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ANALYTICAL CALCULATION OF THE EFFECT OF METAL COATING OF THERMOELECTRIC LEGS ON THE EFFICIENCY OF GENERATOR THERMOELEMENT

The effect of the protective metal coating of the lateral surface of thermoelectric legs on the efficiency of a generator thermoelement has been determined. At the same time, it is taken into account that the metal coating shunts the thermoelectric leg both in terms of electric current and heat flux. Theoretical calculations were made without taking into account eddy thermoelectric currents in the "thermoelectric material - protective coating" system and the temperature dependences of the characteristics of the metal and thermoelectric material for the "bismuth telluride - nickel" couple. The effects of the metal coating on the effective thermoEMF of the leg are taken into account. It is shown that when the influence of the metal coating on the thermoEMF of the leg is taken into account, the efficiency is a sharply monotonically decreasing function of the thickness of the metal coating, so that in order to achieve the efficiency of a thermoelement at a level of about 5%, the coating thickness should be no more than 0.5 μm at a leg height of 1 mm, about 0.9 μm for the leg height of 2 mm and about 1 μm with a leg height of 3 mm. In so doing, it is assumed that the electrical contact resistance is about 10^{-5} Ohm•cm^2, and the thermal contact resistance is absent. However, in the presence of thermal contact resistance at a level of 0.8 K•cm^2 /W, the efficiency of the thermoelement remains at a level of about 5.3% even with a coating thickness of 5 μm. Bibl. 13, Fig. 2, Table 1.

Key words: thermoelement reliability, thermoelectric leg, metal coating, shunt, thermoelectric figure of merit, effective thermoEMF, coating thickness, maximum thermoelement efficiency.

Introduction

Reliability, in particular the resource stability of thermoelectric generator modules, is their even more important parameter than consumer characteristics. This is due to the fact that they are used, in particular, in systems where their replacement in the event of a failure is impossible or difficult, for example, in the space industry and medicine. And the resource is essentially determined by the stability of thermoelements that make up these modules, and, consequently, by the stability of thermoelectric materials of which their thermoelectric legs are made. Among the typical failure mechanisms of thermoelements and thermoelectric generator modules, sublimation of volatile components and alloying impurities from thermoelectric materials and mechanical destruction of thermoelectric legs both in the process of manufacturing thermoelectric generator modules and during their operation are singled out. To prevent or reduce the negative impact of these factors on the consumer characteristics of thermoelectric generator modules, the lateral surface of thermoelectric legs is partially or completely covered with various coatings, in so doing, completely - as a rule, polymer [1], glass-enamel [2] or ceramic [3], and partially - metal [4]. To increase the mechanical stability of thermoelectric generator modules, the mechanical stability, coefficient of linear thermal expansion, Young's modulus, Poisson's ratio, and thermal conductivity of the thermoelectric material are specially coordinated with each other during their design [5 – 7], and special frames are used between the thermoelectric legs to limit their displacement and deformations during the operation of generator modules [8]. In all these cases, reduction of heat flux shunting of thermoelectric legs is achieved [9]. However, for the simultaneous solution of these problems, it seems promising to cover the lateral surface of thermoelectric legs with metal. Since such a coating significantly shunts the thermoelectric leg in terms of electric current and heat flux, the purpose of this article is an approximate assessment of the influence of the geometric characteristics of such a coating on the efficiency of a thermocouple thermoelement in the electric power generation mode.

Physical model of a thermoelement with fully protected legs

A physical model of thermocouple thermoelement with fully protected legs is schematically shown in Fig.1.

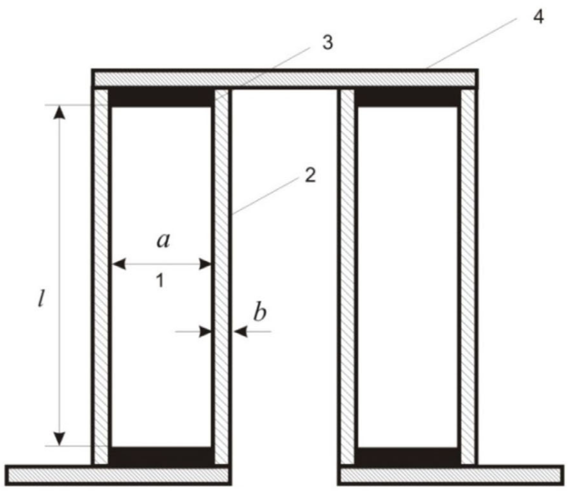

Fig. 1. Physical model of a thermoelement with protected legs:
1 – thermoelectric material;
2 – protective coating; 3 – anti-diffusion layer;
4 – soldered copper interconnect

