal of Vacuum Science and Technology*, vol. 11, No. 411, pp. 411-416, (1974).

13. Keenan, J.A., and Candler, G.V., "Simulation of Graphite Sublimation and Oxidation under Re-Entry Conditions," *AIAA paper 94-2083*, June 1994.
14. Potts, R.L., "Application of Integral Methods to Ablation Charring Erosion, A Review," *Journal of Spacecraft and Rockets*, Vol. 32, No. 2, 1995, pp. 200-209.
15. Zhluktov, S.V. and Abe, T., "Viscous Shock-Layer Simulation of Airflow past Ablating Blunt Body with Carbon Surface," *Journal of Thermophysics and Heat Transfer*, Vol. 13, No. 1, pp. 50-59, (1999).
16. Havstad, M. and Ferencz, R., "Comparison of Surface Chemical Kinetic Models for Ablative Reentry of Graphite," *Journal of Thermophysics and Heat Transfer*, 16 p. 508 (2002).
17. Langmuir, I., "the vapor pressure of metallic tungsten," *The Physical Review*, second series, Vol. II, No. 5, pp. 329-342.
18. <http://www.wolframalpha.com/input/?i=methane>
19. Hatori, H., Yamada, Y., Shiraishi, M., Yoshihara, M., and Kimura, T., "The Mechanism of polyimide pyrolysis in the early stage," *Carbon*, Vol. 34, No. 2, pp. 201-208, (1996).
20. Lua, A.C., and Su, J., "Isothermal and non-isothermal pyrolysis kinetics of Kapton polyimide," *Polymer Degradation and Stability*, Vol. 91, pp. 144-153, (2006)
21. Coats, A.W. and Redfern, J.P., "Kinetic Parameters from thermogravimetric data," *Nature*, Vol. 201, No. 4914, pp. 68-69, (1964).
22. Burger, A., Fitzer, E., Heym, M. and Terwiesch, B., "Polyimides as precursors for artificial carbon," *Carbon*, Vol. 13, No. 3-4, pp. 149-157, (1975).
23. Brown, P.N., Byrne, G.D. and Hindmarsh, A.C., "VODE, A Variable Coefficient ODE Solver," University of California, Lawrence Livermore National Laboratory, Rept. UCRL-98412, June 1988.
24. Belov, I.A. and Terpigor'ev, V.S., *Inzhenerno-Fizicheskii Zhurnal*, **17.6**, 1106-109 (1969).
25. Dain Steffen Holdener, "Convective heating analysis of an IFE target in a high temperature, low Reynolds number xenon environment", Master Thesis, Engineering Sciences (Mechanical Engineering), UC San Diego, 2011.

26. Shapiro, A.B., "TOPAZ3D – A Three Dimensional Finite Element Heat Transfer Code," University of California, Lawrence Livermore National Laboratory, Rept. UCID-20484, 1985.
27. Blackwell, B.F., and Hogan, R.E., "One-Dimensional Ablation using Landau transformation and finite control volume procedure," *Journal of Thermophysics and Heat Transfer*, Vol. 8, No. 2, pp. 282-287, (1994).
28. Puso, M.A., "NIKE3D: A Nonlinear, Implicit, Three-Dimensional Finite Element Code for Solid and Structural Mechanics", Lawrence Livermore National Laboratory, LLNL-SM-563704, 2012.
29. Saltelli, A. Chan, K. and Scott, E. M., *Sensitivity Analysis*, Wiley, ISBN-13: 978-0470743829, 2009.
30. Myers, R., Montgomery, D., and Anderson-Cook, C., *Response Surface Methodology*, Wiley, ISBN-13: 978-0-470-17446-2.
31. Morris, M., "Factorial Sampling Plans for Preliminary Computational Experiments", *Technometric*, 1991, Vol. 33, pages 161-174.
32. Santner, T. J., Williams, B. J., and Notz, W. I., *The Design and Analysis of Computer Experiments*, Springer Series in Statistics, ISBN 978-1-4757-3799-8.
33. Berthold, M., and Hand, D. J., *Intelligent Data Analysis, An Introduction*, Springer, ISBN: 3-540-65808-4.

Figure 1. The sketch of an inertial fusion confinement target

Figure 2. Energy flows for control volume of infinitesimal thickness with top edge coincident with the sublimating surface

Figure 3. Comparison of sublimation pressures for the three materials of interest

Figure 4. Phase diagram for methane [18]

Figure 5. Comparison of temperature histories for substrate and surface protection

Figure 6. Comparison of temperature histories for remesh and fixed mesh computational method

Figure 7. Comparison of temperature histories for the three materials of interest

Figure 8. Comparison of temperature histories for three methane initial thicknesses

Figure 9. Comparison of temperature histories for five levels of sublimation suppression by cover gas

Figure 10. Two dimensional finite element mesh of substate, sublimator and portion of mounting framework

Figure 11. Transient position histories for nodes on top (sublimating) surface

Figure 12. Transient position histories for nodes on top (sublimating) surface where a single underlying brick has been removed

Figure 13. Transient position histories for nodes on top (sublimating) surface where three underlying bricks have been removed

Figure 14. Pie charts of first order indices (left) and main effect plots (right) of temperature of the polyimide exterior surface.

Figure 15. Histogram of polyimide temperature at time = 0.075 seconds

Figure 16. Pie chart of first order (left) indices and main effect plots (right) of the edge thickness at specific time.

Figure 17. Pie charts of first order indices (left) and main effect plots (right) of center sublimation timing

Figure 18. Pie charts of first order indices (left) and main effect plots (right) of edge thickness

Table 1. Key parameters for a sublimating surface protection layer

Table 2. List of parameters and ranges