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Sublimation of a Volatile Component as a Possible Mechanism for Thermoelectric Material Degradation

A physical model of the sublimation of a volatile component from a thermoelectric material has been developed. On its basis, two versions of the mathematical description of the degradation process of thermoelectric material are presented. The first of them takes into account only the diffusion of tellurium as a volatile impurity to the evaporation surface, on which the pressure and, consequently, the concentration of atoms of the volatile component are considered to be known. The second explicitly takes into account the volatility of the evaporating component and, hence, the boundary flux on the evaporation surface. In both cases, an analytical solution of the one-dimensional diffusion equation is obtained taking into account the presence of a temperature gradient along the length of the leg. Further, by computer methods in the Mathcad environment, the time dependence of the thickness of the layer with a reduced concentration of the volatile component and the nature of the distribution of the concentration of this component in it was determined. On this basis, the degradation time of thermoelectric material due to the loss of volatile components is estimated and the requirements for the protective coating of thermoelectric branches are established.

Key words: sublimation**,** diffusion, volatility, layer with a reduced concentration of volatile component, limiting concentration of volatile component, distribution of volatile component in a layer with its reduced concentration, degradation time of thermoelectric leg.

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Introduction

One of the important factors of degradation of thermoelectric legs made of semiconductor materials during their operation as part of generator thermoelectric modules is the sublimation of volatile components from these materials. For example, in Bi-Te-based materials, such a component is tellurium. However, in the present material this volatility is manifested mainly in the case of tellurium excess over the stoichiometric composition of Bi_2Te_3. This is because the "stoichiometric" tellurium is bound in Bi_2Te_3 crystal in the form of quintets of bismuth and tellurium layers and is capable of sublimation only at about 700 K, which significantly exceeds the upper temperature limit of operation of legs of this material in the case of their operation as part of the generator thermoelectric modules.

Similarly, tellurium is a volatile impurity in the medium-temperature *PbTe* material and silicon - in the high-temperature *Si-Ge* material. The loss of these components or impurities due to sublimation does not always favorably change the thermoelectric characteristics of the material and in some cases spoils the thermoelectric module as a whole due to chemical interaction of impurities evaporating from thermoelectric legs with other structural elements. This forces the developers of generator thermoelectric modules to take special measures to suppress the sublimation of volatile impurities from the materials of thermoelectric legs. These include filling the body of the thermoelectric module with an inert gas or coating the side surfaces of thermoelectric legs that are not adjacent to the contact structures with various coatings, for example, polymers [1, 2], glass enamel [3, 4], ceramics [5], or even partial coating them with metal [6].

Therefore, the purpose of this paper is to build a physical model of the sublimation of a volatile component or impurity, its mathematical description both without explicit consideration and taking into account the volatility of this component, an estimate of the temporal change in the thickness of a layer with a reduced concentration of a volatile component or impurity and the concentration distribution of this component or impurity, and an approximate estimate of the degradation time of a thermoelectric leg by the example of a Bi_2Te_3 leg and the development of requirements for a protective coating of thermoelectric legs.

I. Physical model of a thermoelement with unprotected legs in the mode of electrical energy generation

Schematic representation of a thermoelement with unprotected legs and physical model of the sublimation process of a volatile component is given in Fig. 1.

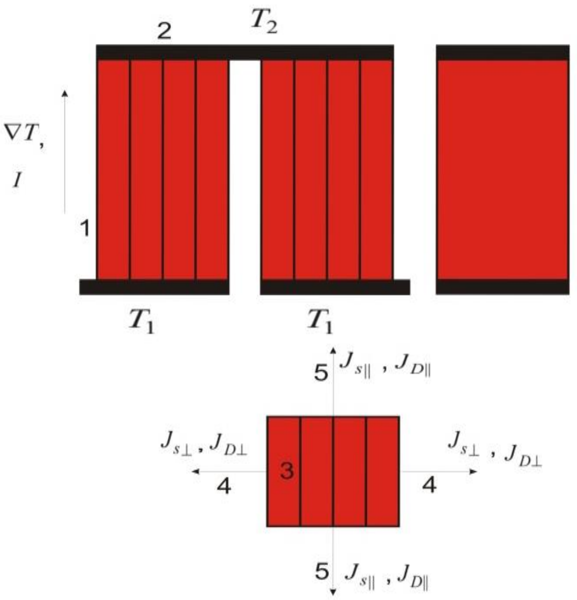

Fig. 1. Schematic representation of a thermoelement and physical model of the sublimation process of a volatile component of a thermoelectric generator module with unprotected legs: 1 – thermoelectric leg, 2 – contacts, 3 – cross-section of the leg and thermoelectric material layers, 4 – sublimation and diffusion flows perpendicular to layers, 5 – sublimation and diffusion flows parallel to layers.