In the model, it is assumed that the leg has the shape of a rectangular parallelepiped with a square cross-section. The metal coating is continuous. In addition, the following assumptions are made in the model at the initial stage of the study: 1) temperature dependences of the thermoelectric parameters of the semiconductor and metal are neglected, i.e. they are considered approximately constant in the temperature range in which the thermoelement operates; 2) there are no eddy currents at the interface between the thermoelectric material and the metal; 3) the end faces of the covering layer are in contact with the metal interconnect electrodes. In this case, the thermoelectric leg is equivalent to two electrical and thermal resistances connected in parallel, if the protective coating completely covers its side surface. In a thermocouple thermoelement, such legs should be considered electrically connected in series and thermally connected in parallel. We also take into account the electrical and thermal contact resistances, which we consider independent of temperature. The intrinsic resistance of metal connections, solder and anti-diffusion coating are neglected.

Calculation of thermoelement efficiency and discussion of its results

To calculate the efficiency of such a thermoelement, first determine the electrical and thermal resistance of each leg. They are equal, respectively:

$$R_E = \frac{\rho_s \rho_m l + 2\rho_{ce}\left[4\rho_s\left(\delta + \delta^2\right) + \rho_m\right]}{a^2\left[4\rho_s\left(\delta + \delta^2\right) + \rho_m\right]}, \tag{1}$$

$$R_T = \frac{\kappa_s^{-1}\kappa_m^{-1} l + 2\rho_{ct}\left[4\kappa_s^{-1}\left(\delta + \delta^2\right) + \kappa_m^{-1}\right]}{a^2\left[4\kappa_s^{-1}\left(\delta + \delta^2\right) + \kappa_m^{-1}\right]}. \tag{2}$$

In these formulae, a is the cross-sectional side of the leg, l is its length, $\delta = b/a$ is the relative thickness of the coating, i.e. the ratio of coating thickness to the side of the square cross-section of the leg, ρ_s, ρ_m are electric resistivities, respectively, κ_s, κ_m are thermal conductivities of semiconductor and metal, respectively, ρ_{ce}, ρ_{ct} are electrical and thermal contact resistivities, respectively.

We move on to determining the efficiency of a thermoelement with partially or fully protected legs. Let the materials of the legs have the same electrical resistivity and thermal conductivity and the Seebeck coefficients α_s of the same magnitude, but opposite in sign. Then the figure of merit of the thermoelectric leg will be equal to:

$$Z = \frac{\alpha_s^2 R_T}{R_E}. \tag{3}$$

With regard to relations (1) and (2), we will find the following expression for it:

$$Z=\alpha_s^2\,\frac{\left\{\kappa_s^{-1}\kappa_m^{-1}l+2\rho_{ct}\left[4\kappa_s^{-1}\left(\delta+\delta^2\right)+\kappa_m^{-1}\right]\right\}\left[4\rho_s\left(\delta+\delta^2\right)+\rho_m\right]}{\left[4\kappa_s^{-1}\left(\delta+\delta^2\right)+\kappa_m^{-1}\right]\left\{\rho_s\rho_m l+2\rho_{ce}\left[4\rho_s\left(\delta+\delta^2\right)+\rho_m\right]\right\}}\,. \tag{4}$$

Assuming in this formula $\delta=0$, $\rho_{ct}=0$, $\rho_{ce}=0$, we will come to the well-known expression for the figure of merit of thermoelectric material:

$$Z_{TEM}=\alpha_s^2/\rho_s\kappa_s\,. \tag{5}$$

Note that formula (4) is also valid for a leg with a circular cross-section, if we understand δ as the ratio of the coating thickness to the diameter of the circular cross-section of the leg.

But, as a matter of fact, one should additionally take into account the effect of the coating on the thermoEMF of the leg, given that a leg with a metal coating, strictly speaking, should be considered not as one with a resistance connected in parallel, but as two sources of electrical energy connected in parallel. The equivalent electrical circuit of the coated leg is shown in Fig. 2.

