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SUBSTRATE TEMPERATURE DURING HIGH-RATE DEPOSITION OF THIN FILMS AND VACUUM COATINGS

Thermal balance of the substrate during deposition of vacuum coatings is studied considering contributions of epy thermal radiation from a vapor source and the heat of condensation released at the substrate. Corresponding expressions are obtained that allow calculating of either the temperature increment of the substrate during the deposition of the coating (without cooling, or the highest acceptable thickness of the coating, at which undesirable overheating will not occur. The main deposition parameters are considered including thickness of the film and its material, dimensions of the substrate and its velocity, deposition and evaporation rates. The presented data must be considered when new coating systems are developed and corresponding experiments are planned.

Keywords: evaporation, condensation, vacuum coatings, substrate temperature.

Тепловой баланс подложки при нанесении вакуумных покрытий изучается с учетом вклада теплового излучения от испарителя и теплоты конденсации, выделяемой на подложке. Получены соответствующие выражения, позволяющие рассчитать либо приращение температуры подложки в процессе осаждения покрытия (без охлаждения) либо наибольшую допустимую толщину покрытия, при которой не произойдет нежелательного перегрева. Учтены все основные параметры осаждения, включая толщину пленки и ее материал, размеры подложки и скорость ее движения, а также скорости осаждения и испарения. Представленные данные необходимо учитывать при разработке новых систем нанесения покрытий и при планировании соответствующих экспериментов.

Ключевые слова: испарение, конденсация, вакуумные покрытия, температура подложки.

INTRODUCTION

Knowledge of the substrate temperature during deposition of thin films and coatings in a vacuum is important, because their main properties depend on the temperature [1-8]. If special measures are not undertaken, the substrate overheating can occur caused by release of the heat due to the condensation of vapors and absorption of the heat emitted by a vapor source. Heat transfer between the source and the substrate due to convection and conduction through residual gases is negligible at pressures not exceeding 1 Pa.

In this paper, correlation between two components of the heat flow absorbed by the substrate is established and analyzed. Heating of fixed and moving substrates during the deposition of vacuum coatings is also studied as a function of other parameters of the process.

CORRELATION BETWEEN THE HEAT OF CONDENSATION AND RADIATION FROM THE EVAPORATOR

There are only scattered data on the correlation between the heat of condensation and the energy absorbed by the substrate due to thermal radiation from the vapor source [1-6]. This relationship will be obtained in this paper as a function of evaporation temperature (or deposition rate) by comparing two heat flows arriving to the substrate and originated one (φ_c) from the heat of condensation, and another (φ_e) from the heat emitted by the evaporator.

Since Knudsen's law of evaporation is similar to Lambert's law of radiation, the correlation between φ_c and φ_e is independent on the geometry of evaporation. Suppose all vapors and emitted heat reach the substrate. Then the heat flow φ_e is as follows [3-5]

$$\varphi_e = k \cdot \sigma (T_e^4 - T_s^4), \tag{1}$$

where k is the blackness coefficient for the evaporator-substrate system, σ is the Boltzmann constant, T_e and T_s are temperatures of the evaporator and the substrate correspondingly. Since T_e is much higher than T_s, the latter can be omitted in Eq. (1). The value of k is almost independent on properties of the substrate, since its surface participates in the heat transfer only during the initial stage of the film deposition. As soon as a continuous film is formed, the both surfaces (substrate and evaporator) are covered by the same metal.

The heat flow φ_c due to the condensation is proportional to the evaporation rate W_e

$$\varphi_c = Q_c W_e, \tag{2}$$

where Q_c is the specific heat of condensation. In its turn, the evaporation rate can be expressed as a function of T_e [7]

$$W_e = W_o \exp(C - 0{,}5 \ln T_e - B / T_e), \tag{3}$$

where B and C are constants for a given metal.

