JOURNAL OF SPACECRAFT AND ROCKETS
Vol. 41, No. 3, May–June 2004

Simulation of Outgassing Processes in Spacecraft Coatings Induced by Thermal Vacuum Influence

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The mathematical models describing the outgassing processes and deposition of volatile products under thermal vacuum exposure to coatings applied to space vehicles are given. The models are based on assumptions that changes of outgassing product concentrations in material under investigation take place as a result of desorption from surface on the material-vacuum boundary, first-order chemical reactions, and diffusion specified by the aforesaid processes, and that a part of the surface deposited mass reevaporates. Analytical expressions for the space–time distribution of outgassing products in material and dependence of mass deposited on unit surface on time were obtained from the model equations for the influence of individual processes on outgassing and deposition kinetics to be investigated numerically. According to the obtained results, an analysis of how parameters of the model, separate and in combination, exert influence on alteration of outgassing product concentrations, on outgassing, and deposition kinetics has been carried out.

Nomenclature

$C_n(x, t)$ = concentration of n component of outgassing process in material
D_i = effective coefficient of diffusion of i component
$F_i(t)$ = dependence of flux of i component emitted from material through the unit of surface on time t
h = thickness of material
k_{ci} = effective coefficient of remission of i volatile component from the surface element
k_i = effective coefficients of desorption of i component
$M_{\mathrm{ci}}(t)$ = dependence of mass of i volatile component deposited on a condensation surface element on time t
$M_{\mathrm{si}}(t)$ = dependence of mass of i volatile component in sample on time t
R_i = concentration of i component in material at initial moment
$S_i(x, t)$ = source function of i component
S_0 = surface area of sample
α_{cs} = geometrical factor depending on positional relationship of volatile components source and element of sensitive surface
β_i = effective first-order reaction rate with i component
λ_k = characterictic value of differential equation
$\sigma_{i\to j}$ = weighting coefficient of thermal destruction of i component through j channel
υ = evaporation rate of material
χ_i = chemical reaction rate with involvement of i component

Introduction

OUTGASSING products of materials working in space environment are one of the main sources that contaminate sensitive surfaces of optical systems, cells of solar batteries, etc. This is, in turn, a factor that potentially limits serviceability and service life of space vehicles. Consequently, elaboration of prediction models describing the outgassing processes of coatings is a present-day problem to predict the sensitive surface contamination. Simulation of this complicated physical-chemical process is possible if some assumptions are made. For example, in Ref. 1 the author suggested that outgassing is a first-order reaction,[2] that is, flux density of each component emitting through the material-vacuum boundary is proportional to its amount remained in material at the given moment. We think this assumption is not always correct because at the given moment flux density of each outgassing component is proportional to its concentration in the near-surface layer that is far from being proportional to its amount remained in material itself. Our models allow for the fact that the outgassing process is a result of some major processes taking place inside the material and on its surface as a response to external influence and that condensation of outgassed products and their reevaporation goes in parallel. When selecting the processes that determine the phenomena under investigation, one should identify the involved components and estimate the influence levels of space factors on an orbit where material is expected to be used.

Model of Outgassing Processes

Application of mathematical formulation permits the assigning of certain mathematical symbols to each aspect of the process under investigation. As a result, interaction between different parameters of the process becomes more evident. In addition, the mathematical model gives a basis for numerical analysis that allows the obtaining of not only descriptive but also prognostic data. We propose the model describing changes of outgassing products concentrations in the material under study and outgassing kinetics through the surface formed by the material-vacuum boundary, under thermal vacuum exposure. Change of concentration $C_n(x, t)$ of the n component (molecules or atoms) of the outgassing process in material applied onto the hermetic substrate is mainly stipulated by the following processes: destruction of material, desorption from the surface on material-vacuum boundary, chemical reactions in material, evaporation of material through the surface on material-vacuum boundary, and diffusion caused by the aforesaid processes.

This model is based on the following assumptions:

1) Thickness of a sample of material is significantly less as compared to other linear dimensions so that one can neglect edge effects, scrutinizing only a one-dimensional problem.

2) Sample temperature is fixed.

Received 8 August 2002; revision received 2 February 2003; accepted for publication 8 August 2003.

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3) Coefficients of diffusion, desorption, and thermal destruction depend by no means on time but are defined by temperature of the given sample of material. Dependence of the first and the second coefficients on temperature is described by the Arrenius correlation.