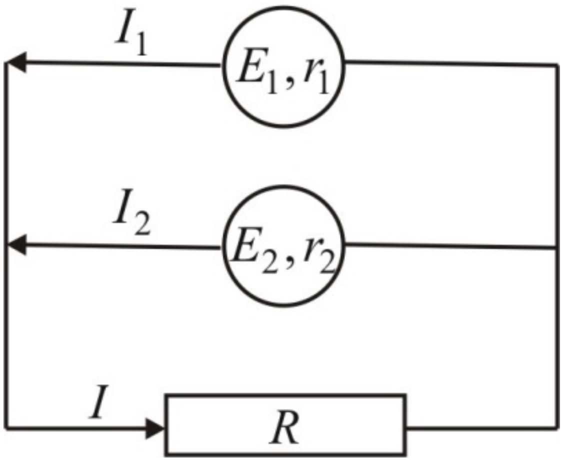

Fig. 2. Equivalent electrical circuit of coated thermoelectric leg.

According to Kirchhoff's rules, we compose an equation for currents:

$$\begin{aligned}&I_1+I_2-I=0\\&I_1r_1+IR=E_1\\&I_2r_2+IR=E_2\end{aligned} \tag{6}$$

From this system we find current *I:*

$$I=\frac{E_1/r_1+E_2/r_2}{\left(1/r_1+1/r_2\right)\left(R+\dfrac{r_1r_2}{r_1+r_2}\right)}\,. \tag{7}$$

From expression (10) it follows that two sources of electrical energy connected in parallel are equivalent to one source with an equivalent EMF equal to:

$$E = \frac{E_1/r_1 + E_2/r_2}{1/r_1 + 1/r_2}, \tag{8}$$

and equivalent internal resistance equal to:

$$r = \frac{r_1 r_2}{r_1 + r_2}. \tag{9}$$

It follows from formula (11) that for a *p*-type leg, the following should be substituted into it:

$$E_1 = \alpha_s \Delta T, \tag{10}$$

$$E_2 = \alpha_m \Delta T, \tag{11}$$

and for an *n*- type leg one should substitute:

$$E_1 = \alpha_s \Delta T, \tag{12}$$

$$E_2 = -\alpha_m \Delta T, \tag{13}$$

where α_m is thermoEMF of metal.
and, moreover, for legs of both types one should substitute:

$$r_1 = \rho_s \frac{l}{a^2}, \tag{14}$$

$$r_2 = \frac{\rho_m l}{4a^2\left(\delta + \delta^2\right)}. \tag{15}$$

Therefore, the expression for the effective figure of merit of the thermoelectric leg will take the following final form:

$$Z_e = \left[\frac{\alpha_s \rho_s^{-1}}{\rho_s^{-1} + \rho_m^{-1}\left(\delta + \delta^2\right)}\right]^2 \times \\ \times \frac{\left\{\kappa_s^{-1}\kappa_m^{-1} l + 2\rho_{ct}\left[4\kappa_s^{-1}\left(\delta + \delta^2\right) + \kappa_m^{-1}\right]\right\}\left[4\rho_s\left(\delta + \delta^2\right) + \rho_m\right]}{\left[4\kappa_s^{-1}\left(\delta + \delta^2\right) + \kappa_m^{-1}\right]\left\{\rho_s \rho_m l + 2\rho_{ce}\left[4\rho_s\left(\delta + \delta^2\right) + \rho_m\right]\right\}}. \tag{16}$$

Now we proceed to the calculation of maximum efficiency of thermoelement in the mode of electric energy generation. The geometrical dimensions of leg without coating will be assumed to be equal to a=1.4 mm, l=1, 2 or 3 mm, the coating thickness b, and, therefore, parameter $\delta = b/a$ will be considered to be variable, and material parameters will be considered to be temperature independent and equal to the following values: $\alpha_s = 160$ μV/K, $\rho_s = 7.143 \cdot 10^{-6}$ Ohm·m, $\rho_m = 7.5 \cdot 10^{-8}$ Ohm·m, $\kappa_s = 1.7$ W/(m·K), $\kappa_m = 90$ W/(m·K), electrical contact resistivity $\rho_{ce} = 10^{-9}$ Ohm·m^2, and thermal contact resistance will be neglected. To calculate maximum efficiency η_{max}, the following formula will be used [10]:

$$\eta_{\max} = \frac{T_h - T_c}{T_h} \cdot \frac{\sqrt{1 + 0.5 Z_e (T_h + T_c)} - 1}{\sqrt{1 + 0.5 Z_e (T_h + T_c)} + T_c / T_h}, \quad (17)$$

where T_h and T_c are the temperatures of the hot and cold thermoelement sides, respectively, Z_e – the effective thermoelectric figure of merit of a coated leg. The results of calculating the efficiency between the extreme temperatures 300 and 500 K are given in Figs.3, 4.

