Mathematical modelling of thin-film polymer heating during obtaining of nanostructured ion-plasmous coatings

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Abstract

Analysis has been carried out and a mathematical model has been developed that describes thermal state of a substrate made of a thin polymer film during deposition of nanostructured coatings on its surface using vacuum ion-plasmous method. Some recommendations are given on choosing optimum parameters of the technological process to stabilize temperature during deposition of loose plies of the coating. Technology of obtaining nanostructured resistive layers of coatings on thin polymer films based on experimental data and mathematical modelling results has been developed. This technology is used to maintain and control thermal conditions in onboard spacecraft systems.

Keywords: nanostructured coatings; thin-film polymer; vacuum ion-plasmous metallization; boundary-value problem of heating and cooling; temperature cycles; optimum cycle frequency

1. Introduction

Various methods of obtaining specific coatings including vacuum ion-plasmous methods on creation of individual parts, units and systems have become widespread. This group of methods allows getting functional coatings on the surfaces of products made of metals, non-metals and polymers [1-4,7]. Lately technologies of coating deposition on the polymers are of great interest because of their high efficiency when using these systems as small-size flexible electrical heaters providing thermal condition for operation of onboard spacecraft systems [2-4,7]. In this technology, the resistive layer is obtained as a nanostructured polymetallic coating that is applied through a specific metal mask on the thin-film (40 – 60) μm high-inert polymer by means of vacuum electroarc method using plant ННВ-6.6И1. Accumulated metal resistive layer is to have thickness (1 – 10) μm to provide required values of electrical resistance. However, necessity of obtaining the coating of such thickness results in considerable heating of the polymer substrate. This requires additional research and correction of technology in order to maintain optimum range of heating temperature during forming of the resistive layer. This article introduces some results of research on choosing of optimum parameters of the technological process for temperature stabilizing during cyclic deposition of a resistive metal layer on a thin polymer film.

2. Manufacturing scheme of metallization process

During metallization process thin polymer film is located in a vacuum chamber inside a special metal device that consists of a foundation and a mask having slots. These slots are used to provide coating deposition and assign required shape of the resistive layer. The layout view of the mask cross-section and the scheme of coating applying are shown in figure 1.

In this spraying scheme the mask rotates in the vacuum chamber with rotation frequency n for a rotation period t_r over time $t_{dep} = k_{dep} t_r$ it is in the spraying zone (fig.1), and over time $t_{cool} = \left(1 - k_{dep}\right) t_r$ is beyond this zone, where $k_{dep} = \alpha / 360^{\circ}$, α – an angular width of a spraying zone (fig.1). Some process parameters are displayed in the table 1.

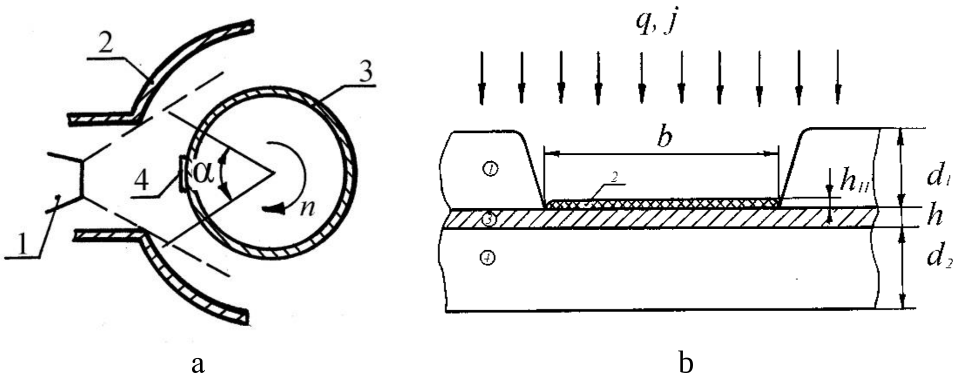

Fig.1. Scheme of coating deposition (a) and scheme of a mask cross-section at the slot area (b).