4) Some components of outgassing process can be produced as a result of destruction of other ones; any other interactions are not considered in the model.

5) Outgassing components in material are involved only in the first-order reactions.

6) Material is evaporated from total surface with a steady rate that depends for the given material only on temperature.

7) Outgassing occurs through the material-vacuum boundary only.

For the present, the macroscopic approach is the only possible one to study the cited processes that occur inside composites and on their surfaces. Hence here we are obliged to speak only about effective diffusion and desorption coefficients that are the parameters by means of which we describe the processes that are observed in laboratory and onboard experiments.

Let us express concentrations of the outgassing components that are not the components that could be generated in the course of destruction of other ones as $C_i(x,t)(i = 1, 2, 3 \ldots N)$. Then change of their concentrations in a sample within the made assumptions can be described by the following differential equations:

$$\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C_i(x,t)}{\partial x^2} - \sum_{j=1}^{M} \sigma_{i \to j} C_i(x,t) - \chi_i C_i(x,t)$$

$$+ S_i(x,t) \quad \text{at} \quad x \in (0, h - \upsilon \cdot t), \quad t > 0, \quad \upsilon \cdot t < h \quad (1)$$

$$C_i(x,t)|_{t=0} = R_i \quad \text{at} \quad x \in [0, h] \quad (2)$$

$$D_i \left. \frac{\partial C_i(x,t)}{\partial x} \right|_{x = h - \upsilon \cdot t} + k_i C_i(x,t)|_{x = h - \upsilon \cdot t} = \left. \frac{\partial C_i(x,t)}{\partial x} \right|_{x=0} = 0$$

$$\text{at} \quad t > 0 \quad (3)$$

The second and the third terms of the second member of Eq. (1) can be combined with the source function; however, all of the variants will not be included then.

The functions $C_i(x,t)$ obtained while solving Eqs. (1–3) with the weighting coefficients $\sigma_{i \to j}$ can enter the analogous equations describing changes of concentration of the j outgassing component ($j = 1, 2, 3 \ldots L$) that can be possibly generated during the destruction of the corresponding i component. Of course, there can arise cases when R_j, $\sigma_{j \to l}$, and $\sigma_{i \to j} = 0$ (where $\sigma_{j \to l}$ is the weighting coefficient of thermal destruction of the j component through the l channel). Thus, having examined all possible outgassing components, we constructed the differential equations system describing changes of $C_n(x,t)$ in a sample of material. For the majority of practical tasks, it is not very difficult to solve this system. Here we present only those that are, in our opinion, of practical interest. While solving Eqs. (1–3), one can determine the outgassing rate of the i component from the unit of surface:

$$\frac{\mathrm{d}F_i(t)}{\mathrm{d}t} = (\upsilon + k_i) \cdot C_i(h - \upsilon \cdot t, t) \quad (4)$$

Temperature of materials in situ and, as a consequence, coefficients of diffusion and desorption is usually a time-dependent function. It is difficult to solve Eqs. (1–3) with such coefficients. That is why the "observation" period was divided into finite intervals to perform computational investigation of influence of variable temperature on outgassing kinetics. Here was also assumed that within each interval the temperature of sample is fixed and undergoes a certain jump at the end. If before the time point t_0 the sample was at the temperature T_1, then, from the moment $t_0 + 0$, it became T_2, values of coefficients D_i, k_i, $\sigma_{i \to j}$, χ_i, and $S_i(x,t)$ change as well, together with temperature, which leads to the change of $C_i(x,t)$ in the material. We got analytical solutions of Eqs. (1–3) for computational analysis of processes taking place with temperature changes in material [here it is given for the case when $S_i(x,t) = 0$ and $\upsilon = 0$]:

$$C_i(x, t \le t_0) = 2R_i \sum_{k=1}^{\infty} A_k^0 \exp\left(-b_i^0 t\right) \cos \lambda_k x,$$

$$A_k^0 = \frac{\sin \lambda_k h}{\lambda_k} \frac{k_i^{0^2} + \lambda_k^2 D_i^{0^2}}{k_i^0 D_i^0 + h\left(k_i^{0^2} + \lambda_k^2 D_i^{0^2}\right)}$$

$$C_i(x, t > t_0) = 2R_i \sum_{n=1}^{\infty} B_n \exp(-\tau \cdot b) \cdot \cos \lambda_n x$$