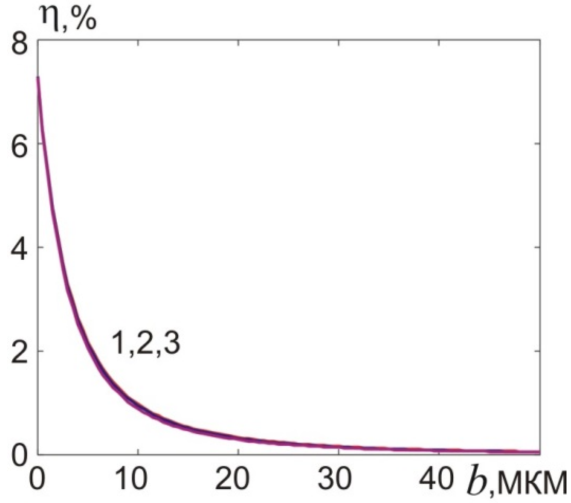

Fig. 3. Dependence of the efficiency on the thickness of the nickel coating of the leg based on Bi-Te in a wide range of thicknesses, with regard to the effect of the coating on the thermal EMF of the leg 1 - for a leg height of 3 mm; 2 – for a leg height of 2 mm; 3 – for a leg height of 1 mm

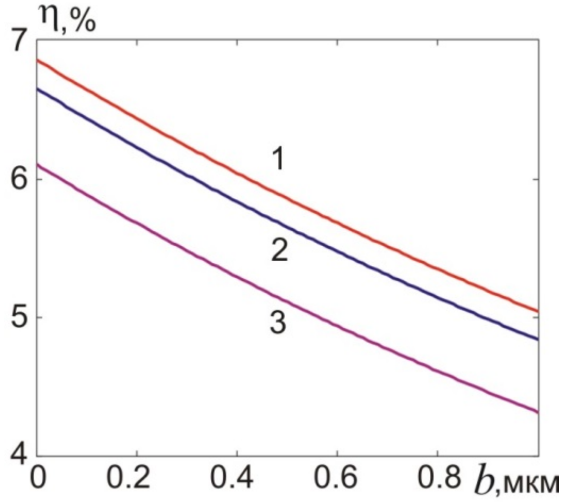

Fig. 4. Dependence of the efficiency on the thickness of the nickel coating of the leg based on Bi-Te in the range of thicknesses at which it is possible to maintain the efficiency of the thermoelement at a level of at least 4%:
1 – for a leg height of 3 mm; 2 – for a leg height of 2 mm;
3 – for a leg height of 1 mm

It can be seen from the figures that, taking into account the effect of the metal coating on the thermal EMF of the leg, the efficiency of the thermoelement is a sharply monotonically decreasing function of the coating thickness. If we disregard the effect of thermal contact resistance, then it turns out that in order to maintain the efficiency of a thermoelement at a level of at least 5 %, a coating with a thickness of no more than 0.9 μm should be produced at a leg height of 2 - 3 mm.

However, the presence of thermal contact resistance to a certain extent neutralizes the negative effect of heat flux shunting the legs. This is illustrated in Fig. 3. At the same time, based on the results of our thermal contact resistance calculations, we believe that the maximum value of the contact resistance can be about $\rho_{ct} = 0.8\ \mathrm{K \cdot cm^2/W}$.

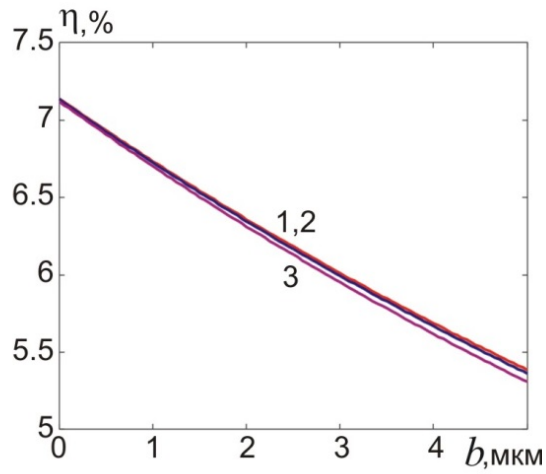

Fig. 5. Dependence of the efficiency on the thickness of nickel coating of the leg, with regard to thermal contact resistances in a wide range of thicknesses. The numbering of the curves is the same as in Fig. 4.