In fig.1a: 1 – cathode, 2 – walls of the vacuum chamber and the generator anode, 3 – rotating cylindrical device to fasten mask , 4- – masks with a polymide film.

In fig.1b: 1 – mask with slots, 2 – coating, 3 – polymide film, 4 – mask foundation.

Table1. Process parameters of coating deposition on the rotating polymide film

Coating material	XH65MB					
Arc current , I , A	70			120		
V_{coat} , μm /min	0.30			0.52		
V_{avg} , μm /min	0.058			0.100		
n, rpm	2	7.5	12	2	7.5	12
Rotation period, t_r , s	30	8	5	30	8	5
t_{dep} , s	5.8	1.6	0.97	5.8	1.6	0.97
$h_{01} = V_{coat} \cdot t_{dep}$, nm	29	8	4.8	50	14	8.4
N for $h = 5$ μm	172	625	1042	100	357	595
t for $h = 5$ μm	86			50		

Note: V_{coat} - rate of coating deposition on the motionless part; V_{avg} - average rate of coating deposition on the rotating part; t_{dep} - spraying time per revolution; h_{01}- layer thickness accumulated per revolution; N and t – total revolution number and time required for deposition of the coating of 5 μm thickness

While the mask slot is in the spraying zone, the coating of 5 μm thickness is formed on the thin-film polymer. Under heat flow effect, the film is heated up to the temperature T_{01} . When the mask slot leaves spraying zone, heat flow density q drops to zero, coating deposition stops, and the temperature of the coating – polymer-film system reduces up to the some values T_{cool} .

One of the main research objectives is to determine process parameters when values T_{01} and T_{cool} for each metallization cycle have constant values and are within the interval limited by the specified minimum $T_{M,1}$ and maximum $T_{M,2}$.

3. Mathematical model of temperature variations

Mathematical modelling of thin-film polymer heating during coating deposition process taking into account cross-section geometrics (fig.1) can be brought to the solution of the task of cyclic heating and cooling of a two-layer plate in a one-dimensional scenario. Thus, the task includes two heat conduction equations for the thin film and for the deposited coating, supplemented with initial conditions, boundary condition of the second for the accumulated surface, boundary condition of the fourth type for the boundary film-coating, and boundary condition of the third type for the film surface taking into account its contact with the surface of manufacturing device.

Fourier criterion per coating deposition cycle is:

$$Fo_1 = \frac{a_1 t}{h_{coat}{}^2(t)} = \frac{a_1}{h_{coat} V_{coat}} > 4,5 \cdot 10^7 , \tag{1}$$

where a_1 – thermal diffusivity of coating material; t – time of coating deposition; h_{coat} – thickness of deposited coating; V_{coat} – rate of coating deposition.

Taking into account condition (1), temperature distribution through the cross-section of the deposited coating is assumed constant. This, in turn, allows the two-layer heat conduction task to be traced to the simpler one-layer one [6]. Since the value of Biot number of this task is substantially smaller than one, and duration of heating and cooling cycles meets Fourier criterion, it is possible to state that temperature variation in the system of coating- thin-film-polymer having the error not exceeding 1 % at the heating and cooling stage is described by the formulas:

$$T_{heat}(Fo) = T_0 + \left[\frac{qh}{\lambda Bi} - (T_0 - T_c) \right] \left[1 - \exp(-BiFo) \right]; \tag{2}$$

$$T_{cool}(Fo) = T_{01} - (T_{01} - T_c)\left[1 - \exp(-BiFo) \right], \quad T_{01} = T_{heat}(Fo_{heat}), \tag{3}$$

where T_0 – initial system temperature; q – thermal flow density; h – thickness of a thin-film polymer; a – thermal diffusivity of a thin-film polymer material; λ – thermal conductivity coefficient of a thin-film polymer material; α, T_c – heat exchange parameters of a thin-film polymer and a manufacturing device surface determined during the experiment; $Bi = \alpha h / \lambda$ – Biot number; $Fo = at/h^2$ – Fourier criterion.