$$B_n = \frac{k_i^2 + \lambda_n^2 D_i^2}{k_i D_i + h\left(\lambda_n^2 D_i^2 + k_i^2\right)} \cdot \sum_{k=1}^{\infty} A_k^0$$

$$\cdot \left[\frac{\sin(\lambda_k - \lambda_n)h}{\lambda_k - \lambda_n} + \frac{\sin(\lambda_k + \lambda_n)h}{\lambda_k + \lambda_n} \right] \exp\left(-b_i^0 t_0\right) \quad (5)$$

where the upper index 0 is attributed to values of parameters existing before the time point:

$$t_0, \tau = t - t_0, \qquad b_i^0 = \beta_i^0 + \lambda_k^2 D_i^0, \qquad b_i = \beta_i + \lambda_n^2 D_i$$

where λ_k, λ_n are solutions of appropriate transcendental equations

$$tg\lambda_k h = k_i^0 \big/ \lambda D_i^0, \qquad tg\lambda_n h = k_i / \lambda D_i \quad (6)$$

β_i^0, β_i are effective first-order reaction rates that occur in material:

$$\beta_i^0 = \sum_{j=1}^{n} \sigma^0{}_{i \to j} + \chi_i^0, \qquad \beta_i = \sum_{j=1}^{n} \sigma_{i \to j} + \chi_i$$

Model of Deposition of Volatile Products

To elaborate on the mathematical model of deposition of volatile products onto the chosen surface element, we made use of the results obtained with the help of the outgassing model keeping designation of parameters unchanged. Thus, mass of i-type volatile component in a sample at any moment t is expressed by its concentration obtained while solving Eqs. (1–3):

$$M_{\mathrm{si}}(t) = S_0 \int_0^{h - \upsilon \cdot t} C_i(x,t)\, \mathrm{d}x \quad (7)$$

and the initial outgassing potential of sample for i volatile component is equal to

$$M_{\mathrm{si}}(0) = h S_0 R_i \quad (8)$$

Change of $M_{\mathrm{si}}(t)$ and $M_{\mathrm{ci}}(t)$ in dependence on time can be described by the set of equations

$$\frac{\mathrm{d}M_{\mathrm{si}}(t)}{\mathrm{d}t} = -S_0 \frac{\mathrm{d}F_i(t)}{\mathrm{d}t} \quad (9)$$

$$\frac{\mathrm{d}M_{\mathrm{ci}}(t)}{\mathrm{d}t} = \alpha_{\mathrm{cs}} S_0 \frac{\mathrm{d}F_i(t)}{\mathrm{d}t} - k_{\mathrm{ci}} M_{\mathrm{ci}}(t) \quad (10)$$

The first member on the right in Eq. (10) is the deposition mass rate of the i-type volatile component on an element of condensation surface; the second one is an ablation rate from this surface due to remission. It is evident that thickness of the deposited layer of material and its composition on the surface under study both can change with time. Hence, in these cases the effective remission coefficient k_{ci} should be time dependent. Usually, in laboratory studies, one can neglect it and consider $k_{\rm ci}$ as being constant when so few molecular layers have been deposited. If the initial mass of i volatile component on a condensation surface $M_{\rm ci}(t)$ is known and initial outgassing potential of sample for i volatile component is determined from Eq. (8), then having integrated Eqs. (9) and (10) we can get the mass of the volatile component deposited on an arbitrary surface element. With the help of expression for function $C_i(x,t)$ obtained from Eqs. (1–3) with fixed boundary material-vacuum, next is the given solution of the system of equations (9) and (10) for the case $[M_{\rm ci}(0) = 0, S_i(x,t) = 0$ and $\upsilon = 0]$ that often occurs in laboratory studies of outgassing and deposition kinetics of volatile components:

$$M_{\rm ci}(t) = 2\alpha_{\rm cs} k_i R_i S_0 \sum_{n=1}^{\infty} \frac{\exp(-k_{\rm ci}t) - \exp(-b_i t)}{(b_i - k_{\rm ci}) \cdot \left[1 + h\left(k_i/D_i + \lambda_n^2 D_i \big/ k_i\right)\right]} \tag{11}$$

The constants here determine outgassing, remission, and deposition rates of volatile products from the condensation surface.

Based on mathematical models, we obtained analytical expressions describing outgassing and deposition kinetics of individual volatile components in dependence on time as well as space–time distribution of their concentrations inside the sample of material. Omitting analytical treatment of said functions, we give only results of computational experiments.

