CHAPTER «PHYSICAL AND MATHEMATICAL SCIENCES»

RELATIONSHIP OF NON-EQUILIBRIUM THERMODYNAMICS IN THE HETEROGENEOUS PERMEABLE THERMOELEMENTS

Vitalii Semeshkin[1]
Radion Cherkez[2]

DOI: https://doi.org/10.30525/978-9934-26-364-4-1

Abstract. A significant number of thermoelectric processes are described with fundamental law of thermodynamics. This paper describes thermoelectric processes in the permeable thermoelements, which are described with the help of relationships of non-equilibrium thermodynamics. The thermoelectric effects, which are described in this work, are laid in the basis of the work of thermoelectric elements, which make up the modules of generators and coolers. Any thermoelectric module can work in refrigerating regime as well as in generator regime. The difference is that, in order to generate energy and to work in the refrigerating regime, the different temperatures and different semiconductors are optimal, which are used in development of thermoelectric modules. The heterogenous materials, which are used to create new thermoelectric modules, can be defined as materials with different sharp heterogeneity of durability from one phase to the other. This heterogeneity of durability may be caused by microstructure of diversity, heterogeneity of the crystal structure or compositional diversity. The size of phases may be in the range from micrometers to millimeters, the geometry of phases may change and create different

---

[1] Doctor of Philosophy Degree Candidate,
Postgraduate Student of the Thermoelectricity and Medical Physics Department,
Yurii Fedkovych Chernivtsi National University, Ukraine
[2] Doctor of Physical and Mathematical Sciences,
Professor of the Thermoelectricity and Medical Physics Department,
Yurii Fedkovych Chernivtsi National University, Ukraine

material systems. The object of this research is the processes in non-equilibrium thermodynamic systems. The subject of the research is the flow of thermodynamic processes in heterogeneous materials, relationship of non-equilibrium thermodynamics in the heterogeneous permeable thermoelements. The methodology of the research is based on the common scientific methods of analysis and synthesis, induction and deduction, observation and abstraction, which are used to systemize results and calculations of thermoelectric systems. The aim of the work is familiarization with the relationship of non-equilibrium thermodynamics, its systematization and calculation of optimal parameters of permeable thermoelement on its basis. This paper describes the physical nature of thermodynamic and thermoelectric phenomenon, based on the newest actual and classic works of the branch of thermoelectricity, non-equilibrium thermodynamics, applied and thermoelectric material science, and their practical application. The analytical review of the literature about the problematics of non-equilibrium thermodynamics in heterogeneous systems was done. We observed the advantages and disadvantages of these systems. The practical part of this work consists of the calculation of parameters of permeable thermoelement made of thermoelectric material on the base of BismuthTtelluride for thermoelectric cooler or, as it used to say in the field of thermoelectricity, thermoelectric heat pump, calculation of dependence of its parameters on amount and size of channels of permeable thermoelement. While investigating the relationship of non-equilibrium thermodynamics, exactly Gibbs' equation, Boltzmann's equation, the equation of coolant and heat flow, equation of cooling coefficient, we systemized them and calculated the optimal parameters for the permeable thermoelectric element of cooling on the base of diverse semiconducting alloy Bi_2Te_3. On the basis of these calculations, we graphically represented the dependence of parameters of semiconducting permeable thermoelectric element on width of its channel, showed optimal definition of width of channel of permeable thermoelectric element. The results of research showed that, by means of the system of channels with the heat carrier, which make changes in the gradient and the temperature's distribution on the element, is the significant advantage of the cooling factor of the thermoelectric electric over impenetrable.

1. Introduction

In 1930's Lars Onsager suggested the theoretical description of non-equilibrium thermodynamic processes, where bound thermodynamic powers and forces are described in a very general view. Thermodynamic theory of thermoelectric phenomena in isotropic environments was first developed by Callen. Usually it is described as the Onsager-de Groot-Callen theory, but also it might be called the theory of "first approximation", which gives coordinated and very accurate thermodynamic description of thermoelectric processes on phenomenological level [1–4].

This work describes physical essence of thermodynamic and thermoelectric phenomenon based on actual newest researches and on classical works in the field of non-equilibrium thermodynamics, material science, thermoelectricity and their practical usage.

The problematics of non-equilibrium thermodynamics in heterogeneous systems is now actively researched by many educational establishments in the world, especially: Japan (universities in Osaka and Tokyo, private Waseda University), Belgium (Brussel University), Mexico (National Autonomous University in Mexico in Mexico), USA (Lafayette University) and others.

It is problematic to embrace the whole spectrum of the given subject in the border of one research, but we will examine some of them. The result of our research will be the demonstration of applied usage of this subject in the engineering of thermoelectric devices.

Starting with general theories and concepts in the first chapters of this work, in the fourth chapter we will calculate the parameters for permeable thermoelectric element on the basis of bismuth telluride (Bi_2Te_3) for thermoelectric cooler (TEC), or, as it is named among experts of the branch of thermoelectricity – thermoelectric heat pumps (THP).

The aim of the given work is an acquaintance with correlations of non-equilibrium thermodynamics, their generalization, calculation on their basis of optimal parameters of permeable thermoelement. The object of the research of this work is processes of non-equilibrium thermodynamic systems. The subject of the research is the flow of thermodynamic processes in heterogeneous materials, and also a correlation of non-equilibrium thermodynamics in heterogeneous permeable thermoelements. The methodology of research is based on general scientific methods of analysis and synthesis, induction and deduction, observation and abstraction, which are used for the systematization of the results and calculations of thermoelectric systems. The novelty of this paper lies in calculation of correlations of non-equilibrium thermodynamics in heterogeneous permeable thermoelements.

2. Thermal conductivity and thermoelectric effects

2.1. Thermal conductivity and local entropy

As it is known, in the classic thermodynamics, the irreversible processes in the isolated systems are conducted with the rise of entropy [1]. Let's examine the source of rise of local entropy and dependence of entropy on system's parameters.

First, we shall examine the easiest case – heat conductivity in the solid homogeneous body. In the case if the temperature of the body changes from one point to the other, then the inner energy per unit mass in the general case depends on coordinates and moments in time.

That very statement is fair for the heat flow Q. In such case, the law of energy conservation may be put down as:

$$\rho \times \left[\frac{dU}{dt} \right] + \nabla \vec{Q} = 0, \tag{1}$$

where ρ – density, U – inner energy, t – time.

For the full description of heat conductivity, we should take into account the relation of the inner energy and U and temperature T in a differential form:

$$dU = cdT, \tag{2}$$

where c – specific heat capacity.

Also, we have to consider Fourier law, which binds the heat flow Q to temperature's gradient:

$$\bar{Q} = -\chi gradT = -\chi \nabla T, \tag{3}$$

where χ – is coefficient of heat conductivity.

Specific internal energy is bound to specific entropy by combined expression of first and second laws of thermodynamics. Since we research the heat exchange processes in the solid body, we can neglect the changes of volume, so we get:

$$dU = TdS, \tag{4}$$

where S – is entropy.

From equations (1) and (4) we see:

$$\rho\frac{dS}{dt}=\frac{-\nabla\vec{Q}}{T}, \tag{5}$$

Then the next equations are fair:

$$\nabla\frac{\vec{Q}}{T}=\frac{1}{T}\vec{\vec{Q}}-\frac{1}{T^2}\vec{Q}gradT, \tag{6}$$

$$\frac{1}{T}\nabla\vec{Q}=\nabla\frac{\vec{Q}}{T}+\frac{1}{T^2}\vec{Q}gradT, \tag{7}$$

that is why we get:

$$\rho\frac{dS}{dt}+\nabla\frac{\vec{Q}}{T}=\frac{-1}{T^2}\vec{Q}gradT. \tag{8}$$

The given expression we can consider as the equation of the continuity of the flow of entropy *S*. Then we shall bind the increasement of entropy to the right part of the equation (8). Let’s integrate the equation (8) for a heat-conducting body, while using Gauss theorem:

$$\rho\frac{d}{dT}\int SdV+.\ \left(\frac{\overrightarrow{Q^n}}{T}\right)d\sigma=-\int\left(\frac{1}{T^2}\vec{Q}gradT\right)dV. \tag{9}$$

If the surface of the solid body is isolated adiabatically, then the normal component of the heat flow *Q* equals zero. In such case, in the left part of the equation (9) the velocity of change of body’s entropy may remain, which is shown as temperature *T*, the temperature’s gradient (*T*) and the heat flow (*Q*).

Since the velocity of entropy’s change is expressed as volume’s integral (*dV*), then, in such case, the sub-integral expression – is the local velocity of entropy’s generation:

$$\sigma=\frac{-1}{T^2}\vec{Q}gradT. \tag{10}$$

The velocity of entropy’s generation depends only on the state of system at the relevant moment in time at the appropriate elementary volume.

If we decline the adiabatically isolated surface of a thermally conductive body, and we imagine the given surface bound to heat reservoir, then the magnitude Q^n – is the flow of heat through a single body surface to the heat reservoir, which, in this case, equals the flow of heat, because $dV = 0$. Then:

$$\vec{J} = \frac{\vec{Q}}{T}, \tag{11}$$

where J – is the flow of entropy.