We can see that the effect of thermal contact resistances slows down the drop in the efficiency of the thermocouple with the increase in the thickness of the nickel coating of the legs. Thus, if the assessment of thermal contact resistances is done correctly, it can be assumed that the efficiency of the thermocouple in the case of covering the lateral surface of the leg based on *Bi-Te* with a nickel and anti-sublimation layer 5 μm thick will remain at a level of 5.3-5.4 %.

Let us compare these results with those of [11] where, among other things, the influence of the presence of electrically conductive nickel layers on the isothermal faces of a zone-inhomogeneous thermoelement based on *Bi-Te* on its efficiency was studied. It is shown that the efficiency of such a thermoelement is a monotonically increasing function of the coating thickness, which quickly reaches saturation when the ratio of coating thickness to the linear size of the thermoelement coil is about 0.06. The efficiency value in this case reaches about 5.1 %, which, as follows from Fig. 3, is close to our results for a nickel anti-sublimation layer thickness of about 5 μm. However, a strict comparison of these results is not correct, because the equivalent electrical circuits of a thermocouple thermoelement with a protective conductive layer on each leg and a zone-inhomogeneous thermoelement, in which the conductive layer electrically connects the *n*-and *p*-regions, are fundamentally different from each other.

Conclusions

1. Without taking into account eddy currents in the "thermoelectric leg – anti-sublimation protective metal coating" system and the temperature dependences of thermoelectric parameters of thermoelectric material and metal, the thermoelectric figure of merit of a leg with a completely protected lateral surface is calculated.
2. It is shown that in the absence of thermal contact resistances, the maximum efficiency of a thermoelement with fully protected legs will remain at a level of about 5 % if, at a leg height of 2 - 3 mm, the coating thickness does not exceed 0.9 - 1 μm.
3. In the presence of thermal contact resistances of about 0.8 Kcm^2/W, the maximum efficiency of a thermoelement with fully protected legs will remain at a level of about 5.3 % if, at a leg height of 1 - 3 mm, the coating thickness does not exceed 5 μm.

References

1. WO/2015/126272. V. I. Grishin, D. V. Kotlov. Method of manufacturing semiconductor legs for thermoelectric module and thermoelectric module.
2. Sabo E. P. (2006). Mechanisms that determine the resource possibilities of thermoelectric converters. *J. Thermoelectricity*, 2, 59 - 70.
3. Salvo M., Smeacetto F., D'Isanto F. et al. (2018) Glass-ceramic oxidation protection of higher manganese silicide thermoelectrics Journal of European Ceramic Society. https://doi.org/10.1016/j.jeurceramsoc.2018.01.007
4. *US patent No US 7480984 B1* (2009). J. S. Sakamoto, T. Caillat, J.-P. Fleurial, G. J. Snyder. Method of suppressing sublimation in advanced thermoelectric devices.
5. Wereszczak A. A., McCarty R., Thompson, Sharp J. (2012). Thermoelectric mechanical reliability. *Vehicle technologies annual merit review and peer evaluation meeting*. Arlington VA. 15 May 2012.
6. Liu W., Jie Q., Kim H.S., Ren Z. *Current progress and future challenges in thermoelectric power generation: from materials to devices*. – Preprint of department of physics and Texas center for superconductivity (TcSUH) – University of Houston, Texas 77204, USA. – 60 p.
7. Karri N.K., Mo C. (2017). Reliable thermoelectric module design under opposing requirements from structural and thermoelectric considerations. *Journal of Electronic Materials*. November, 2017, 1-10. – https://doi:10.1007/s11664-017-5934-6 .
8. Yi Yan. (2019). Vertical self-defined thermoelectric legs for use in thin-film micro thermo electric generators (μ-TEG)/ Yi Yan . *A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Electrical Engineering) in the University of Michigan*.
9. Song Lv., Liu M., Xe W. et al. (2020). Study of thermal insulation material influence on the performance of thermoelectric generators by creating a significant effective temperature difference. *Energy Conversion and Management*, Vol.207, 112516-1 – 112516-9.

10. Anatychuk L. I. (1979). *Termoelementy i termoelectricheskiie ustroistva. Spravochnik. [Thermoelements and thermoelectric devices. Guidebook]*. Kyiv: Naukova Dumka.
11. Anatychuk L. I., Kuz R. V., Luste O. J. (2005). Optimization of zone-inhomogeneous thermoelement with electrically conductive layers on isothermal faces. *J.Thermoelectricity*, 3, 68 - 73.