Results and Discussion of Numerical Computation

To determine the influence of individual processes on outgassing and condensation here were performed numerical experiments; their results are given and discussed next. We confined ourselves to the i component alone, calling it as a volatile component (VC) and omitting indexes of parameters. To simplify perception of results here were chosen $R = 1\ \mu\text{m}^{-3}$, $S_0 = 1\ \mu\text{m}^2$, $\alpha_{\rm cs} = 0.075$, and $h = 100\ \mu$m (characteristic thickness of temperature control coatings), whereas other parameters were being varied.

To show separate processes and determine their influence on outgassing, Fig. 1 gives plots of time dependence of VC concentration in material with different model parameters. With the same values of parameters $D(\mu\text{m}^2/\text{s})$, $k(\mu\text{m/s})$, and $\beta(\text{s}^{-1})$, the plots of Figs. 1a and 1b represent behavior of change of $C(x,t)$ for $\upsilon = 0$ and $\upsilon = 0.015(\mu\text{m/h})$, respectively. The given set of model parameters in the second case $C(x,t)$, on the substrate side, with time becomes

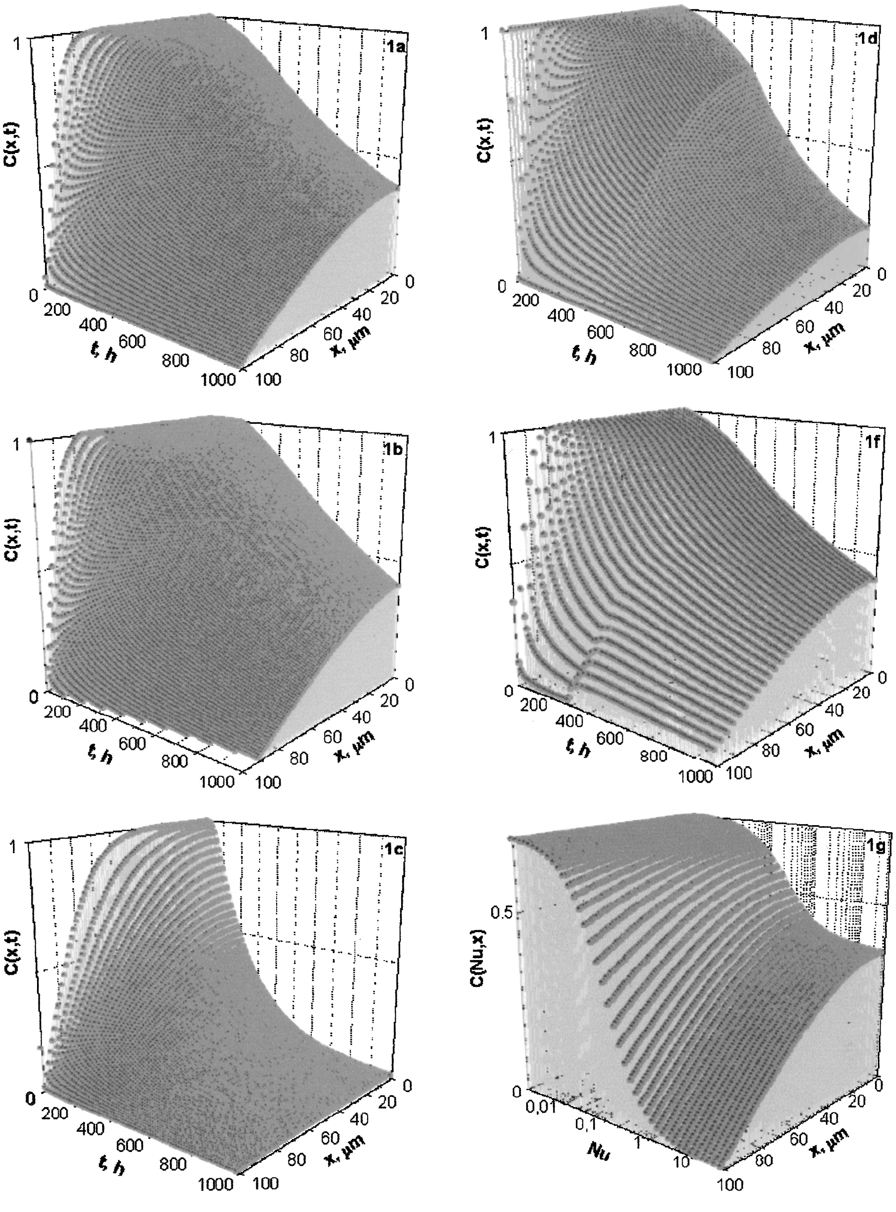


Fig. 1 Space–time distribution of VC concentration in material with different model parameters: a) $D = 0.001$, $k = 0.01$, $\beta = 10E{-}7$, $\upsilon = 0$; b) $D = 0.001$, $k = 0.01$, $\beta = 10E{-}7$, $\upsilon = 0.015$; c) $D = 0.005$, $k = 