2.2. The conductivity of anisotropic bodies

Since all characteristics of anisotropic solid bodies depend on orientation relative to the crystal axes, then their heat conductivity characteristics can not be described by the scalar values. Each component of the heat flow, which flow through crystal, depend on all three components of gradient's temperature [2; 9]. So, the description of thermal conductivity feature of crystal needs the all nine values in the system of three equations:

$$\begin{cases} w_1 = -\chi_{11}\dfrac{dT}{dx_1} - \chi_{12}\dfrac{dT}{dx_2} - \chi_{13}\dfrac{dT}{dx_3}, \\ w_2 = -\chi_{21}\dfrac{dT}{dx_1} - \chi_{22}\dfrac{dT}{dx_2} - \chi_{23}\dfrac{dT}{dx_3}, \\ w_3 = -\chi_{31}\dfrac{dT}{dx_1} - \chi_{32}\dfrac{dT}{dx_2} - \chi_{33}\dfrac{dT}{dx_3}. \end{cases} \tag{12}$$

The statement (12) states that the thermal flow and the temperature's gradient in any crystal is antiparallel [2].

Let's modify the equation of velocity of entropy's generation (10), taking into account anisotropy of heat conductivity:

$$\sigma = -\left[\frac{1}{T^2}\left(w_1\frac{dT}{dx_1} + w_2\frac{dT}{dx_2} + w_3\frac{dT}{dx_3}\right)\right], \tag{13}$$

We should take into account that for any of temperature's gradient should be fulfilled the condition $\sigma \geq 0$, that is:

$$\sum_i \sum_k \chi \frac{dT}{dx_i}\frac{dT}{dx_k} \geq 0, \tag{14}$$

The statement (14) means that tensor χ_{ik} – is essential. Thus, it is logical:

$$X_{ik} = \chi_{ki}(i,k = 1,2,3). \tag{15}$$

2.3. Thermoelectric effects

Currently we know three main thermoelectric effects or phenomenon: Seebeck effect, Peltier effect and Thomson effect. Their essence lies in the given:

1) If the two different conductors with different temperature contact, then the thermoelectric driving force occurs;

2) When the electric current flows through the temperature-homogeneous system, the heat is set apart or absorbed in the place of contact of two different conductors (Peltier's heat). If the heat is set apart, i.e. the contact is warmed up, then the Peltier effect is called a positive one, if not – then the negative one;

3) When the current is flown in the temperature heterogeneous system, except Joule heat, the additional Thomson heat is distinguished, what is proportional to the power of flow and temperature's gradient.

Let's look at the metal in which the electric current is flown and the drop of temperature occurs. We shall write down the law of energy conservation and withdraw the relevant equation of the entropy's balance [10]. If the current is absent, use the equation (8).

Let's assume that the specific internal energy *U* and the specific entropy *S* are not depended on vector current density *j*. While formulating the law of energy conservation, we should take into account that energy is produced per unit volume per unit time the energy *jE* is conducted, that in the future, as a result of increasement of charge of the given volume on $-\nabla\vec{j}$, the additional potential energy appears – $\varphi\nabla\vec{j}$, where $\varphi-$ is an electrical potential, $\bar{E}=-grad\varphi.$ Then the law of energy conservation gets the next look:

$$\rho\frac{dU}{dt}=-\nabla\vec{j}+\overrightarrow{jE}-\varphi\nabla\vec{j}, \tag{16}$$

Seebeck effect occurs only in the circles with the contact of two heterogeneous conductors with different temperatures. Such couple of providers are called the thermocouple and it is characterized by contact difference of potentials, which is caused by the difference of Fermi level in two providers on the contacts:

$$U_{к}=\frac{F_2-F_1}{e}, \tag{17}$$

where $U_к$ – is a contact difference of potentials, F – is Fermi level of the conductor, e – is the charge of electron.

Generated by Seebeck effect of thermoelectrics, driving force is defined as:

$$\varepsilon = \int_{T_1}^{T_2} \alpha_{12}(T)\,dT, \tag{18}$$

where ε – is thermoelectric driving force, α_{12} – is a coefficient of thermoelectric driving force, T_1 and T_2 – are temperatures of conductors.

Reversed to Seebeck effect is Peltier effect, which is characterized by Peltier effect:

$$\Pi = \alpha T, \tag{19}$$

where α – is the researched before thermoelectric driving force.

$$\Pi_{12} = \Pi_1 - \Pi_2, \tag{20}$$

where Π_{12} – is Peltier coefficient of junction of two conductors, Π_1 i Π_2 – is Peltier coefficient of each conductor apart.

With the help of Peltier coefficient, the quantity of allocated or absorbed heat is calculated, depending on how we use thermoelectric element – as a heater or as a coolant:

$$Q = \Pi_{12} It \tag{21}$$

where Q – is quantity of allocated or absorbed heat, I – is current's power, t – is the time of the current flow in the circle. For Thomson effect, the quantity of non-Jouel's heat, which is stood out in the volume, is defined through the temperature gradient with the next formula:

$$dQ^T = -\tau\left(gradT \cdot \vec{j}\right)dtdV, \tag{22}$$

where τ – is Thomson coefficient, where $[\tau] = [B]$.

Exactly the thermoelectric effects, which were described, are laid in the work of thermoelements, which generators' or coolers' thermoelectric modules are made of. At the same time, any thermoelectric module can work in the generator's regime, and in the cooler's or heater's regime as well. The difference is, that for the generation of energy and for the work in the cooler's/heater's regime, the different temperatures are optimal, accordingly different semiconducting chemical effects are optimal, which are used in the development of other thermoelectric modules. The example of thermoelectric module is shown on the Figure 1.

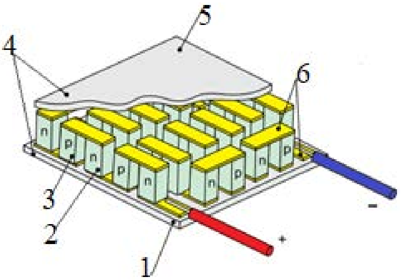

Figure 1. Schematic figure of thermoelectric module cut.
1 – the cold side, 2 – semiconductor thermoelement of n-type,
3 – semiconductor thermoelement p-type, 4 – ceramic plates,
5 – hot side, 6 – metallic contacts

3. Heterogeneous materials

3.1. Structure of heterogeneous materials

Heterogeneous materials become the next relevant scientific field after the age of nanomaterials. After almost a century of researches we almost reached the boundaries where we can improve the mechanic features of metals and alloys. Our commonly accepted knowledges from books and literature lie in strengthening of the weak matrix by the stronger base, as the part of second phase. During the last few years were researched the combinations of strength and flexibility in different metals and alloys, which are processed with different microstructures, including gradient structure, heterogeneous structure of lamellas, bimodal structure, harmonious structure, laminate structure, dual-phase steel, nano-phase structure, strung with grains, etc. These materials have one common feature: its solidity is sharply different on different phases, also sizes and geometry of phases may vary [5; 11]. In other words, these materials have enormous microstructure heterogeneity. That is why these materials might be considered as heterogeneous materials.

The principle of their creation is in layering in one system of some phases with different peculiarities. It is called the composite principle, which was used in order to reach the great progress in this or other field of study. Such layering is used in the modern metallurgy to create the reliable alloys, and in the thermoelectricity to create materials with higher quality.

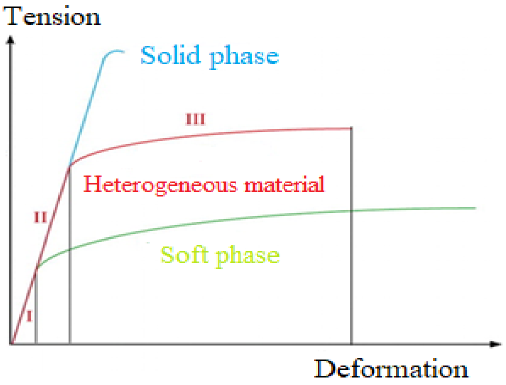

Figure 2. Three phases of deformation of heterogeneous materials

The heterogeneous materials may be defined as materials with sharp heterogeneous solidity from one phase to the other. The solidity of this heterogeneity may be caused by the microstructure heterogeneity, heterogeneity of crystal structure or compositional heterogeneity [6]. The sizes of phases may be in the range of micrometers to millimeters, geometry of phases may be changed while creating very diverse material systems.

The heterogeneous materials may be defined as materials with sharp heterogeneous solidity from one phase to the other. The solidity of this heterogeneity may be caused by the microstructure heterogeneity, heterogeneity of crystal structure or compositional heterogeneity [6]. The sizes of phases may be in the range of micrometers to millimeters, geometry of phases may be changed while creating very diverse material systems.

During the deformation, for example, the draft test of heterogeneous materials with the increasement of applied strain, the process of deformation may be classified by three stages (Figure 2). At the first stage, both, soft and solid, phases are deformed resiliently, that looks like the usually homogeneous material. At the second stage, the soft phases will start the dislocation slip, while the solid materials will stay elastic, which creates the mechanic incompatibility. The soft phases should be deformed with the solid neighboring phases, that is why they can't freely plastically deform. The strain on the phase surface of the fracture must be continuous, despite the weaker phases usually consist more strain because they are plastically deformed. Because of that, the plastic gradient of deformation appears. This gradient of deformation should correspond to the geometrically required dislocations, that will make the phase of enhancement softer, which leads to synergistic improvement of material characteristic in order to increase the general measured border of material fluidity.