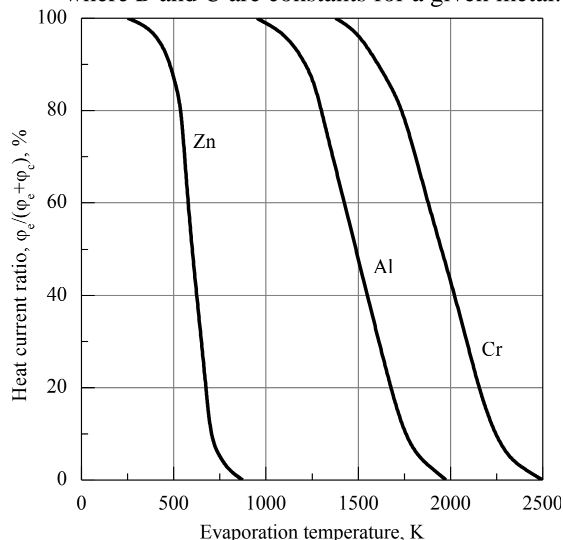


Fig. 1. Heat current ratio, emitted from the evaporator (φ_e) to the total ($\varphi_e+\varphi_c$), vs evaporation temperature

The correlation between φ_e and a total heat flow absorbed by the substrate ($\varphi_e+\varphi_c$) is shown in Fig. 1 as a function of evaporation temperature, indicating that the radiant energy can be neglected during high-rate deposition processes. However, the absorbed radiation plays the main role in the thermal balance of the substrate at the low-rate processes.

To obtain quantitative data on φ_e and φ_c one should consider dimensions of the substrate and the

evaporator and their mutual arrangement. It is performed by introducing the angle coefficient α showing what part of the radiant energy (or vapors) arrives to the substrate

$$\varphi_e = k \cdot \sigma \cdot \alpha \cdot T_e^4 (A_e / A_s), \quad (4)$$

$$\varphi_c = \alpha \cdot Q_c W_e (A_e / A_s), \quad (5)$$

where A_e and A_s are the surface areas of the evaporator and the substrate.

As shown in Fig. 2 where *Cu* is taken as an example (α = 0.06), there are three different processes depending on the deposition rate. If the rate is between $5 \cdot 10^{-4}$ and 10^{-2} μm/s, the both components of the heat flow must be considered as being of the same order (zone II in Fig. 2). However, one of the components can be neglected at lower and higher deposition rates (zones I and III in Fig. 2).

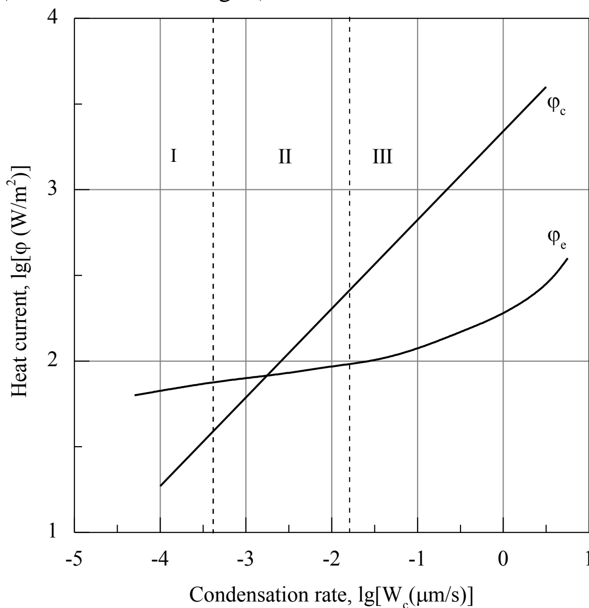


Fig. 2. Heat currents due to condensation (φ_c) and radiation (φ_e) arriving at the substrate vs condensation rate of Cu vapours

TEMPERATURE OF FIXED SUBSTRATES

Since thermal energy is absorbed by a very thin layer of the substrate surface, its temperature is higher than that of the bulk. Time dependence of the surface temperature in the case of a fixed substrate can be found by solving heat transfer equations and considering the constant heat flow (φ=φ_e+φ_c) arriving to the surface

$$\lambda_s \frac{\partial^2 T}{\partial x^2} = c_s \rho_s \frac{\partial T}{\partial t}, \quad \left(\frac{\partial T}{\partial x}\right)_{x=d} = 0, \quad \left(\lambda_s \frac{\partial T}{\partial x}\right)_{x=0} = -\phi \quad (6)$$

where d is the substrate thickness, λ_s is its thermal conductivity, c_s is the specific heat of the substrate, ρ_s is the substrate density. Axis x is perpendicular to the substrate surface. It is assumed that the heat does not leave the substrate that is quite reasonable for the high-rate deposition process.