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АНАЛІТИЧНИЙ РОЗРАХУНОК ВПЛИВУ МЕТАЛЕВОГО ПОКРИТТЯ ТЕРМОЕЛЕКТРИЧНИХ ГІЛОК НА ККД ГЕНЕРАТОРНОГО ТЕРМОЕЛЕМЕНТА

Визначено вплив захисного металевого покриття бічної поверхні термоелектричних гілок на ККД генераторного термоелемента. При цьому враховано, що металеве покриття шунтує термоелектричну гілку як за електричним струмом, так і за тепловим потоком. Теоретичні розрахунки зроблено без врахування вихрових термоелектричних струмів у системі «термоелектричний матеріал – захисне покриття» і температурних залежностей характеристик металу і термоелектричного матеріалу для пари «телурид вісмуту – нікель». Враховано впливу металевого покриття на ефективну термоЕРС гілки. Показано, що при врахуванні впливу металевого покриття на термоЕРС гілки ККД є різко монотонно спадною функцією товщини металевого покриття, так що для досягнення ККД термоелемента на рівні близько 5% товщина покриття повинна складати не більше 0.5 мкм за висоти гілки 1 мм, близько 0.9 мкм за висоти гілки 2 мм і близько 1 мкм за висоти гілки 3 мм. При цьому вважається, що електричний контактний опір складає близько 10^{-5}Ом·см^2, а тепловий контактний опір відсутній. Однак за наявності теплового контактного опору на рівні 0.8 К·см^2/Вт ККД термоелемента зберігається на рівні близько 5.3% навіть за товщини покриття 5 мкм.

Ключові слова: *надійність термоелемента, термоелектрична гілка, металеве покриття, шунт, термоелектрична добротність, ефективна термоЕРС, товщина покриття, максимальний ККД термоелемента.*
елементи, телурид вісмуту.

References

1. WO/2015/126272. V. I. Grishin, D. V. Kotlov. Method of manufacturing semiconductor legs for thermoelectric module and thermoelectric module.
2. Sabo E. P. (2006). Mechanisms that determine the resource possibilities of thermoelectric converters. *J. Thermoelectricity*, 2, 59 - 70.
3. Salvo M., Smeacetto F., D'Isanto F. et al. (2018) Glass-ceramic oxidation protection of higher manganese silicide thermoelectrics Journal of European Ceramic Society. https://doi.org/10.1016/j.jeurceramsoc.2018.01.007
4. *US patent No US 7480984 B1* (2009). J. S. Sakamoto, T. Caillat, J.-P. Fleurial, G. J. Snyder. Method of suppressing sublimation in advanced thermoelectric devices.
5. Wereszczak A. A., McCarty R., Thompson, Sharp J. (2012). Thermoelectric mechanical reliability. *Vehicle technologies annual merit review and peer evaluation meeting*. Arlington VA. 15 May 2012.
6. Liu W., Jie Q., Kim H.S., Ren Z. *Current progress and future challenges in thermoelectric power generation: from materials to devices*. – Preprint of department of physics and Texas center for superconductivity (TcSUH) – University of Houston, Texas 77204, USA. – 60 p.
7. Karri N.K., Mo C. (2017). Reliable thermoelectric module design under opposing requirements from structural and thermoelectric considerations. *Journal of Electronic Materials*. November, 2017, 1-10. – https://doi:10.1007/s11664-017-5934-6 .
8. Yi Yan. (2019). Vertical self-defined thermoelectric legs for use in thin-film micro thermo electric generators (μ-TEG)/ Yi Yan . *A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Electrical Engineering) in the University of Michigan*.
9. Song Lv., Liu M., Xe W. et al. (2020). Study of thermal insulation material influence on the performance of thermoelectric generators by creating a significant effective temperature difference. *Energy Conversion and Management*, Vol.207, 112516-1 – 112516-9.
10. Anatychuk L. I. (1979). *Termoelementy i termoelectricheskiie ustroistva. Spravochnik. [Thermoelements and thermoelectric devices. Guidebook]*. Kyiv: Naukova Dumka.
11. Anatychuk L. I., Kuz R. V., Luste O. J. (2005). Optimization of zone-inhomogeneous thermoelement with electrically conductive layers on isothermal faces. *J.Thermoelectricity*, 3, 68 - 73.

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