In the extreme or ideal case, the soft phases will be fully surrounded by the solid phases, so that the soft phase will not change its form, as it is needed from plastic deformation, till the matrix of the solid phase starts to deform plastically [7]. The geometrically needed dislocations will accumulate on the borders of soft phases, as the matrix of the solid phase, making the global force of output much higher than it is provided for this mixture.

At the third phase, both, soft and solid phases, are plastically deformed, but the soft phases withstand the much higher strain, than the solid phases, what creates the so-named strain deformation. When the neighboring phases maintain the different plastic strain, it is expected that the gradients of deformation will exist near the phase borders of both, soft and solid, fields. These gradients of deformation will increase with the increasement of deformation, so it will cause the hardening under the pressure [12–17]. The hardened work hardening will help to prevent the appearance of the cords during the tensile tests, thus improving the plasticity [18].

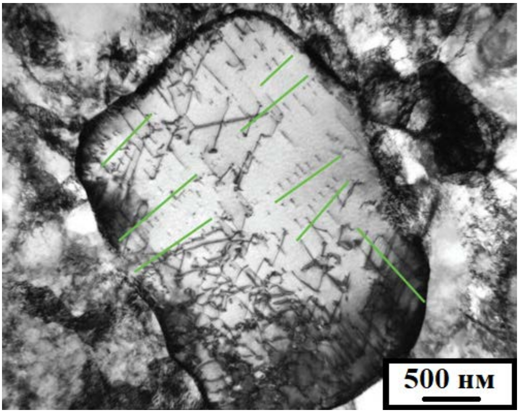

Figure 3. Soft grain 4 mkm size, surrounded by the solid ultrathin grained matrix in the heterogeneous lamella Ti. The dislocated accumulations are marked with green lines

3.2. Dislocations in heterogeneous materials and Burgers vector

In the plastic deformation of heterogeneous materials and alloys, usually, two types of dislocations take place: edge and screw. The flow intensity as a function of dislocation density is conventionally calculated as:

$$H = \alpha G b\left(\sqrt{\rho_S} + \sqrt{\rho_G}\right), \tag{23}$$

where H – is shear flow intensity, α – is a constant, G – is shear module, b – is value of Burgers vector, ρ_S and ρ_G – are densities of edge and screw dislocations.

Dislocation – is a linear crystallographic defect or the irregularity in the structure of crystal, which contains the sharp change of the atom's dislocation. The crystal order recovers from the both sides of dislocation, but atoms from one side transfer or slide. Dislocations mark the border between sliding and not high area of the material, and can't end in the border of grid, and should rather expand to the free edge, or create loop in the crystal. Dislocation may be characterized by distance and direction of motion, which is caused in atoms of a grid, what is called Burgers vector. This vector of dislocation stays permanent, even if the form of dislocation may change. There are multitude of types of dislocations, whereby there are movable and immovable dislocations. The motion of movable dislocations allows atoms to slide one over another when the level of strain is low. This effect is useful for alloy of metals, which are used in the industry, because movement of dislocation causes flexibility of given materials. The movement of dislocations may be enhanced or hampered by the presence of other materials in the crystal, and, by the flow of time, these elements might diffuse to dislocation and create Cottrel atmosphere. Clamping and detachment of these elements explain some unusual compliant behaviors, which are observed with steels [19].

Dislocations act like they are clear essence in the crystal material, where some types of dislocations may transfer because of binding of material and the change of form of the object. The dislocations are created by the deformation of crystal material, such as metals, which might cause their origin from surfaces, especially, when the strain is concentrated, or within material when the bead has defects. The quantity and location of dislocations cause many features of materials, such as flexibility, solidity and strength. Thermal treatment, alloy content and "cold" treatment may change the quantity and location of dislocation set, and the way of their transfer, and the interaction with the aim to create the useful feature.

It is worth noting, that in semiconducting materials assigned for the thin electronics, dislocation is tried to be avoided, because it causes many failures in the work of fine equipment [20].

The vectoral characteristics of dislocation in the crystal is Burgers vector. It represents direction and size of defections in the structure of crystal grid.

For the visual representation of Burgers vector, first, the "ideal" model of crystal grid is built without defects, then Burgers vector is set on it, visualizing distortions in the material structure.

The direction of vector depends on surface of dislocation, which is usually located on the one of the nearest packed crystallographic surfaces. The magnitude is usually presented with the next equation:

$$\| b \| = (a/2)\sqrt{h^2 + k^2 + l^2}, \tag{24}$$

where α – is an edge of a unit cell, *b* – is Burgers vector, *h, k, l* – are components of Burgers method.

It is worth noting, that formula (24) is good for calculating of Burgers vector only for grids, which are composed of volume-centered (VC) and face-centered (FC) unit cells.

Directly Burgers vector for VC and FC are calculated as:

$$b = \frac{a}{2}(hkl), \tag{25}$$

The magnitude of Burgers vector and directly Burgers vector for the primitive cubic grid:

$$b = a\sqrt{h^2 + k^2 + l^2}, \tag{26}$$

$$b = a(hkl), \tag{27}$$

At the edge dislocations, Burgers vector and the line of dislocations are perpendicular to each other, and at the edge ones – are parallel.

Transmission electron microscopy (TEM) method may be used to observe the dislocations inside the microstructure of the material [3]. Ultra-thin foil materials are prepared to make them transparent for electronic ray of microscope. Electronic ray is diffracted by the usual crystal lattice planes into a diffraction pattern, and this diffraction creates contrast in the image, as well as thickness fluctuations and various types of deformations.

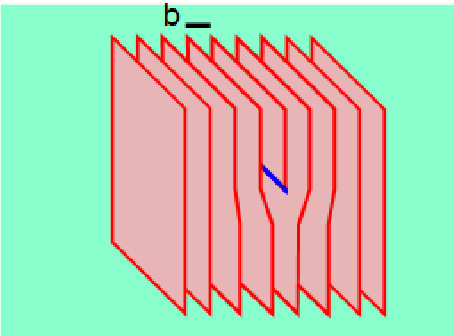

Figure 4. Schematic diagram of the edge dislocation. Burgers vector is marked with the black line, and the direction of edge dislocation – blue one

Dislocations have different local structure of atom and produce a deformation field, that is why they make the electrons in the microscope scatter in different ways.

Besides TEM, the field ion microscopy and atomic probing methods are used. The given methods allow to zoom in on the object of observation 3 million times and more and allow to observe the dislocations on the atomic level [21–23].

In order to observe the dislocations in the semiconductors we can use chemical pickling method. When the line of dislocation crosses the surface of metallic material, the associated strain field locally increases relative susceptibility of the material to acid digestion and digestion results. Thus, dislocations in silicon, for example, can be observed indirectly, using an interference microscope. The crystal orientation may be defined by the form of digestive pits, connected to dislocations.

If the material deforms and is digested repeatedly, then the series of digestive pits may be created, by which the movement of dislocations may be effectively tracked.

3.3. Heterogeneous systems

Heterogeneous systems exchange the heat, the mass and the charges with their surroundings. Systems are homogeneous phases, divided by interfacial area. They are electroneutral, but polarize. The interfacial area is also called the fracture surface [5].

Let's look at two stages of multi-component system which are balanced. System polarizes in the electric area. The last feature is relevant for electrochemical systems. In the systems, which transfer only heat and mass, this feature is not relevant. Homogeneous phases (index ^{i} and index ^{o})

have their inner energy, U^i and U^o, entropy, S^i i S^o, molar numbers, N_j^i and N_j^o components j, and also their polarization in the direction to the surface P^i, P^o. For the general system we have an equation:

$$U = U^i + U^s + U^o, \tag{28}$$

where U – is general energy of system, U^i and U^o – are energies of homogeneous stages which are divided by fracture surface, U^s – is energy of interfacial area.

So, we get analogous to equation (28) phrases for entropy, molar numbers and polarization:

$$S = S^i + S^s + S^o, \tag{29}$$

$$N_j = N_j^i + N_j^s + N_j^o, \tag{30}$$

$$P = P^i + P^s + P^o. \tag{31}$$

Thus, the surface is made of one or several layers of atoms or molecules with the insignificant volume, then we neglect the volume of interfacial surface:

$$V = V^i + V^o. \tag{32}$$

Density of polarization is the same for both, homogeneous phases and surface. The system might contain free charges, polar and apolar molecules. Electric field leads to polarization of apolar molecules and to orientation of polar molecules [24]. Besides, it leads to reallocation of free charges. In all cases, polarization occurs in the way where homogeneous phases and surface are kept electroneutral.

Out of second Maxwell quotation and of condition of electroneutrality we get:

$$\frac{d}{dx} D = 0, \tag{33}$$

where D – is displacement field. dx = equals zero.

That is why the normal component of displacement field is permanent in the whole heterogeneous system. Assuming that the system is invariant along the surface, follows, that the electric fields, displacement fields and polarization are normal for the surface. The displacement field is related to electric fields in two phases:

$$D = \varepsilon_0 E^i + P^i = \varepsilon_i E^i ; \Rightarrow D = \varepsilon_0 E^o + P^o = \varepsilon_o E^o, \tag{34}$$

where ε_i and ε_0 – are dielectric steels of phases ^{i} and ^{o} accordingly, ε_0 – is the dielectric constant of the vacuum, defined as:

$$\varepsilon_0 = \frac{1}{\mu_0 c_0^2} \approx 8.8542 \times 10^{-12} \left(\frac{\Phi}{м} \right). \tag{35}$$

Similar to (34) correlation may be written down for the electric field of the surface:

$$D^s = 0 = \varepsilon_0 E^s + P^s \rightarrow P^s = -\varepsilon_0 E^s . \tag{36}$$

Formula (36) shows that polarization of the surface equals negative dielectric constant multiplied by the surface of electric field. Field offset is characterized by sum ε_0 multiplied by electric field and density of polarization. Field offset is continuous on the surface, that is why the sum of electric field, which exceeds ε_0 plus density of surface polarization, should equal zero.