Taking into account functional dependence of thermal flow density from the rate of coating deposition $q = gV_{II}$ relations (2-3) are written as:

$$T_{heat}\left(t\right)=T_0+\left[A_1V_{coat}-\left(T_0-T_c\right)\right]\left[1-\exp\left(-A_2t\right)\right]; \quad (4)$$

$$T\left(t\right)=T_{01}-\left(T_{01}-T_c\right)\left[1-\exp\left(-A_2t\right)\right],\quad T_{01}=T_{heat}\left(t_{heat}\right), \quad (5)$$

where $A_1=g/\alpha$; $A_2=\alpha a/\lambda h$.

During coating deposition process the manufacturing device with the thin-film polymer being inside the vacuum chamber moves round a circle. At the time moment $t=0$, the thin-film polymer having initial temperature T_0 gets to the thermal flow effect zone. By the time moment $t=t_{dep}=k_{dep}t_r$ that corresponds leaving of the thermal flow effect zone, the temperature of the thin-film polymer is determined by the formula:

$$T_{heat}\left(t_{heat}\right)=T_{01}=T_0+\left[A_1V_{coat}-\left(T_0-T_c\right)\right]\left[1-\exp\left(-A_2k_{dep}t_r\right)\right]; \quad (6)$$

On subsequent rotation of the manufacturing device and complete revolution for the time period $t=t_{cool}=\left(1-k_{dep}\right)t_r$ cooling takes place. Thin-film polymer temperature at this moment according to (5) is written as:

$$T\left(t_{cool}\right)=T\left(\left(1-k_{dep}\right)t_r\right)=T_{01}-\left(T_{01}-T_c\right)\left[1-\exp\left(-A_2(1-k_{dep})t_r\right)\right], \quad (7)$$

Having performed required transformations, taking into account (6-7) we get the formula for determination of temperature of the thin-film polymer from the moment of entry to the thermal flow zone to the next entry to this zone since the manufacturing device will have performed one complete revolution:

$$T\left(t_{cool}\right)-T_0=\exp\left(-A_2t_r\right)\left\{A_1V_{coat}\left[\exp\left(A_2k_{dep}t_r\right)-1\right]-\left(T_0-T_c\right)\left[\exp\left(A_2t_r\right)-1\right]\right\}, \quad (8)$$

Similarly, for determination of temperature of the thin-film polymer from the moment of entry to the thermal flow zone to the entry to this zone after completion of complete $i+1$ revolutions the formula takes the form:

$$\Delta T\left(i+1,\, i\right)=T\left(t_{cool,i+1}\right)-T\left(t_{cool,i}\right)=\exp\left(-A_2t_r\right)\left\{A_1V_{coat}\left[\exp\left(A_2k_{dep}t_r\right)-1\right]-\left[T\left(t_{cool,i}\right)-T_c\right]\left[\exp\left(A_2t_r\right)-1\right]\right\}, \quad (9)$$

where $i=0,\,1,\,2...$; $T\left(t_{cool,0}\right)=T_0$.

Substituting (5) into (6) and having done needed transformations, it is found that temperature variations of the film from the moment of its entry to the spraying zone to the moment of its entry to this zone since it has performed one revolution are determined by the relation:

$$T(t_{cool})-T_0=e^{-A_2t_r}\left[A_1V_{\Pi}\left(e^{A_2k_{dep}t_r}-1\right)-\left(T_0-T_c\right)\cdot\left(e^{A_2t_r}-1\right)\right]. \quad (10)$$

Similarly, considering a certain ($i+1$) revolution of rotation it is found that at any rotation cycle, film temperature variation from the moment of its entry to the spraying zone $T(t_{cool,i})$ to the moment of its entry to this zone since it has performed one complete revolution $T(t_{cool,i+1})$ is:

$$\Delta T_{cool}\left(i+1,i\right)=T(t_{cool,i+1})-T(t_{cool,i})=e^{-A_2t_r}\cdot\left[A_1V_{coat}\left(e^{A_2k_{dep}t_r}-1\right)-\left(T(t_{cool,i})-T_c\right)\cdot\left(e^{A_2t_r}-1\right)\right], \quad (11)$$

where i=0,1,2..; $T\left(t_{cool,0}\right)=T_0$.