Solving Eq. (6) at x = 0, we obtain

$$\Delta T = T - T_o = \frac{2\varphi \cdot a_s}{\lambda_s} f(\alpha) \sqrt{\frac{t}{\pi}}, \quad 7)$$

where

$$f(\alpha) = 1 + 2\sum_{n=1}^{\infty} \left\{ \exp(-n^2\alpha^2) - \sqrt{\pi} n \cdot \alpha \left[1 - \Phi(n\lambda)\right] \right\}$$

$$\alpha = \frac{d}{a_s \sqrt{t}} \text{ is the dimensionless coefficient,} \quad (7a)$$

$$a_s^2 = \frac{\lambda_s}{c_s \cdot \rho_s};$$

$$\Phi(n\alpha) = \frac{2}{\sqrt{\pi}} \int_0^{n\alpha} \exp(-\beta^2) d\beta \cdot \quad (7b)$$

T_o is the initial temperature of the substrate.

If the coating is deposited at a thick substrate during a short period of time, the value of $f(\alpha)$ is almost equal to unity. However, $f(\alpha)$ is more than one for all other processes. It can be shown that the error in calculating ΔT under assumption of $f(\alpha)=1$ does not exceed a certain value β, for which the following expression can be written

$$\frac{\beta}{2} > \exp(-\alpha^2) - \sqrt{\pi}\alpha\left[1 - \Phi(\alpha)\right], \quad (8)$$

For instance, if the error of 10% is acceptable, the condition (8) is satisfied under $\alpha \geq 1.2$. Then the following simplified equations can be used for the temperature increment

$$\Delta T = \frac{2\varphi \cdot \alpha_s}{\lambda_s} \sqrt{\frac{t}{\pi}} \cdot \quad (9)$$

Expression (7) can be simplified at low values of α as well, i.e. in the case of thin substrates and prolonged depositions. Then, expression (7) diminishes to

$$\Delta T = \frac{\varphi \cdot t}{c_s \rho_s d} \cdot \quad (10)$$

If Eq. (10) is used instead of Eq. (7), the error β is described by the following expression

$$\beta < 1 - \frac{\sqrt{\pi}}{2\alpha \cdot f(\alpha)} \cdot \quad (11)$$

For instance, $\beta \leq 10\%$ at $\alpha \leq 0.65$.

As an example, we have found the temperature increment during the deposition of *Al* coatings on steel and polyethylene substrates (d = 0.4 mm) at the rate of 0.5 μm/s (φ=$2.04 \cdot 10^4$ W/m^2). ΔT achieves 82 K for steel and 167 K for polyethylene.

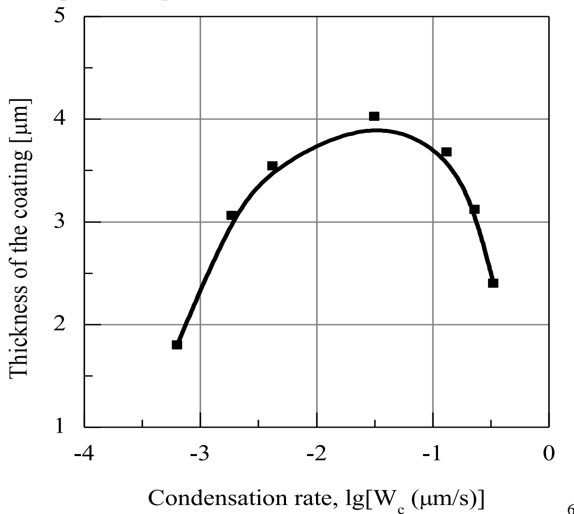
HOW DEPOSITION PARAMETERS DEPEND ON THE HIGHEST ACCEPTABLE SUBSTRATE TEMPERATURE

Substrate overheating prevents deposition of thick coatings, especially at the high-rate processes where heat transfer from the substrate is much lower than the rate of the heat absorption. It is clear that the highest acceptable thickness of the coating δ_o depends on the maximum temperature T_m that the substrate still can sustain. Eliminating time from Eq. (7) and considering (7a) and (7b), we obtain

$$\delta_o = \frac{\sqrt{\pi} \cdot W_c \cdot \lambda_s \cdot d \cdot \Delta T_m}{2\varphi \cdot a_s^{\ 2} \cdot \rho_c \cdot \alpha_o f(\alpha_o)}, \qquad (12)$$

where $\Delta T_m = T_m - T_o$, $\alpha_o = \frac{d}{a_s}\sqrt{\frac{W_c}{\delta_o \rho_c}}$, W_c is the rate of condensation, ρ_c is the density of the coating.