Thermodynamic potential of the system is defined as Gibbs energy. In the classic case, Gibbs equation is shown as:

$$G = U + PV - TS, \tag{37}$$

where U – is inner energy, P – is pressure, V – is volume, T – is an absolute temperature, S – is entropy.

For heterogeneous polarized systems we can write down the inner energy as a total differential of variables $S, N_j, V, \Omega, P^i, P^o$ i P^s by adapting Gibbs equation accordingly:

$$dU = TdS - \rho dV + \gamma d\Omega + \sum_{j=1}^{n} \mu_j dN_j + D_{eq} d \left(\frac{P^i}{\varepsilon_i} + \frac{P^s}{\varepsilon_0} + \frac{P^o}{\varepsilon_o} \right), \tag{38}$$

where D_{eq} – is displacement field resulting from the inverse transformation, P – is pressure, Ω – is surface area, μ – is a chemical potential, T – is the temperature, γ – is the surface tension.

By integrating the equations (2, 3, 10) we will get the definition of the energy of system:

$$U = TS - \rho V + \gamma \Omega + \sum_{j=1}^{n} \mu_j dN_j + D_{eq} \left(\frac{P^i}{\varepsilon_i} + \frac{P^s}{\varepsilon_0} + \frac{P^o}{\varepsilon_o} \right). \tag{39}$$

We shall write down Gibbs equation for phases ^{i} and ^{o} of the system and for the fracture surface accordingly:

$$dU^i = TdS^i - \rho dV^i + \sum_{j=1}^{n} \mu_j dN_j + D_{eq} d \frac{P^i}{\varepsilon_i}, \tag{40}$$

$$dU^o = TdS^o - \rho dV^o + \sum_{j=1}^{n} \mu_j dN_j + D_{eq} d\frac{P^o}{\varepsilon_o}, \tag{41}$$

$$dU^s = TdS^s + + \sum_{j=1}^{n} \mu_j dN_j + D_{eq} d\frac{P^o}{\varepsilon_o}. \tag{42}$$

By integrating these equations, we get:

$$U^i = TS^i - \rho V^i + \sum_{j=1}^{n} \mu_j dN_j + D_{eq} \frac{P^i}{\varepsilon_i}, \tag{43}$$

$$U^o = TS^o - \rho V^o + \sum_{j=1}^{n} \mu_j dN_j + D_{eq} \frac{P^o}{\varepsilon_o}, \tag{44}$$

$$U^s = TS^s + \gamma\Omega + \sum_{j=1}^{n} \mu_j dN_j^s + \frac{D_{eq}}{\varepsilon_o} P^s. \tag{45}$$

For equations (38-45) fair is equality of temperatures and chemical potentials: $\mu_j^i = \mu_j^o = \mu_j^s = \mu_j$; $T^i = T^o = T^s = T$. Pressure *P*, which is used in calculations, is also equal for both equations.

4. Nonequilibrium thermodynamics

4.1. Thermodynamics of small-scale systems

Thermodynamics may be applied only to systems with limitless quantity of particles located in the specific limitless volume with the constant density. Such conditions are called thermodynamic border. Taking into account these circumstances, we can accept the approximated description of the system, which provides the existence of the great quantity of particles and justifies absence of fluctuations. Thermodynamic border may be asymptotically approximated with the help of statistical mechanics. Thermodynamics deals with large-scale systems. Absence of thermodynamic border has important consequences to the behavior of the whole system. The reduction of size leads to the other script, where the input in the system of energy is absent in thermodynamic border, for example, in the surface energy [26–29]. This makes impossible the usual thermodynamic approach.

The typical example may be the limited little shares' cluster *N*. Let's express Gibbs energy for such cluster:

$$G = \mu N + \alpha N^{\beta}, \tag{46}$$

where G – is Gibbs energy of system, μ – is a chemical potential, α – is a random function, $\beta < 1$.

As it is seen in formula (46) – if the quantity of share N increases, then the total relative contribution of the second component of the equation (46) in relation to the first one falls down.

Let's look at the corresponding equation under the condition of a sufficiently large value N, where the condition $\mu N \gg \alpha N^{\beta}$ is fair:

$$G \approx \mu N. \tag{47}$$

Such approximation simplifies the practical calculation of thermodynamic potential of the system under the condition of a sufficient large value N.

In the case, when we can't use phrase (46) instead of phrase (47), it means that in order for the system to be investigated, we can't use only thermodynamic approach, because then Gibbs energy is not extensive energy in the system, and fluctuations start to play a great role in its description.

Thermodynamics of small systems is well-formulated for the equilibrium states. Therefore, in many experimental systems instead of using the tranquility state, we use non-equilibrium in the time configurations. Such situation usually happens in such kinetic processes [6; 7], as inception and growth of small clusters [8], in the non-covalent association of proteins, and in the active transportation of substances through biological membranes.

4.2. Mesoscopic non-equilibrium thermodynamics

The reduction of scale of observation by system's time and length usually leads to increasement of quantity of non-equilibrium degrees of freedom [30]. Such degrees of freedom, marked as $\gamma \equiv (\gamma_i)$, may, for example, present the velocity of colloidal particle, magnetic moment orientation, size of macromolecule or any parameter of coordinate or arrangement, whose meanings define the state of system in the phase space. The characteristics of system's state at the mesoscopic level flows out P (γ, t) density of probabilities of system's finishing in the state γ at the time moment t. In order to bring the system to a state, which is characterized by a certain value γ, we need to make some effort. The minimal needed reversible work $\Delta W(\gamma)$ is defined as:

$$\Delta W = \Delta U - T\Delta S + \rho\Delta V - \mu\Delta M + y\Delta Y, \tag{48}$$

where E – is an inner energy, S – is entropy, V – is volume, M – is mass, μ – is a chemical potential, y – is an intensive parameter, Y – is an aggregate variable.

The expression of work converges to different thermodynamic potentials, making restrictions, which define these potentials. For example, in the case of permanent temperature, volume, quantity and particles, the minimal work corresponds to free Gelmgols energy [31].

We shall consider, that the evolution of stages of freedom is described by the process of diffusion in gamma-space and we shall write down the appropriate form of Gibbs equation:

$$dS = -\frac{1}{T}\int \mu(\gamma)\,dP(\gamma,t)\,d\gamma, \tag{49}$$

which corresponds to the law in the non-equilibrium thermodynamics, which is used for the research of diffusive processes. In this equation μ(γ) – is a generalized chemical potential, related to density of probability.

As an alternative, variants of entropy may be calculated through the postulate of Gibbs entropy:

$$S = S_{eq} - k_B \int P(\gamma,t)\,ln\left(P\frac{(\gamma,t)}{P_{eq}(\gamma)}\right)d\gamma, \tag{50}$$

where S_{eq} – is the entropy of system in the equilibrium state for which the density of probability is defined as:

$$P_{eq} = exp\left(\frac{-\Delta W(\gamma)}{k_B T}\right), \tag{51}$$

where k_B – is Boltsman constant.

Let's write down the variations (50):

$$dS = -k_B \int dP(\gamma,t)\,ln\left(P\frac{(\gamma,t)}{P_{eq}(\gamma)}\right)d\gamma, \tag{52}$$

$$dS_{eq} = \frac{-1}{T}\int \mu_{eq}(\gamma)\,dP(\gamma,t)\,d\gamma, \tag{53}$$

where μ_{eq} – is a chemical potential in an equilibrium state.

The comparison of two equations helps to define the generalized thermodynamic chemical potential in the equation:

$$\mu(\gamma,t) = k_B T\left[ln\left(\frac{P(\gamma,t)}{P_{eq}(\gamma)}\right)\right] + \mu_{eq}, \tag{54}$$

which, taking into account (51) may be written down as following:

$$\mu(\gamma,t) = k_B T\left[ln\left(P(\gamma,t)\right)\right] + \Delta W. \tag{55}$$

The evolution of system is characterized by the generalized diffusive process in the space of mesoscopic variables γ. The process is set into action by the thermodynamic force:

$$F_T = \frac{d}{d\gamma}\frac{\mu}{\mathrm{T}}. \tag{56}$$

The production of entropy by the process is defined by the equation:

$$\sigma = \frac{-1}{\mathrm{T}}\int J\frac{d\mu}{d\gamma}d\gamma, \tag{57}$$

this very equation, but using chemical potential:

$$\sigma = -k_B\int J(\gamma,t)\frac{d}{d\gamma}\left(ln\frac{P(\gamma,t)}{P_{eq}(\gamma)}\right)d\gamma. \tag{58}$$

In the next equation we may identify thermodynamic forces as the gradient in the space of mesoscopic variables of logarithm's relation of density of probability to its equilibrium meaning. Current and thermodynamic power may be related in a linear way.

$$J(\gamma,t) = k_B L\left(\gamma, P(\gamma)\right)\frac{d}{d\gamma}ln\left(\frac{P(\gamma,t)}{P_{eq}(\gamma)}\right), \tag{59}$$

where $L(\gamma,P(\gamma))$ – is Onsager coefficient, which, generally, is function in $P(\gamma)$ and coordinate γ (gamma). In order to get this equation, the locality in the gamma-surface was taken into account, for which only the powers with same meaning γ connect. Current may be replaced by the equation of continuity:

$$\frac{dP}{dt} = -\left[\frac{dJ}{d\gamma}\right], \tag{60}$$

$$\frac{dP}{dt} = \frac{d}{d\gamma}\left(DP_{eq}\frac{d}{d\gamma}\frac{P}{P_{eq}}\right), \tag{61}$$

where the diffusion coefficient is calculated as:

$$D(\gamma) \equiv \frac{k_B L(\gamma, P)}{P}. \tag{62}$$

4.3. Boltsman equation

Boltsman equation describes the evolution of allocation of particles of non-equilibrium thermodynamic system by speeds and in the space of coordinates [33].