0.01$, $\beta = 10E{-}7$, $\upsilon = 0$; d) $D^0 = 0.001$, $k^0 = 0.01$, $\beta^0 = 1.0E{-}7$, $D = 0.002$, $k = 0.024$, $\beta = 1.80E{-}7$, $\upsilon = 0$; f) $D^0 = 0.001$, $k^0 = 0.01$, $\beta^0 = 1.0E{-}7$, $D = 0.001$, $k^0 = 0.001$, $\beta = 1.0E{-}7$, $\upsilon = 0$; and g) dependence of $C(x,t)$ on parameter $Nu = k \cdot h/D$.

significantly greater then in the first one. This is because of the evaporation of the desorption depleted near-surface layer, which, in turn, reduces gradient of VC concentration in it. The value of parameter D is five times greater in Fig. 1c as compared with Fig. 1a that is appreciably affected on behavior of the function $C(x, t)$. Figures 1d and 1f show the influence of augmentation of parameter values k, D, β, and the abrupt decrease of value k respectively on the distribution of concentrations at time point $t_0 = 400$ h. The plot Fig. 1g shows dependence of change of $C(x, t)$ on the nondimensional parameter $Nu = k \cdot h/D$ during 1000 h in the case of a fixed boundary. Here is seen that desorptive inhibition of outgassing process occurs when the value of Nu is ≤ 0.01 and diffusive inhibition is ≥ 50, respectively. We are so detailed in studying the influence of parameter values on $C(x, t)$ in order to give more clearness of comprehension of outgassing process. Having received information on influence of model parameters on $C(x, t)$ then, we examined