In the case of $\alpha_o \geq 1.2$ and $\alpha_o \leq 0.65$ the following simplified expressions can be used to calculate δ_o



Solid line – theory; points – experiment. ΔT_m = 50 K [6]

Fig. 3. The highest admissible thickness of Cu coatings on polyethylene vs condensation rate

$$\delta_o = \frac{c_c \rho_s W_c \Delta T_m}{\varphi \cdot \rho_c}, \qquad \alpha \leq 0.65; \qquad (13)$$

$$\delta_o = \frac{\pi \cdot W_c \cdot \lambda_s^{\ 2} \Delta T_m}{4\varphi^2 \cdot a_s^{\ 2} \cdot \rho_c}, \qquad \alpha \geq 1.2, \qquad (14)$$

where c_c is the specific heat of the coating. Expressions (13) and (14) are derived from Eqs. (9) and (10).

By analyzing Eqs. (12) to (14) we have found that there must be optimum combination of W_c and d corresponding to the highest value of δ_o at a given ΔT_m. Experimental evidence is presented in Fig. 3 for *Cu* coatings deposited on polyethylene sheets (d = 1.5 mm) under vacuum of $2 \cdot 10^{-2}$ Pa.

The error in the calculated value of δ_o caused by a negligence of the heat transfer from the substrate can be corrected using the experimental curve of the natural substrate cooling. Then, the value of Dt_o must be added to T_m, where D is the experimentally observed rate of cooling, t_o is the deposition time. The correction is especially important in the case of thin substrates and low deposition rates. For instance, we deposited 6 μm-thick coating on the polyimide substrate of 50 μm thickness at the rate of 0,1 μm/s at ΔT_m=350 K, although calculation without correction gave only 2.6 μm, as the highest admissible thickness of the coating.

TEMPERATURE OF MOVING SUBSTRATES

There are two extremes in the case of moving substrates. If the substrate is thin and its velocity is low, the temperature increment is the same as in the case of a fixed substrate. Then, the corresponding value of α is lower than 0.65 and α is described by the following expression

$$\alpha = \frac{d}{a_s}\sqrt{\frac{v}{l}}$$

where l is the length of the deposition zone, v is the substrate velocity. We consider here a continuous coating process, such as vacuum metallization of polymer films or deposition of vacuum coatings on steel strip.

If $\alpha \geq 1.2$, the substrate can be considered as having infinite thickness, since the temperature of its surface s opposite to the source remains constant. For intermediate values of α in a range between 0.65 and 1.2, the following expression is valid similar to Eq. (7)

$$\Delta T = \frac{2\varphi \cdot a_s^2 \cdot l \cdot \alpha \cdot f(\alpha)}{\sqrt{\pi}\lambda_s \cdot v \cdot \alpha}. \qquad (15)$$

Calculations show that α = 0.03-0.6 in the case of continuous deposition of vacuum coatings on steel strip (d=0.1-0.5 mm, v = 0.5-10 m/s). Then $\alpha \cdot f(\alpha)$ approaches $\frac{\sqrt{\pi}}{2}$. Considering also that the heat of condensation prevails over the radiant energy at the high-rate processes, we obtain

$$\Delta T = \frac{\varphi \cdot a_s^2 \cdot l}{\lambda_s \cdot v \cdot \alpha} = \frac{Q_c \rho_c \delta}{c_s \cdot \rho_s \cdot d}. \qquad (16)$$

For example, ΔT= 200 K, if *Al* coating of 5 μm thickness is deposited at the rate of 10 μm/s on the 0.25 mm -thick steel strip moving with the velocity of 1 m/s . The approach described here was also tried to calculate substrate overheating in semi continuous coating systems for vacuum metallization of polymer films.

CONCLUSION

Substrate overheating is a serious problem for physical vapor deposition (PVD) processes at the high rate, because it affects substrate properties and put limitations on thickness of the coatings. Depending on the deposition rate, the main contribution to the substrate heating has either the heat of condensation, or the radiant energy emitted by the evaporator. The heating processes have been analyzed here in details and recommendations were given on how to calculate the temperature increment and the highest admissible thickness of the coating. The data must be considered while developing new coating systems and planning corresponding experiments.