Let's specify Boltsman equation to define the time evolution for the function of distribution of particles fi:

$$\frac{df_i}{dt} + \overrightarrow{v_i}\frac{df_i}{d\vec{r}} + \frac{1}{m_i}\left(\overrightarrow{F_i} + e_i\overrightarrow{v_i} \times B\right)\frac{df_i}{d\overrightarrow{v_i}} = \sum_{i,j=a}^{b} J\left(f_i, f_j\right). \tag{63}$$

$$\overrightarrow{F_i} = \overrightarrow{F_i^{(e)}} + e_i\vec{E}, \text{for}\, i, j = a, b. \tag{64}$$

Here $\overrightarrow{F_i^{(e)}}$ is an outer conservative force, vector $\vec{E}$ and $\vec{B}$ – are electric and magnetic fields. These fields – are coherent, generated by plasma, defined from Maxwell equations:

$$J\left(f_i, f_j\right) = \iiint\left[f\left(\overrightarrow{v_i^{'}}\right)f\left(\overrightarrow{v_j^{'}}\right) - f\left(\overrightarrow{v_i}\right)f\left(\overrightarrow{v_j}\right)\right]\sigma\left(\overrightarrow{v_i}, \overrightarrow{v_j} \to \overrightarrow{v_i^{'}}, \overrightarrow{v_j^{'}}\right)g_i d\overrightarrow{v_i} d\overrightarrow{v_i^{'}} d\overrightarrow{v_j^{'}}. \tag{65}$$

We should notice, that for equation (65) dependence of fi to r and t is not taken into account.

The magnetic induction B is accepted by the averaged magnetic field, defined out from Maxwell equations, where the current's density will depend upon distribution functions f_i. Actually, we should write $B = B_{av} + B_e$, де B_e – is the outer field, which might be, or might not be the permanent field [32]. The intersection of σ pleases the principle microscopic reversibility, namely, it is the invariant in the space and time imprint, that's why:

$$\sigma\left(\overrightarrow{v_i}, \overrightarrow{v_j} \to \overrightarrow{v_i^{'}}, \overrightarrow{v_j^{'}}\right) = \sigma\left(\overrightarrow{v_i^{'}}, \overrightarrow{v_j^{'}} \to \overrightarrow{v_i}, \overrightarrow{v_j}\right). \tag{66}$$

4.4. Physical model of heterogeneous permeable thermoelement

The physical model of random permeable thermoelement for the thermoelectric cooling is shown at the Figure 5. It contains semi-conduct branches of *n*- and *p*-types of conductivity, every branch contains of N_p segments allocated at the distance hк from each other. The width of

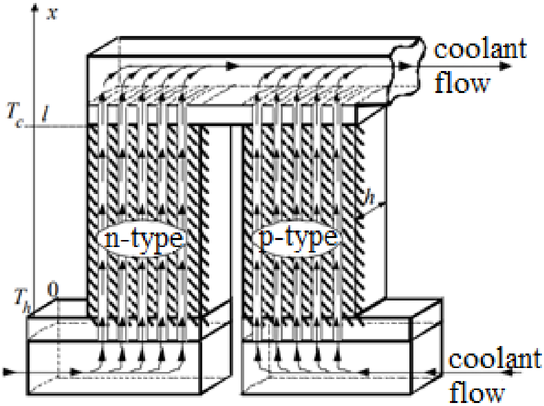

Figure 5. Model of permeable thermoelement for thermoelectric heat pump

the segment *h*, and its thickness h_p. The gaps between segments create channels, where the air or liquid coolant is pumped for its cooling – warm and cold spikes of thermoelement under the meanings $T_{г}$ and T_x accordingly. The coolant is pumped in the direction from cold spikes to the warm ones.

5. Calculation of energetic characteristics of permeable thermoelement based on bismuth telluride

Let's calculate the characteristics on the basis of 1-D model of permeable thermoelectric element. Our calculations will be based upon calculations of equation system (67) for the coolant and semi-conduct material of branches of conductor *n*- and *p*-types of conductivity:

$$\begin{cases} \dfrac{dT}{d\chi} = \dfrac{-\alpha j}{\kappa} T - \dfrac{q}{\kappa}, \\ \dfrac{dq}{d\chi} = \dfrac{\alpha^2 j}{\kappa} T + \dfrac{\alpha j}{\kappa} q + i^2 \rho - \dfrac{\alpha_T P_K N_K l^2}{(S - S_K) j} (T - t), \\ \dfrac{dt}{d\chi} = \dfrac{\alpha_T P_K N_K l}{V c_p S_K} (T - t), \end{cases} \tag{67}$$

where T and t temperature of branch's material and coolant at the point χ accordingly, $\chi = x/l$ – is dimensionless coordinate; S_K – is a cross-sectional area of all channels; S – is a cross-section of the branch with channels; P_K – is channel's parameter; N_K – is quantity of channels in the branch; V – is mass velocity of coolant in the channels; α_T – is a coefficient of heat transfer in the channel; j – is a density of the current, which is defined as:

$$j = i \times l, \tag{68}$$

where i – is a specific current density, l – is a height of branches of thermoelectric element, q – is the given specific heat flow, which is defined by formula:

$$q = \frac{1}{j}\left(\alpha j T - \kappa \frac{dT}{d\chi}\right). \tag{69}$$

In order to find a solution of the task, let's use the principle of Pontryagin maximum form mathematic theory of optimal control [38–40], which gives the needed conditions of optimality:

1) Optimal meanings of specific current density in branches of thermoelement have to satisfy equalities:

$$-\left[\frac{dJ}{dj}\right]_{np} + \sum_{np}\int_0^1 \left[{}_1\frac{df_1}{dj} +{}_2 \frac{df_2}{dj} +{}_3 \frac{df_3}{dj}\right]_{np} d\chi = 0, \tag{70}$$

where J – is a functional, which characterizes the effectiveness of the energy's transformation process from thermal to electric and vice versa. For thermoelectric generator – efficiency factor, for thermoelectric refrigeration – cooling coefficient; $\Psi = (\Psi_1, \Psi_2, \Psi_3)$ – it is vector-function of impulses;

2) Optimal meanings of required parameters of permeable element ω_i are defined in the system of differential equations:

$$-\left[\frac{dJ}{d\omega_i}\right]_{np} + \sum_{np}\int_0^1 \left[\varepsilon_1 \frac{df_1}{d\omega_1} + \varepsilon_2 \frac{df_2}{d\omega_2} + \varepsilon_3 \frac{df_3}{d\omega_3}\right]_{np} d\chi = 0, \tag{71}$$

Taking into account the given correlations, by using the method of successive approximations, multiple methods for solving the system of equations (67) and Newton method, and using the computer program to project the permeable thermoelectric element, we calculated the meanings of parameters of thermoelectric refrigeration (Table 1) and we created graphs of dependence of cooling coefficient of thermoelectric elements on mass velocity of the coolant in it, and dependence of heat current on channels perimeter.