In the model, the main physical processes that determine the degradation of the thermoelectric leg in the process of functioning as part of the thermoelement are sublimation of tellurium through the lateral faces of the leg and its diffusion to these faces due to the formed gradient of tellurium concentration. These processes are characterized by the corresponding sublimation and diffusion fluxes $J_{s\|}, J_{s\perp}, J_{D\|}, J_{D\perp}$ indicated in the diagram. Additional factors of possible influence on the process are the temperature gradient ∇T and electric current *I*. The mathematical description of this physical model is carried out in two versions, in accordance with which different model assumptions are made. In the first version, the volatility of the volatile component or impurity is explicitly disregarded, in the second it is taken into account by introducing the boundary flux of impurity atoms through the unprotected side faces of the thermoelectric leg.

II. Mathematical description of the physical model without explicit consideration of the volatility of the volatile component or impurity and its consequences

If the volatility of the alloying impurity is not explicitly taken into account, the model assumes that:

1) the tellurium vapor near the evaporation surfaces is saturated, and therefore the boundary fluxes of atoms through the side faces are absent;

2) during the growth of a layer with a reduced concentration, the preferred diffusion of tellurium to the lateral faces of the leg occurs in a direction parallel to the layers of the material, since the corresponding diffusion coefficient is 7 orders of magnitude greater than the diffusion coefficient in the perpendicular direction and is considered equal to the tellurium self-diffusion coefficient;

3) the effect of the temperature gradient along the height of the leg on the growth of the layer thickness with a reduced concentration of the volatile component or impurity in each of the cross sections of the leg is due to the temperature dependences of the diffusion coefficient of the volatile component or impurity, and the pressure of its saturated vapor, and, consequently, the concentration of atoms on the evaporation surfaces;

4) the temperature gradient along the leg is determined exclusively by the temperatures at the ends of the leg and the temperature dependence of the thermal conductivity of the thermoelectric material.

The model neglects:

1) the effect of concentration of tellurium, as a doping impurity, on its diffusion coefficient;

2) the effect of the concentration of tellurium as a doping impurity, on the temperature distribution along the leg, since this effect changes the temperature along the leg by less than 1%;

3) the effect of electric current on the temperature distribution along the leg, since the heat fluxes generated by electric current are considered small compared to the heat flux consumed by the thermoelement.

The distribution of the concentration of the volatile component or impurity that is sublimated in accordance with the above physical model in the one-dimensional approximation satisfies the equation:

$$\frac{\partial n}{\partial t} = D\,\frac{\partial^2 n}{\partial x^2}, \tag{1}$$

where *D* is the diffusion coefficient of the volatile impurity or component in the material, *n* is its concentration, *t* is the time, *x* is the coordinate calculated from the surface from which the sublimation occurs, deep into the material.

The boundary conditions for Eq.(1) in conformity with Fig. 1 are as follows:

$$n(0,t) = n_s \tag{2}$$
$$n(l,t) = n_0 \tag{3}$$

where n_0 is the concentration of component to be sublimated in the source material, l is the thickness of sublimation layer with reduced volatile impurity or component.

The solution of Eq. (1) can be represented as:

$$n(x,t) = n_0 \operatorname{erf}\left(x/2\sqrt{Dt}\right) \tag{4}$$

where erf (…) is the so-called error integral.