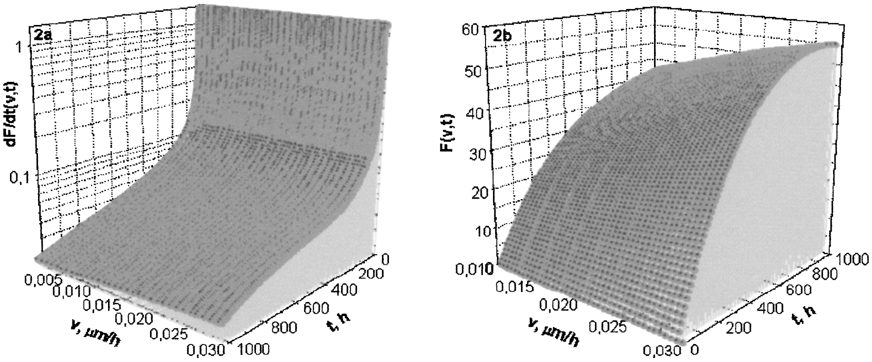
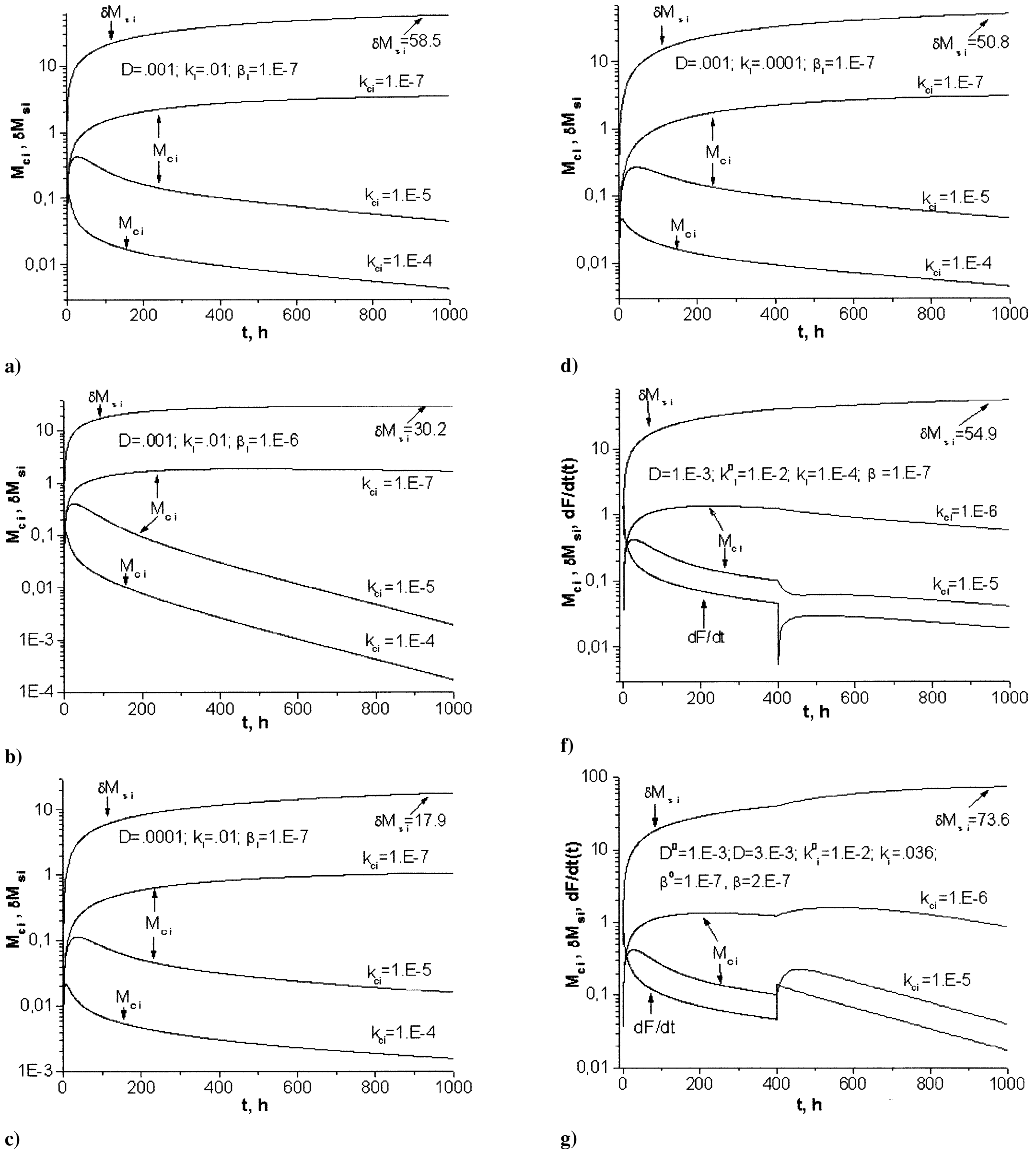


Fig. 2 Plots of VC a) outgassing rate and b) integral flux through the unit of surface in dependence on time and evaporation rate of material υ with fixed values of other model parameters: $D = 0.001$, $k = 0.01$, and $\beta = 10E-7$.



a) d) b) f) c) g)

Fig. 3 Outgassing and deposition kinetics for various models parameters [at $\upsilon = 0$ and $S(x, t) = 0$].