Table 1

Results of calculations of parameters of thermoelectric refrigeration

Quantity of channels: N_k = 10; Height of branch: TEEl = 1 [sm]; Heat transfer coefficient: A_t = 0.0100 [Watt/(sm^2*K)]; Temperature of hot side: T_h = 300 [K]; Temperature of cold side: T_c = 250 [K]; Temperature of air at the hot side: T_{h_v} = 303 [K]; Contact resistance: R_o infinitesimally small.

l, sm	V, (g×sm)/sec	ε	Q, Watt	t(l)-K	Sк/S	Sm/Sк	Hк, sm	S-Hк, sm
1.00	1.11427	0.600877	1.187644	254.587	0.0110	89.9091	0.0011	0.0989
1.00	0.57740	0.601020	1.175924	254.545	0.0210	46.6190	0.0021	0.0979
1.00	0.38690	0.601162	1.164200	254.502	0.0310	31.2581	0.0031	0.0969
1.00	0.28933	0.601306	1.152470	254.459	0.0410	23.3902	0.0041	0.0959
1.00	0.23003	0.601450	1.140736	254.416	0.0510	18.6078	0.0051	0.0949
1.00	0.19017	0.601594	1.128997	254.373	0.0610	15.3934	0.0061	0.0939
1.00	0.16155	0.601739	1.117253	254.329	0.0710	13.0845	0.0071	0.0929
1.00	0.13999	0.601884	1.105504	254.286	0.0810	11.3457	0.0081	0.0919
1.00	0.12317	0.602030	1.093750	254.243	0.0910	9.9890	0.0091	0.0909
1.00	0.10969	0.602177	1.081992	254.200	0.1010	8.9010	0.0101	0.0899
1.00	0.09863	0.602323	1.070228	254.156	0.1110	8.0090	0.0111	0.0889
1.00	0.08941	0.602471	1.058460	254.113	0.1210	7.2645	0.0121	0.0879
1.00	0.08159	0.602618	1.046686	254.069	0.1310	6.6336	0.0131	0.0869
1.00	0.07489	0.602767	1.034908	254.026	0.1410	6.0922	0.0141	0.0859
1.00	0.06907	0.602916	1.023124	253.982	0.1510	5.6225	0.0151	0.0849
1.00	0.06398	0.603065	1.011335	253.938	0.1610	5.2112	0.0161	0.0839
1.00	0.05948	0.603215	0.999541	253.894	0.1710	4.8480	0.0171	0.0829
1.00	0.05190	0.603516	0.975938	253.806	0.1910	4.2356	0.0191	0.0809
1.00	0.04868	0.603667	0.964128	253.762	0.2010	3.9751	0.0201	0.0799
1.00	0.04576	0.603819	0.952314	253.718	0.2110	3.7393	0.0211	0.0789
1.00	0.04311	0.603971	0.940493	253.674	0.2210	3.5249	0.0221	0.0779
1.00	0.04069	0.604124	0.928668	253.630	0.2310	3.3290	0.0231	0.0769
1.00	0.03643	0.604432	0.905001	253.541	0.2510	2.9841	0.0251	0.0749
1.00	0.03280	0.604741	0.881311	253.452	0.2710	2.6900	0.0271	0.0729
1.00	0.03118	0.604897	0.869459	253.408	0.2810	2.5587	0.0281	0.0719
1.00	0.02967	0.605053	0.857600	253.363	0.2910	2.4364	0.0291	0.0709
1.00	0.02826	0.605209	0.845736	253.319	0.3010	2.3223	0.0301	0.0699
1.00	0.02695	0.605367	0.833866	253.274	0.3110	2.2154	0.0311	0.0689
1.00	0.02571	0.605524	0.821991	253.229	0.3210	2.1153	0.0321	0.0679
1.00	0.02455	0.605683	0.810110	253.184	0.3310	2.0211	0.0331	0.0669

(Continuation of Table 1)

l, sm	V, (g×sm)/sec	ε	Q, Watt	t(l)-K	Sк/S	Sm/Sк	Hк, sm	S-Hк, sm
1.00	0.02346	0.605841	0.798223	253.139	0.3410	1.9326	0.0341	0.0659
1.00	0.02243	0.606001	0.786330	253.094	0.3510	1.8490	0.0351	0.0649
1.00	0.02146	0.606161	0.774432	253.049	0.3610	1.7701	0.0361	0.0639
1.00	0.02054	0.606321	0.762527	253.004	0.3710	1.6954	0.0371	0.0629
1.00	0.01967	0.606482	0.750617	252.958	0.3810	1.6247	0.0381	0.0619
1.00	0.01885	0.606644	0.738701	252.913	0.3910	1.5575	0.0391	0.0609
1.00	0.01807	0.606806	0.726779	252.868	0.4010	1.4938	0.0401	0.0599
1.00	0.01732	0.606969	0.714850	252.822	0.4110	1.4331	0.0411	0.0589
1.00	0.01661	0.607132	0.702916	252.776	0.4210	1.3753	0.0421	0.0579
1.00	0.01594	0.607296	0.690976	252.731	0.4310	1.3202	0.0431	0.0569
1.00	0.01529	0.607461	0.679029	252.685	0.4410	1.2676	0.0441	0.0559
1.00	0.01468	0.607626	0.667076	252.639	0.4510	1.2173	0.0451	0.0549
1.00	0.01409	0.607791	0.655117	252.593	0.4610	1.1692	0.0461	0.0539
1.00	0.01353	0.607957	0.643152	252.547	0.4710	1.1231	0.0471	0.0529
1.00	0.01299	0.608124	0.631180	252.501	0.4810	1.0790	0.0481	0.0519
1.00	0.01247	0.608292	0.619202	252.455	0.4910	1.0367	0.0491	0.0509
1.00	0.01197	0.608460	0.607217	252.409	0.5010	0.9960	0.0501	0.0499
1.00	0.01150	0.608628	0.595226	252.363	0.5110	0.9569	0.0511	0.0489
1.00	0.01104	0.608798	0.583229	252.317	0.5210	0.9194	0.0521	0.0479
1.00	0.01060	0.608967	0.571225	252.270	0.5310	0.8832	0.0531	0.0469
1.00	0.01017	0.609138	0.559214	252.224	0.5410	0.8484	0.0541	0.0459
1.00	0.00977	0.609309	0.547197	252.177	0.5510	0.8149	0.0551	0.0449
1.00	0.00937	0.609480	0.535173	252.130	0.5610	0.7825	0.0561	0.0439
1.00	0.00899	0.609653	0.523143	252.084	0.5710	0.7513	0.0571	0.0429
1.00	0.00863	0.609826	0.511105	252.037	0.5810	0.7212	0.0581	0.0419
1.00	0.00793	0.610173	0.487010	251.943	0.6010	0.6639	0.0601	0.0399
1.00	0.00760	0.610348	0.474952	251.896	0.6110	0.6367	0.0611	0.0389
1.00	0.00728	0.610524	0.462887	251.849	0.6210	0.6103	0.0621	0.0379
1.00	0.00697	0.610700	0.450815	251.802	0.6310	0.5848	0.0631	0.0369
1.00	0.00668	0.610876	0.438736	251.754	0.6410	0.5601	0.0641	0.0359
1.00	0.00639	0.611054	0.426650	251.707	0.6510	0.5361	0.0651	0.0349
1.00	0.00611	0.611232	0.414557	251.660	0.6610	0.5129	0.0661	0.0339
1.00	0.00583	0.611410	0.402457	251.612	0.6710	0.4903	0.0671	0.0329
1.00	0.00557	0.611590	0.390349	251.564	0.6810	0.4684	0.0681	0.0319

(End of Table 1)

l, sm	V, (g×sm)/sec	ε	Q, Watt	t(l)-K	Sк/S	Sm/Sк	Hк, sm	S-Hк, sm
1.00	0.00507	0.611950	0.366111	251.469	0.7010	0.4265	0.0701	0.0299
1.00	0.00482	0.612132	0.353982	251.421	0.7110	0.4065	0.0711	0.0289
1.00	0.00459	0.612314	0.341845	251.373	0.7210	0.3870	0.0721	0.0279
1.00	0.00436	0.612496	0.329700	251.325	0.7310	0.3680	0.0731	0.0269
1.00	0.00414	0.612679	0.317548	251.277	0.7410	0.3495	0.0741	0.0259
1.00	0.00393	0.612863	0.305388	251.229	0.7510	0.3316	0.0751	0.0249
1.00	0.00372	0.613048	0.293220	251.180	0.7610	0.3141	0.0761	0.0239
1.00	0.00351	0.613234	0.281045	251.132	0.7710	0.2970	0.0771	0.0229
1.00	0.00331	0.613420	0.268862	251.084	0.7810	0.2804	0.0781	0.0219
1.00	0.00312	0.613606	0.256671	251.035	0.7910	0.2642	0.0791	0.0209
1.00	0.00293	0.613794	0.244472	250.986	0.8010	0.2484	0.0801	0.0199
1.00	0.00275	0.613982	0.232266	250.938	0.8110	0.2330	0.0811	0.0189
1.00	0.00257	0.614171	0.220051	250.889	0.8210	0.2180	0.0821	0.0179
1.00	0.00240	0.614360	0.207828	250.840	0.8310	0.2034	0.0831	0.0169
1.00	0.00223	0.614551	0.195597	250.791	0.8410	0.1891	0.0841	0.0159
1.00	0.00206	0.614742	0.183358	250.742	0.8510	0.1751	0.0851	0.0149
1.00	0.00190	0.614933	0.171111	250.693	0.8610	0.1614	0.0861	0.0139
1.00	0.00174	0.615126	0.158855	250.644	0.8710	0.1481	0.0871	0.0129
1.00	0.00159	0.615319	0.146591	250.594	0.8810	0.1351	0.0881	0.0119
1.00	0.00144	0.615513	0.134318	250.545	0.8910	0.1223	0.0891	0.0109
1.00	0.00129	0.615708	0.122037	250.495	0.9010	0.1099	0.0901	0.0099
1.00	0.00115	0.615903	0.109747	250.446	0.9110	0.0977	0.0911	0.0089
1.00	0.00101	0.616099	0.097449	250.396	0.9210	0.0858	0.0921	0.0079
1.00	0.00087	0.616296	0.085141	250.346	0.9310	0.0741	0.0931	0.0069
1.00	0.00075	0.616474	0.074056	250.301	0.9400	0.0638	0.0940	0.0060
1.00	0.00073	0.616494	0.072824	250.296	0.9410	0.0627	0.0941	0.0059
1.00	0.00060	0.616692	0.060497	250.246	0.9510	0.0515	0.0951	0.0049
1.00	0.00047	0.616891	0.048159	250.196	0.9610	0.0406	0.0961	0.0039
1.00	0.00035	0.617091	0.035806	250.146	0.9710	0.0299	0.0971	0.0029