Then it follows from conditions (2.3) that the thickness l of the sublimation layer and the time are not independent, but are related by the following relation

$$\operatorname{erf}\left(l/2\sqrt{Dt}\right) = n_s/n_0 = \nu \tag{5}$$

If sublimation occurs in vacuum, the concentration of atoms on the surface will increase from zero only until the vapor of the impurity that is sublimated becomes saturated. The handbook [7] states that the saturated tellurium vapor pressure at temperature $t_s^0 = 329^0$C is $h_s = 10^{-3}$ mm Hg. Then the ratio ν, considering the saturated tellurium vapor as an ideal gas, can be calculated as follows:

$$\nu = \frac{\rho_{Hg} g h_s M_{sc}}{R(t_s^0 + 273)\rho_{sc}\nu_{ms}}, \tag{6}$$

where ρ_{Hg} – the density of mercury, g – the acceleration of gravity, M_{sc} – the molecular weight of the semiconductor, ρ_{sc} – the density of the semiconductor, ν_{ms} – the atomic fraction of the sublimated impurity. Therefore, $\nu = 4.5368 \cdot 10^{-9}$. Substituting this value of ν into Eq. (6), we obtain the following law of motion for the lower limit of the evaporation layer:

$$l = 8.2922\sqrt{Dt}, \tag{7}$$

whence it follows that in the case of the presence of a saturated vapor of a volatile component on the evaporation surface, the thickness of the layer with a reduced concentration of this component increases at least twice as fast as indicated in [8].

But even if the degree of evacuation of the evaporation surface corresponds to the presence, for example, of only one particle per cubic centimeter (and such a vacuum is considered extreme), then instead of law (7) for the case of Bi_2Te_3, we obtain the following law of growth of the layer thickness with a reduced concentration of the volatile component with time:

$$l = 13{,}7278\sqrt{Dt}, \tag{8}$$

Therefore, for an arbitrary concentration of atoms on the surface, the law of motion of the lower boundary of the sublimation layer is as follows:

$$l = K\sqrt{Dt}, \tag{9}$$

The dependence of the coefficient K on the relative concentration of atoms of the volatile component on the surface is shown in Fig. 2.

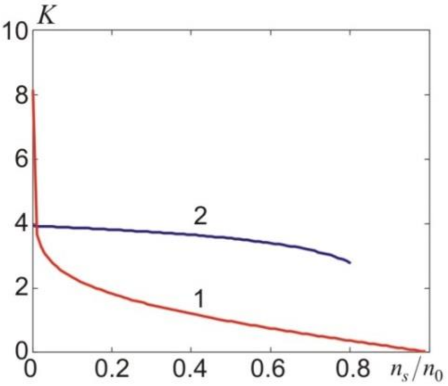

Fig. 2. Dependence of the coefficient K on the relative concentration of atoms on the evaporation surface for Bi_2Te_3: 1 - in accordance with the proposed model approach; 2 - in accordance with the results of [8].

The figure shows that in accordance with the proposed approach, the growth rate of the layer with a reduced concentration of a volatile component in the case of vacuum on the surface is at least twice as high as in [8], but, on the other hand, with increasing concentration of volatile components on the surface within the proposed approach decreases much more sharply than in accordance with [8]. The main error of [8] from this point of view is the assumption of the independence of the rate of diffusion motion of volatile impurity atoms to the surface in contact with the vacuum or saturated vapor of this impurity on the concentration of impurity on the concentration of impurity atoms near the vaporization surface in the process of sublimation.

Possible distributions of tellurium atoms in a layer of thermoelectric material, in which their concentration has decreased, in the case of sublimation into vacuum and reaching the surface with a surface concentration of $0.9n_0$ are shown in Fig. 3.

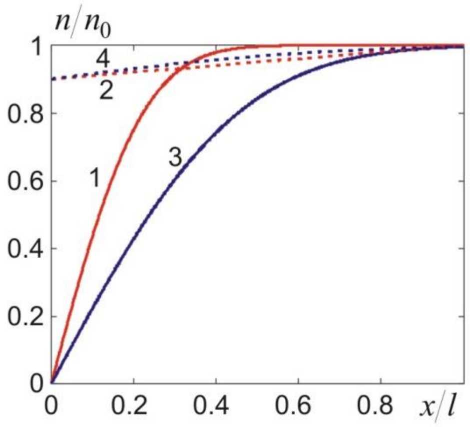

Fig. 3. Possible distributions of tellurium atoms in the layer with reduced tellurium concentration: 1 - in the case of evaporation in saturated vapor atmosphere in accordance with the proposed model approach; 2 - in the case of evaporation at $n_s = 0.9n_0$ in accordance with the proposed model approach; 3 - in the case of evaporation in vacuum in accordance with [8]; 4 - in the case of evaporation at $n_s=0.9n_0$ in accordance with [8].