their influence on outgassing kinetics through the material-vacuum boundary. If we know $C(h - \upsilon \cdot t, t)$, we can determine the outgassing rate from Eq. (4). Integrating it by time, we get the value of VC flux emitted through the unit of surface during the time interval t. When making a numerical analysis of influence of the evaporation rate of material on outgassing kinetics, this parameter has been chosen in such a way that evaporation of material was 5–30% while observing the process. Figure 2a shows the outgassing rate $\mathrm{d}F/\mathrm{d}t$ in dependence on time and evaporation rate of material. At first, as is shown on the plot, the outgassing rate is maximum, the value of parameter υ making insignificant influence on the rate because the outgassing process at this time interval is mainly defined by desorption from the near-surface layer. Influence of parameter υ becomes noticeable with time. It is stipulated by two reasons. First, growth of its value brings more rapid evaporation from the VC desorption depleted by the near-surface layer. Second, evaporation gives a contribution to the outgassing process that is equal to $\upsilon \cdot C(h - \upsilon \cdot t, t)\,\mathrm{d}t$ within any given small time interval from t until $t + \mathrm{d}t$. The aforesaid influence of evaporation rate can be also referred to the integral flow function $F(\upsilon, t)$ emitting through the unit of surface on the material-vacuum boundary. Figure 2b shows the behavior of this function in dependence on time and evaporation rate. To demonstrate influence of separate processes on outgassing kinetics and VC deposition, Fig. 3 shows plots of mass loss of VC $\delta M_{\mathrm{si}}(t)$ and mass of VC $M_{\mathrm{ci}}(t)$ deposited on the surface element in dependence on time for various values of models parameters. If parameters $D, k, k_{\mathrm{ci}}(k_{\mathrm{ci}} = 10^{-4}, 10^{-5}, 10^{-7})$ are equal, Figs. 3a and 3b present plots of outgassing kinetics and VC deposition for $\beta = 10^{-7}$ and 10^{-6}, respectively. One can see from the plots that in the second case mass of VC emitted from the sample of material δM_{si} during 1000 h is almost half as great as in the first one, whereas mass of deposited VC M_{ci} within this period of time reaches maximum value and then decreases for all values of remission coefficients. Hence, a disregard of processes that are described using the parameter β can lead to essential errors when making prognostic calculations. Functions $\delta M_{\mathrm{si}}(t)$ and $M_{\mathrm{ci}}(t)$ in Figs. 3c and 3d differ from ones given in Fig. 3a by values of effective diffusion D and desorption k coefficients reduced by 10 and 100 times respectively with other model parameters being equal. Reduction of the first coefficient affects, most of all, behavior of functions $\delta M_{\mathrm{si}}(t)$ and $M_{\mathrm{ci}}(t)$, although in the second case there take place significant changes if compared with plots of Fig. 3a as well. In the first case mass of VC emitted from the sample of material, $\delta M_{\mathrm{si}}(t)$ during 1000 h was reduced by more than three times, whereas in the second case its reduction is only 13%. Figures 3f and 3g show variations of functions $\delta M_{\mathrm{si}}(t)$, $M_{\mathrm{ci}}(t)$, and $\mathrm{d}F(t)/\mathrm{d}t$ for stepwise changes of model parameters at the moment of $t_0 = 400$ h. Stepwise reduction of the desorption coefficient k with time leads to augmentation of the VC concentration (Fig. 1f) in the near-surface layer because of diffusion from the inside of the material that partly compensates decrease of outgassing rate $\mathrm{d}F(t)/\mathrm{d}t$ (Fig. 3f). Total mass loss δM_{si} during 1000 h is reduced only by 5.2% in comparison with the case (Fig. 3a), where $k = k_0 = 0.01$. Growth of parameters D, k, β in the moment of time t_0 causes a faster reduction of VC concentration in material (Fig. 1d) and essential growth of mass loss $\delta M_{\mathrm{si}}(t)$ (Fig. 3g) as compared with the case given in Fig. 3a at the expense of increase of outgassing rate. The same situation is observed in experiments when the abrupt rise of temperature of the sample on outgassing kinetics is studied.

It is obvious that experimental determination of all parameters of the model with adequate accuracy is a complicated problem. But having a good model, the present-day nonlinear regression analysis methods (NRAM) may help to determine missing parameters using sets of experimental point.[3] Having determined the parameters for the prediction model with the help of NRAM, one should carry on test experiments on outgassing kinetics to make them more precise.

Conclusions

The goal of the work is an attempt to create the mathematical models that could form the basis for the engineering prediction method of outgassing of coatings that are applied to space vehicles, under the influence of space environment. Using the models, numerical calculations of how different processes exert influence on outgassing and deposition of volatile products have been carried out. Analysis of results shows that each of physical-chemical phenomena accountable in the mathematical model give a significant contribution to the outgassing processes. It confirms the major regular dependencies observed in investigations of outgassing processes under steady and alternating temperatures of the sample being carried out in our laboratory. These results helped us to highlight correctly the key point while preparing and carrying on experiments concerning investigation of outgassing kinetics and deposition of volatile products that, in turn, so far confirm qualitatively the correctness of principal model's aspects. The present model of condensation of outgassed products is suitable only for making estimations when thin films are deposited and reevaporation process is considered to be the first-order reaction. In other cases one should allow for the physical-chemical phenomena analogous to those that are used in the model of outgassing process.

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Associate Editor