At the Figure 6 the accurate linear growth of cooling coefficient when the size of channel of permeable thermoelectric element increases. This correlation may be written down as following:

$$\varepsilon = \frac{Q_{refr}}{W_{TE}} f\left(H_{\kappa}, N_{\kappa}\right), \tag{72}$$

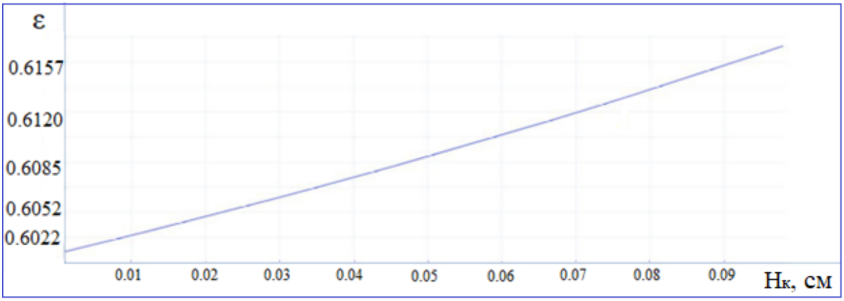

Figure 6. Graph of dependence of cooling coefficient of thermoelectric element for thermoelectric refrigerator on width of channel of permeable element

where Q_{refr} – is a refrigeration capacity, W_{TE} – is a capacity of power of cooling element, $H_{к}$ and $N_{к}$ – are width of channel of permeable element and quantity of channels accordingly.

From graphs on Figure 7 we can accurately see the sharp fall of velocity of the coolant in the channel during the growth of channels' sizes. The function of velocity's decline has an asymptotic nature [38]. Approximately descending function of dependence of velocity's fall of the coolant reminds the function $y = \frac{1}{x}$, for x>0.

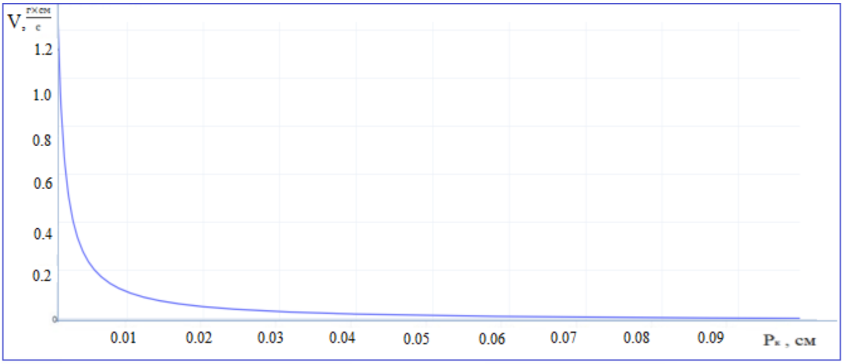

Figure 7. Dependence of mass velocity of the coolant on width of channel

Justification of velocity’s descendance of the coolant is given in the formula:

$$V_{н} = \frac{v_{н}}{S_{ch} \times N_{ch}}, \tag{73}$$

where $v_{н}$ – is volume of the coolant, $V_{н}$ – its velocity, S_{ch} – is a cross-sectional area of the channel, N_{ch} – is a quantity of channels.

The allocation of velocities in the permeable thermoelectric element and its correlation with the distribution of temperatures in the coolant is shown at the Figure 8.

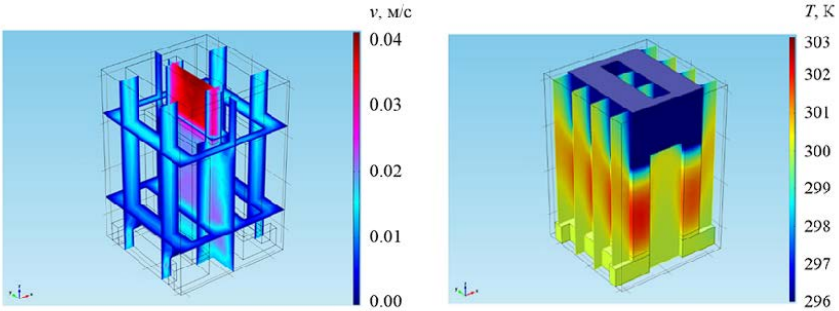

Figure 8. Allocation of velocities of the coolant and the distribution of temperatures in the coolant of permeable thermoelement accordingly [25]

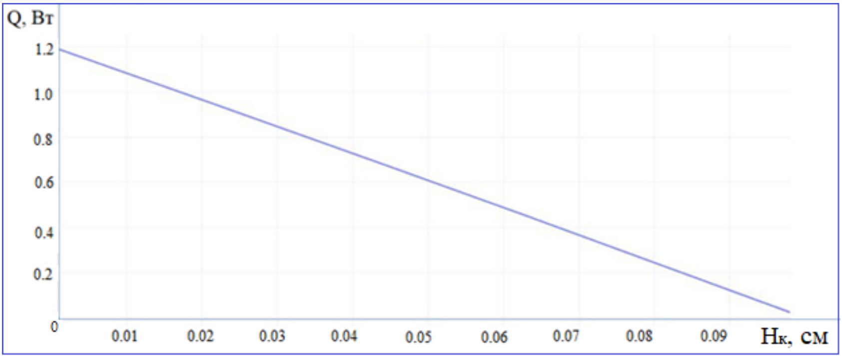

Figure 9. Dependence of the concentration of the heat flow on the width of the channel

The linear descendance of the concentration of the heat flow in the channel while it is getting bigger is shown at the Figure 9.

This is due to better dispersion of the warmth when the diameter of the channels is bigger in the permeable thermoelectric element:

$$Q = f\left(H_{\kappa}, N_{\kappa}\right), \tag{74}$$

$$f\left(H_{\kappa}, N_{\kappa}\right) = \sum_{N_{\kappa}} S_{\kappa i.}. \tag{75}$$

Here Q is defined as function H_{κ} and N_{κ}, which is accordingly defined as sum of cross-sectional areas of all channels of the permeable thermoelectric element.

By applying graphs of dependences of the calculated characteristics of the permeable thermoelectric elements, graphically we find the point of intersection of dependences of cooling coefficient ε and of heat flow Q on H_{κ} (Figure 10). The point X_{opt} points to the optimal width of the channel of the permeable thermoelement.

Comparative analysis of the permeable and impermeable thermoelements is shown on the graph (Figure 11).

It is clearly seen on the Figure that permeable thermoelement prevails the impermeable one. The graph is built up on the example of comparison of ε thermoelements with the same temperature drop $\Delta T = 50$ K.

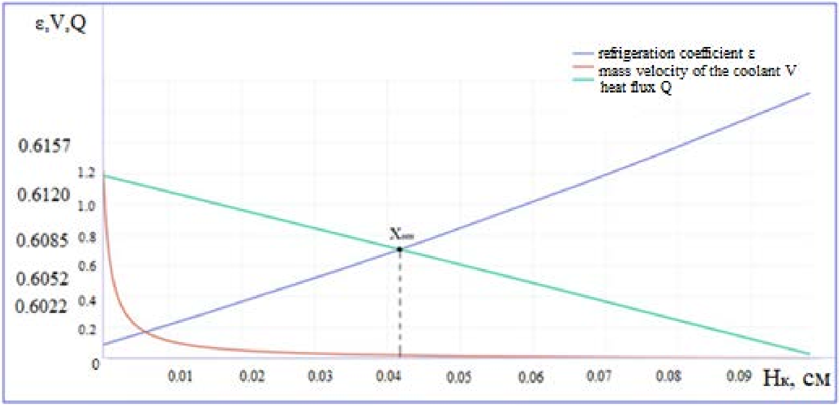

Figure 10. Summarized graph of dependences ε, *V*, *Q* on the width of channel

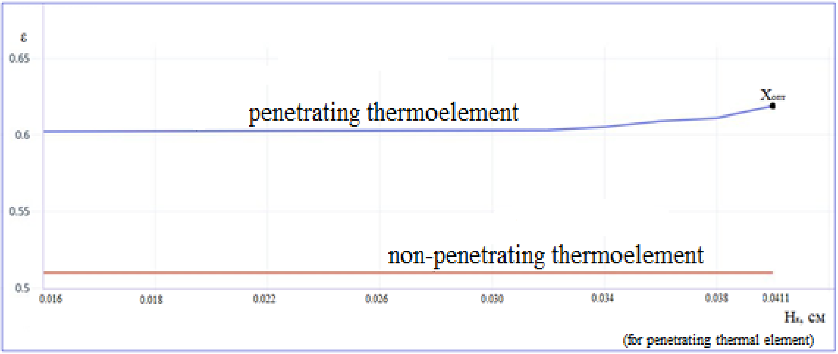

Figure 11. Comparison of the cooling coefficients of the permeable and impermeable thermoelectric element on the base of Bi-Te with the temperature difference $\Delta T = (T_г - T_x) = 50$ K

6. Conclusions

The analysis of the processes in the non-equilibrium thermodynamic systems and the flow of thermodynamic processes in the heterogeneous materials was done. The similar processes are described in the analytical review of the literature. The analogous calculations were done for thermoelectric processes, which are described with correlations of non-equilibrium thermodynamic.