It can be seen from the figure that the distributions of tellurium atoms in the sublimation layer, in accordance with the proposed approach and the results of [8], differ significantly from each other in the case of a vacuum on the surface, but almost do not differ at $n_s = 0.9n_0$. In the case of a vacuum on the surface, a layer with a reduced concentration of a volatile impurity or component grows much faster and the concentration of this impurity or component has a significantly sharper distribution in the layer than is suggested by [8].

From such a mathematical description of this physical model, it follows that it is possible to suppress sublimation in two ways. The first is to pump air or an inert gas into the free space under sufficient pressure. The second way consists in limiting this free space by covering the part of the surface of the thermoelectric leg free from contacts with such a protective layer that would practically not let the atoms of a volatile doping impurity or component pass through itself. However, since in real operating conditions there is a temperature gradient along the thermoelectric leg, and the diffusion coefficient of a volatile impurity and the pressure of its saturated vapor depend significantly on temperature [7, 9], it makes some sense to study the dependence of the reduced concentra-tion layer thickness on the coordinate measured along the height of the leg, for example, from its cold end. Without dwelling on the details of such a study, we additionally note that during the study, the temperature distribution along the leg was determined both based on experimental data and by calculation, using well-known approaches and formulae of microscopic theory to determine the temperature dependence of the thermal conductivity of the material. As a result of the study, we obtained a number of dependences of the sublimation layer thick-ness on the coordinate along the height of the leg for different times counted from the beginning of the subli-metion process. These dependences are shown in Fig. 4.

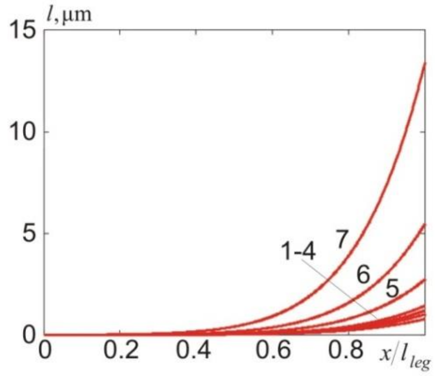

Fig. 4. Distribution of the thickness of the layer with reduced tellurium concentration along the height of the leg after:1 – 300 s, 2 – 500 s, 3 – 700 s, 4 – 1000 s, 5 – 1 h, 6 – 4 h, 7 – 1 day.

It can be seen from the figure that after about 0.5 of the leg height, starting from the hot side, the thickness of the depleted layer drops sharply. That is why it is possible to apply an anti-sublimation coating only to a part of the leg [6].

III. Mathematical description of the physical model with explicit consideration of the volatility of the doping impurity and its consequences

Taking into account the boundary fluxes J_s caused by sublimation on the lateral faces of the thermoelectric leg, the solution of equation (1) by applying the Fourier transform in the coordinate and Laplace transform in time can be obtained in the form:

$$n(x,t) = n_0 \operatorname{erf}\left(x/2\sqrt{Dt}\right) + \frac{2J_s\sqrt{Dt}}{D\sqrt{\pi}}\left[1 - \exp\left(-\frac{x^2}{4Dt}\right)\right] + \frac{J_s x}{D}\operatorname{erfc}\left(x/2\sqrt{Dt}\right), \qquad (10)$$

Equating the left side of formula (10) to n_0 we find the law of motion of the lower boundary of the evaporation layer. In this case, in the limit $t \to \infty$ the distribution law of the concentration of a volatile impurity or component in a layer with its reduced concentration becomes linear:

$$n(x,\infty) = \frac{J_s x}{D}, \qquad (11)$$

Therefore, the steady-state thickness Δ of the layer with a reduced concentration of a volatile impurity or component is equal to:

$$\Delta = \frac{Dn_0}{J_s}, \qquad (12)$$

Thus, it is the larger, the higher the diffusion coefficient and the concentration of the volatile impurity or component and the lower the boundary flux of this impurity. If we assume that the growth of the layer thickness with a reduced concentration of a volatile impurity or component occurs according to a law of the form (9), then for the coefficient K we obtain the equation:

$$\operatorname{erf}(K/2) + \frac{2\sqrt{Dt}}{\Delta\sqrt{\pi}}\left[1 - \exp\left(-\frac{K^2}{4}\right)\right] + \frac{K\sqrt{Dt}}{\Delta}\operatorname{erfc}(K/2) = 1, \qquad (13)$$