4. Modelling result analysis and optimum rotation frequency of a product

It is clear from (10) that in the considered scheme of spraying of coating, depending on the rotation time t_r (or rotation frequency n) three variants of film temperature variation at the moment of its reentry to the spraying zone are possible:

$$T\left(t_{cool}\right)=T_0;\ T\left(t_{cool}\right)>T_0;\ T\left(t_{cool}\right)<T_0. \quad (12)$$

In the first case $T\left(t_{cool}\right)=T_0$, it is clear from (11) that since the first rotation cycle, the film having constant temperature T_0 enters to the spraying zone and it leaves this zone with the constant temperature (5). Condition resulting from (10) is the requirement of optimum spraying cycle:

$$A_1V_{coat}\left(e^{A_2k_{dep}t_r}-1\right)=\left(T_0-T_c\right)\cdot\left(e^{A_2t_r}-1\right), \quad (13)$$

and there is a heating temperature constraint after leaving spraying zone:

$$T_{м,2}>T_0+\left[A_1V_{coat}-\left(T_0-T_c\right)\right]\left(1-e^{-A_2k_{dep}t_r}\right). \quad (14)$$

This relation (13) can be considered as an equation for finding optimum value $t_{r,opt}$ or n_{opt} depending on three parameters

$$\Gamma_1=\frac{A_1V_{coat}}{T_0-T_c}=\frac{gV_{coat}}{\alpha\left(T_0-T_c\right)}=\frac{q}{\alpha\left(T_0-T_c\right)},\ A_2=\frac{\alpha\cdot a}{\lambda h}. \quad (15)$$

In the second case, condition $T\left(t_{cool}\right)>T_0$ results in $\Delta T_{cool}\left(i+1,i\right)$ in (11) is more than zero and $T\left(t_{cool},i\right)$ goes up with the i growth. Consequently, such rotation cycle $i=s$ comes at which decreasing positive difference of summands in the square brackets (11) becomes zero. As a result, under the following rotation film temperature $T\left(t_{cool,s}\right)$ when it enters the spraying zone will have constant value determined from equation (11) by the relation:

$$T\left(t_{cool,s}\right)=T_c+A_1V_{coat}\left(e^{A_2k_{dep}t_r}-1\right)\Big/\left(e^{A_2t_r}-1\right). \qquad (16)$$

It is clear, that is happens when $t_r<t_{r,opt}$ or $n>n_{opt}$.

Applying (5), it is easy to show, that at the moment of leaving spraying zone in each subsequent cycle polymer temperature is of constant value determined by the relation:

$$T\left(t_{cool,s}+t_{dep}\right)=T_c+A_1V_{coat}\left(1-e^{-A_2k_{dep}t_r}\right)\Big/\left(1-e^{-A_2t_r}\right). \qquad (17)$$

In the third case, $T\left(t_{cool}\right)<T_0$ reduction of film temperature, when it enters to the spraying zone, results in $\Delta T_{cool}\left(i+1,i\right)$ in relation (11) is less than zero, and $T\left(t_{cool},i\right)$ reduces with the *i* growth. Consequently, such rotation cycle comes $i=s_1$, at which decreasing in absolute magnitude negative difference of summands in the square brackets (11) becomes zero. As a result, on further rotation, film temperature $T\left(t_{cool,s}\right)$ at its entry to the spraying zone also takes constant value determined by the same relation (16), and on the exit from the spraying zone its temperature is determined by the relation (17). It is clear, that this case takes place at $t_r>t_{r,opt}$ or $n<n_{opt}$.