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ИССЛЕДОВАНИЕ КИНЕТИКИ ПРОЦЕССА СУШКИ ЯГОДНОГО СЫРЬЯ ПРИ РАЗЛИЧНЫХ СПОСОБАХ ЭНЕРГОПОДВОДА

Сделан обзор существующих методов расчета кинетики процесса сушки. Экспериментально получены кривые сушки и скорости сушки черники, красной и черной смородины при различных способах энергоподвода (конвективный, конвективный с прокалыванием, конвективный с ИК-излучением). Дан анализ и математическая обработка результатов экспериментов. Получены зависимости, описывающие кинетику сушки различных ягод.

Ключевые слова: конвективный энергоподвод, ИК-излучение, ягодное сырье, кривые сушки и скорости сушки, кинетика сушки.

A review of existing methods for the drying kinetics calculating is done. Drying curves and drying rate curves of blueberries, red and black currant are experimentally obtained for different methods of energy supply (convection, convection with piercing, convective IR radiation). The analysis and mathematical treatment of the experiments results are done. The dependences which describe drying kinetics of different berries are obtained.

Keywords: convective energy supply, IR radiation, berry raw materials, the curves of drying and drying rate, drying kinetics.

В настоящее время многие сельскохозяйственные предприятия Республики Беларусь специализируются на выращивании и сборе различных ягод. Большая их часть либо экспортируется в другие страны, либо подвергается заморозке. Сушка, как метод переработки ягод практически не применяется. Однако существует множество направлений использования высушенного ягодного сырья, одним из которых является производство из сушеных ягод тонкодисперсных порошков и дальнейшее их применение в качестве биологически активных пищевых добавок, красителей и ароматизаторов.

На предприятиях кондитерской промышленности используются сушеные ягоды импортного производства. Поэтому сушка ягод в промышленных масштабах на территории Республики Беларусь позволит не только расширить ассортиментный перечень выпускаемой кондитерскими предприятиями продукции, но и решит вопрос импортозамещения.

Использование известных способов сушки ягод сопровождается рядом недостатков: большая продолжительность сушки, невозможность использования высоких температур воздуха ввиду вероятности перегрева и пригорания ягод, потерь витаминов и биологически-активных веществ, образование пленки на поверхности ягод, затрудняющей процесс испарения влаги.

Поэтому актуально проведение теоретических и экспериментальных исследований кинетики сушки ягод с целью выбора наиболее рационального способа подвода энергии и проведения процесса, а также создания необходимой экспериментальной базы для разработки уточненной методики инженерного расчета сушильных процессов.

На основе литературного обзора изучены методы расчета кинетики сушки различных материалов, а именно А. В. Лыкова, В.В. Красникова, Г.К. Филоненко, Б.С. Сажина, А.В. Акулича и др.

Установлено, что метод А.В. Лыкова, основанный на замене действительной кривой сушки, имеющей сложный вид, прямой линией, описывается уравнением

$$-\frac{dW}{dt} = K \cdot (W - W_p) = \chi \cdot N \cdot (W - W_p)\,, \quad (1)$$

где W, W_p – текущая и равновесная влажности материала, %;

t – время сушки, с;

χ – относительный коэффициент сушки, зависящий от свойств материала и его начальной влажности;

K – коэффициент сушки, $ч^{-1}$ (зависит от режима сушки и прямо пропорционален скорости сушки в первый период N).

Г.К. Филоненко установил, что кривые сушки, полученные при разных режимах, совмещаются в одну общую кривую, если их перестроить в системе координат: скорость сушки $dW/d\tau$ – приведенная скорость сушки ψ [1]. Последняя представляет собой отношение скорости сушки в любой момент к скорости сушки в первый период N. В.В. Красников в своей работе дал развитие метода А. В. Лыкова, предложив рассчитывать второй период сушки по зонам, в каждой из которых зависимость скорости сушки и влажности линейна [1]. В работе [2, 3] предложено обобщенное уравнение для расчета кинетики сушки материалов в аппаратах с активной гидродинамикой

$$dW/dt = -K \cdot (A - W)^m \cdot (W - B)^n\,, \quad (2)$$

где A и B – начальная и конечная влажность материала; m и n – показатели степени, выбираемые для каждого конкретного случая.

Однако все эти методы применимы только для периода постоянной и падающей скорости сушки, или при кусочно-линейной аппроксимации функции по частям.

На основе теоретических и экспериментальных исследований кинетики сушки ягод установлено, что