From (13) it can be seen that in the absence of a boundary flux, the steady-state thickness of the layer with a reduced concentration of a volatile impurity or component becomes infinitely large, and therefore, equation (13) takes the form:

$$\operatorname{erf}(K/2) = 1, \qquad (14)$$

And this simply means that for the formation of an infinitely thick layer with a reduced impurity concentration over the elapsed time, an infinite diffusion rate of a volatile impurity or component to the evaporation surface is required. That is, in the absence of a limiting flux, the formal solution to equation (10) for all times is $x=\infty$. Therefore, in the case of neglecting the limiting flux, it is necessary either to solve this equation not exactly, but with a certain error, which is arbitrarily assigned by the researcher in order to avoid non-physical results, and then it turns out that the growth rate of the layer with a reduced impurity concentration is also essentially assigned by the researcher, which is incorrect or significantly depends on surface conditions, which is understandable.

We have neither the exact value of the limiting flux J_s for tellurium, nor information on its anisotropy. But calculations show that if it were equal, for example, to the volatility of cadmium in *CdSb,* determined on the basis of the calculated value of the mass loss given in [8], which, as indicated in the same work, satisfactorily coincides with the experiment, then we should put $J_s = 3 \cdot 10^{18}$m^{-2} s^{-1}, and, therefore, the steady-state thickness of the layer with a reduced tellurium concentration would be 7.1 µm. But, since the diffusion mode becomes steady-state, then in this mode the volatile component is lost at a constant rate and the evaporation layer, without changing the thickness, descends as a whole. Therefore, for example, with a steady-state limiting flux and a thermoelectric leg thickness equal to 3 mm, the complete loss of the volatile component would occur in about 100 days.

In order for it to occur, for example, only after 100 years, the protection of the surface of the material should be organized in such a way that the limiting flux is reduced at least 365 times. Note that the following values of other parameters included in the relation (10) were taken into account in the calculations: $n_0 = 8.6923\cdot10^{21}$ cm^{-3}, $D = 2.465\cdot10^{-11}$cm^2/s.

The limiting flux reduced in this way corresponds to the steady-state thickness of the layer with a reduced tellurium concentration, equal to about 2.6 mm. The law of variation of the layer thickness with time for this case is shown in Fig. 5.

The distribution of tellurium in the layer with its reduced concentration at different time intervals is shown in Fig. 6.

At first glance, it might seem that the distributions shown in Fig. 6 for different points in time do not correspond to the initial condition $n(x,0)=n_0$. But it should be borne in mind that in the phenomenological consideration of physical processes, the atomic structure of matter is ignored. Therefore, a certain value of the coordinate corresponds to an infinitely thin layer, the number of atoms in which at their finite concentration will be vanishingly small. And the limit condition to equation (1) in this case corresponds to the instantaneous "switching on" of the limiting flux of a finite quantity. Therefore, it is clear that this layer evaporates instantly.

The limiting flux, as an explicit quantitative characteristic of the volatility of an impurity or component, has a significant effect on the steady-state thickness of the layer with a reduced concentration of the specified impurity or component and the time to reach it, and on the degradation of the thermoelectric leg as a whole due to the movement of the specified layer as a whole inward from the surface from which evaporation occurs. The lower the limiting flux, the greater the steady-state thickness of a layer with a reduced impurity or component concentration.

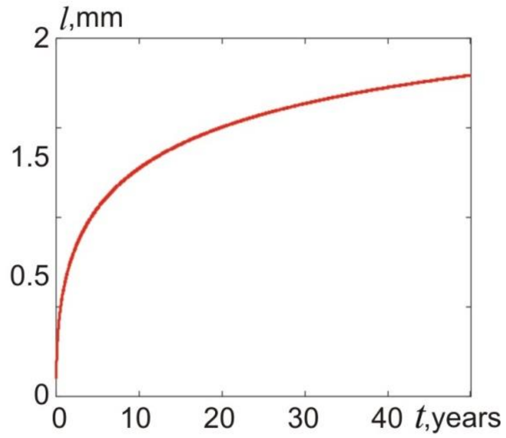

Fig. 5. The law of increasing the thickness of layer with a reduced tellurium concentration.