Thus, on cyclic spraying on the rotating product optimum rotation frequency n_{opt} may exist. At this rotation frequency film temperature variation from the first rotation cycle alters within the limits from T_0 to $T_{heat}\left(t_{heat}\right)<T_{м,2}$. This optimum frequency is determined by conditions (13) and (14) and it depends on three generalized mode parameters (15). If rotation frequency values more or less than optimum ones, the mode comes in some rotation cycles at which film temperature will also change in each rotation cycle within the limits from $T\left(t_{cool,s}\right)$ (16) to $T\left(t_{cool,s}+t_{dep}\right)$ (14), if these limits meet requirements

$$T_{м,1}<T_{heat}\left(t_{cool,s}\right),\ T\left(t_{cool,s}+t_r\right)<T_{м,2}, \qquad (18)$$

then these modes can be used to spray the coating.

Let us determine the optimum rotation frequency n_{opt}.

Analysis (13) shows that solution of this equation exists only when performing certain correlation between parameters (15). Actually, one root of the equation has trivial value $t_r=0$. Therefore, nontrivial solution root $t_r>0$ exists only when the graph of the left part of the equation (10) at $k_{dep}<1$ is higher than the graph of the right part of this relation and this results in their intersection at the second point at $t_r>0$. Consequently, the derivative of the left part of the relation (10) of t_{dep} at the point $t_r=0$ is to be more than the derivative of the right part of this relation at the same point, that is:

$$\Gamma_1k_{dep}=\frac{A_1V_{coat}k_{dep}}{T_0-T_c}=\frac{qk_{dep}}{\alpha\left(T_0-T_c\right)}>1. \qquad (19)$$

Particularly, it results from this relation that, if the rotation period t_r meets the requirement $A_2t_r<<1$, then there is no solution for the equation (13). Really, using requirement $A_2t_r<<1$, we get $\Gamma_1k_r=1$, but this contradicts (19). Given example shows that experimental approach for determination of optimum cycle of temperature variation under impulse powerful thermal flows at the expense of choosing high revolutions of the product (low values t_r) being apparent and often used in technology, but it does not give desired result without taking relation (19) into consideration.

5. Practical application of modelling results

The results obtained are used to stabilize thermal cycle of obtaining nanostructured coating made of material XH65MB on the polymide film with thickness $h=60$ μm. It has been obtained from the preliminary experimental research that thermal flow density of a plasma jet is connected with condensation rate of the coating by the relation $q=6{,}8\cdot10^3V_{coat}$ (in this relation V_{coat} is measured in μm /min). Heat exchange parameters for given conditions of spraying are α = (11,3 ± 0,2) W/m^{2}K and T_c = (38 ± 5) °C, and limits of temperature range for obtaining qualitative coating on the polymide film are to be $T_{M,1}$ = T_0 = 80 °C and $T_{M,2}$ = 160 °C.

In the fig. 2 there is the graph of roots of equation (13) depending on parameter Γ_1 at $A_2=0.107$ and $k_н=0.194$. This graph of rotation period $t_{r,опт}$ or rotation frequency n_{opt} gives values of these parameters at optimum cycle of temperature variation of the polymide film for chosen parameter values Γ_1, A_2 и k_{dep}. For example, for the manufacturing mode at the coating spraying rate $V_{coat}=0.5$ μm /min parameter value Γ_1 is $\Gamma_1=7.33$ and this gives rotation period $t_{r,opt}=7.6$ sec and rotation frequency $n_{опт}=7.9$ rev/min. Using this data, let us check fulfillment of condition (14) $T_{heat}\left(t_{heat}\right)=T_0+\left[A_1V_{coat}-\left(T_0-T_c\right)\right]\left(1-e^{-A_2k_{dep}t_{r,opt}}\right)=120^0\ C<T_{M,2}$.