While researching the correlation of non-equilibrium thermodynamic, namely Gibbs equation, Boltsman equation, equation of coolant and heat flow, cooling coefficient equation and by its summarizing, we calculated the optimal parameters for the permeable thermoelectric element of cooling on the base of heterogeneous semi-conductive alloy Bi2Te3.

Basing on the correlations given in the work, using the method of coherent approximations, multiple methods of the solution of the system' equations and Newton method, and using the computer program of projecting the permeable thermoelectric element, we calculated the meanings of parameters of thermoelectric refrigerator.

On the basis of conducted calculations, we graphed the dependences of parameters of semi-conduct permeable thermoelement, exactly the cooling coefficient, mass velocity of the coolant and the heat flow on the width of the channel. The consolidated schedule of the dependence of these parameters was created and the point, which indicates the optimal width of the channel of permeable thermoelement was shown. According to the calculations, the optimal meaning of the channel width for the investigated permeable thermoelectric element is the meaning where $H_к = 0.0411$ sm.

The comparative analysis of the cooling coefficient between permeable and impermeable thermoelements was done. Its results are shown in the schedule. The results of the comparison show that the permeable element has more optimal meanings. The advantage of cooling coefficient of the permeable thermoelement over the impermeable exists because of the system of channels with the coolant, which changes the gradient and the allocation of temperatures on the thermoelement.

References:

1. B. Flem, Q. Xu, S. Kjelstrup and Å. Sterten (2001) Thermoelectric powers of cells with NaF-AlF3-Al2O3 melts. J. Non-Equilib. Thermodyn., 26: 125–151.
2. T. Førland and S. Kjelstrup Ratkje (1981) Irreversible thermodynamic treatment of frost heave. Engineering Geol., 18: 225–229.
3. T. Suzuki, K. Iwano, R. Kiyono and M. Tasaka (1995) Thermoosmosis and transported entropy of water across hydrocarbonsulfonic acid-type cationexchange-membranes. Bull. Chem. Soc. Jpn., 68: 493–501.
4. Y. Demirel (2002) Non-equilibrium Thermodynamics. Transport and Rate Processes in Physical and Biological Systems. Elsevier, Amsterdam.
5. Hull, D., Bacon, D. J. (2001) Introduction to dislocations (4th ed.). Butterworth-Heinemann.
6. Gibbs, J. Willard (May 1877 – July 1878). "On the Equilibrium of Heterogeneous Substances".
7. D.G. Miller (1960) Thermodynamics of irreversible processes. The experimental verification of the Onsager reciprocal relations. Chem. Revs., 60: 15–37.
8. F. Bresme, B. Hafskjold and I. Wold (1996) Nonequilibrium molecular dynamics study of heat conduction in ionic systems. J. Phys. Chem., 100: 1879–1888.
9. R. Haase (1969) Thermodynamics of Irreversible Processes. Addison-Wesley, Reading, MA.
10. L. Waldmann (1967) Non-equilibrium thermodynamics of boundary conditions. Z. Naturforschung, 22a: 1269–1280.
11. D. Bedeaux (1986) Nonequilibrium thermodynamics and statistical physics of surfaces. Adv. Chem. Phys., 64: 47–109.
12. J. Meixner (1941) Zur Thermodynamik der Thermodiffusion. Ann. Physik 5. Folge, 39: 333–356.
13. S.R. de Groot and P. Mazur (1984) Non-Equilibrium Thermodynamics. Dover, London.

14. Kaye, J. and Welsh, J.A. (eds) (1960) Direct Conversion of Heat to Electricity, John Wiley & Sons, Inc.

15. Sutton, G.W. (ed.) (1966) Direct EnergyConversion, Inter-University Electronics Series, vol. 3, McGraw-Hill BookCompany.

16. Seebeck, T.J. (1823) Magnetische Polarisationder Metalle und Erze durch-Temperatur-Differenz. Technical report, (1822–1825) Reports of the Royal Prussian Academy of Science, Berlin.

17. Nolas, G.S., Sharp, J., and Goldsmid, H.J. (2001) Thermoelectrics: Basic Principles and New Materials Development, Springer Series in Material Science, vol. Springer-Verlag, Berlin.

18. Riffat, S.D. and Ma, X. (2003) Thermoelectrics: a review of present and potential applications. Appl. Therm. Eng.

19. Rowe, D.M. and Bhandari, C.M. (1983) Modern Thermoelectrics, Reston Publishing Company, Inc., Reston, VA.

20. Anatychuk, L. I. (1998) Physics of Thermoelectricity, Thermoelectricity, vol. 1, Institute of Thermoelectricity, Ukraine.

21. Anatychuk, L. I. (2003) Thermoelectric Power Converters, Thermoelectricity, Thermodynamics and Thermoelectricity, vol. 2, Institute of Thermoelectricity, Kyiv-Chernivtsi.

22. Anatychuk L. I., Vykhor L. M. (2012) *Termoélektrychestvo, tom IV. Funktsyonal'no-hradyentnye termoélektrycheskye materyaly* [Thermoelectrics, volume IV. Functional gradient thermoelectric materials]. Chernovtsy: Instytut termoelektrychestva. (in Ukrainian)

23. Vykhor L. M., Horskyy P. V. (2015) Elektrychnyy opir kontaktu termoelektrychnyy material – metal [Electrical resistance of the contact thermoelectric material – metal]. *Termoelektryka – Thermoelectricity*, no. 2. (in Ukrainian)

24. Mykhaylovskyy V. Ya., Vykhor L. M., Maksymuk M. V., Mochernyuk R. M. (2015) Proektuvannya termoelektrychnykh kaskadnykh moduliv z sektsiynymy vitkamy na osnovi Bi2Te3-PbTe-TAGS [Design of thermoelectric cascade modules with sectional branches based on Bi2Te3-PbTe-TAGS]. *Termoelektryka – Thermoelectricity*, no. 2. (in Ukrainian)

25. Cherkez R. H. (2016) Pro modelyuvannya pronyknykh termoelementiv [On modelling permeable thermocouples]. *Termoelektryka. – Thermoelectricity*, no. 1. (in Ukrainian)

26. Anatychuk L. I., Kobylyans′kyy R. R., Konstantynovych I. A., Kuz′ R. V., Manyk O. M., Nitsovych O. V., Cherkez R. H. (2016) Tekhnolohiya vyhotovlennya termoelektrychnykh mikrobatarey [Technology for manufacturing thermoelectric microbatteries]. *Termoelektryka – Thermoelectricity,* no. 6. (in Ukrainian)

27. Cherkez R. (2018) Capabilities of permeable thermoelectric elements // 18th International Balkan Workshop on Applied Physics. Constanta, Romania, July 10–13. Book of Abstracts. P. 49.

28. Anatychuk L. I., Vikhor L. M. (2013) "Fiziko-tekhnicheskiye problemy sovremennogo materialovedeniya" ["Physical and technical problems of modern materials science"]. *Funktsional'no-gradiyentnyye termoelektricheskiye*

materialy. Tom 2 [Functional-gradient thermoelectric materials, vol. 2]. Kyiv: Akademperiodika. (in Ukrainian)

29. E.M. Hansen and S. Kjelstrup (1996) Application of nonequilibrium thermodynamics to the electrode surfaces of aluminium electrolysis cells. J. Electrochem. Soc., 143: 3440–3447.

30. A. Bejan (1982) Entropy Generation Through Heat and Fluid Flow. Wiley, New York.

31. D. Bedeaux (2004) Nonequilibrium thermodynamic description of the threephase contact line. J. Chem. Phys., 120: 3744–3748.

32. D. Bedeaux and S. Kjelstrup (2004) Irreversible thermodynamics – a tool to describe phase transitions far from global equilibrium. Chem. Eng. Sci., 59: 109–118.

33. Anatychuk L. I., Prybyla A. V. (2016) Porivnyalnyy analiz termoelektrychnykh ta kompresiynykh teplovykh nasosiv dlya indyvidual'nykh kondytsioneriv [Comparative analysis of heat-electric and compressor heat pumps for individual consumers]. *Termoelektryka – Thermoelectricity*, no. 2. (in Ukrainian)

34. H.B. Callen (1985) Thermodynamics and an Introduction to Thermostatistics. John Wiley and Sons, Inc., New York.

35. Hermann von Helmholtz – Ueber Die Thermodynamik Chemischer Vorgange; 1882.

36. H. Reiss (1996) Methods of Thermodynamics. Dover, New York.

37. S.R. de Groot and P. Mazur (1984) Non-Equilibrium thermodynamics. Dover, New York.

38. Cherkez R. (May 2012) Theoretical studies on the efficiency of air conditioner based on permeable thermoelectric converter. *Applied Thermal Engineering*, vol. 38, pp. 7–13. DOI: http://dx.doi.org/10.1016/j.applthermaleng.2012.01.012

39. Cherkez R. G. (2013) Energy Characteristics of Permeable Thermoelements. *Journal of Electronic Materials*, vol. 42, no. 7, pp. 1558–1563.

40. Cherkez R. G., Lastivka M. S., Gukova A. S. (2021) Optimization of the efficiency of permeable thermoelectric elements for air conditioner applicatons. *Physics and Chemistry of Solid State*, vol. 22, no. 2, pp. 269–277.