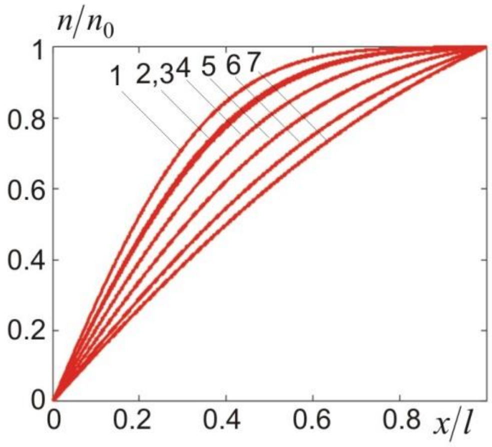

Fig. 6. Tellurium distribution in a layer with a reduced concentration thereof after: 1 – 5 min, 2 – 4 h, 3 – 1 day, 4 – 1 month, 5 – 1 year, 6 – 10 years, 7 – 50 years.

Therefore, we conclude that the protective layer should be made of such a material that it is able to weaken the limiting flux by at least 400 times or more, given that volatility is an increasing function of temperature.

IV. Requirements for the protective coating of thermoelectric legs

Thus, the research results imply the following requirements for the protective coating of thermoelectric legs:

1) it must weaken the sublimation of volatile components or impurities by at least 400 times;
2) coefficient of diffusion of volatile impurities through the coating material should be as low as possible;
3) it must be as electrically insulating as possible and have a low thermal conductivity so as not to shunt thermoelectric legs in terms of electric current and heat

flux;

4) it must have sufficient adhesion to the material of thermoelectric legs so as not to peel off during the manufacture and operation of thermoelectric generator modules;

5) it must be non-toxic;

6) it must be chemically inert to the material of thermoelectric legs and other structural members of thermoelectric generator module.

Conclusions

A physical model of the process of sublimation of volatile component of thermoelectric material as one of the possible mechanisms of its degradation is developed.

Within the framework of the developed model, the change in the thickness of a layer with a reduced concentration of the volatile component in the material with time was studied using the example of tellurium in *Bi-Te* based material with regard to the effect of the temperature gradient along the leg on the sublimation process. In so doing, this study was carried out both without explicit consideration and taking into account the volatility of the volatile component. It is shown that in order for the degradation of the thermoelectric leg due to the loss of tellurium as a component to last at least 100 years, the limiting flux of tellurium atoms through the side surfaces of thermoelectric leg should not exceed $J_s = 7.5 \cdot 10^{15}$ m^{-2}s^{-1}

Based on the results of calculations, the requirements for the protective coating of thermoelectric legs are determined.

Gorskyi P.V. – Dr. Sci., senior researcher of subgroup 1.1.

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П.В. Горський

Сублімація леткої компоненти як можливий механізм деградації термоелектричного матеріалу

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Розроблено фізичну модель сублімації леткої компоненти з термоелектричного матеріалу. На її основі запропоновано два варіанти математичного опису процесу деградації термоелектричного матеріалу. Перший з них враховує виключно дифузію телуру як леткої домішки до поверхні сублімації, тиск, а, отже і концентрація атомів леткої компоненти на якій вважаються відомими. Другий враховує у явному вигляді леткість компоненти, яка випаровується, і, отже, граничний потік на поверхні випаровування. У обох випадках отримано аналітичний розв'язок одновимірного рівняння дифузії з урахуванням наявності градієнту температури по довжині гілки. Далі комп'ютерними методами у середовищі Mathcad визначено часову залежність товщини шару зі зниженою у порівнянні з основним матеріалом концентрацією леткої компоненти та характер розподілу концентрації цієї компоненти в ньому. На цій основі оцінено час деградації термоелектричного матеріалу внаслідок втрати леткої компоненти і встановлено вимоги до захисного покриття термоелектричних гілок.

Ключові слова: сублімація**,** дифузія, леткість, шар зі зниженою концентрацією леткої компоненти, гранична концентрація леткої компоненти, розподіл леткої компоненти у шарі з її зниженою концентрацією, час деградації термоелектричної гілки.