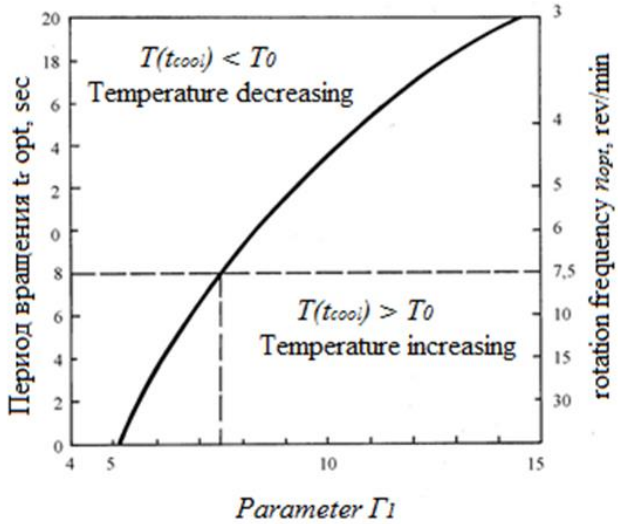

Fig. 2. Period $t_{r,opt}$ and rotation frequency n_{opt} at optimum cycle of temperature variation of the polymide film depending on the parameter $\Gamma_1 = q/\alpha(T_0 - T_c)$ when $k_{dep} = 0.194$ and $A_2 = 0.107$.

As this condition is fulfilled, for the spraying mode of material XH65MB with the arc current 120A at the spraying rate $V_{coat} = 0.5$ μm/min on the polymide film in the designed manufacturing device rotation frequency is to be set $n_{opt} = 7.9$ rev/min if the film is initially heated up to T_0 = 80 ºC.

Upon that, for a revolution of the device the layer of 0,013 μm =13 nm thickness is deposited, to obtain the layer of total thickness 5 μm, for example, about 385 revolutions are to be performed and the spraying time is about 52 minutes.

Note that if the rotation frequency $n > n_{opt}$ during spraying, the situation happens that is determined by the second condition (12) and the film temperature, as it rotates, increases until it will take the value (16). If the rotation temperature is $n < n_{opt}$, the third condition is fulfilled (12) and the film temperature, as it rotates, reduces until it will take value (12).

Revealed regularities allow us to suggest highly effective technique to control thermal cycle of coating spraying on rotating products. If during the process of coating spraying the optical temperature registration system registers that the product temperature increases from revolution to revolution, then it is necessary to reduce rotation frequency to decrease the product temperature, but if the temperature decreases, it is necessary to increase rotation frequency. Besides, this required frequency variation could be selected experimentally by means of some stages of its alterations or could be calculated according to mentioned relations.

Numerical analysis of accuracy tolerances of determination of value n_{opt} depending on the accuracy of parameter determination (12) at conditions (18) shows that the considered mode of spraying with the film temperature variations within the range from 60 ºC to 160 ºC is provided at scattering of mode parameters within limits not exceeding 20 %. Consequently, developed scheme of cyclic spraying on products located at the rotating cylindrical manufacturing device is resistant to scattering of spraying mode parameters.

6. Conclusion

Undertaken research has permitted to describe the process and to develop mathematical model of cyclic heating and cooling of a thin-film polymer during spraying of metal coating using vacuum ion-plasmous method. Undertaken experimental research has proved adequacy and adaptability of the developed model. On the basis of obtained analytical tool optimum parameters of technological process for stabilizing of thermal mode of the system thin-film-polymer-coating on rotation of sprayed product together with the vacuum chamber carousel have been found. Effective methods of control have been suggested; technology of obtaining nanostructured resistive coating on thin-film polymer has been developed and patented. On the basis of the technology developed thin-film flexible electrical heaters for thermal control of onboard spacecraft systems have been manufactured, have passed the whole scope of tests and have been applied in industry.

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