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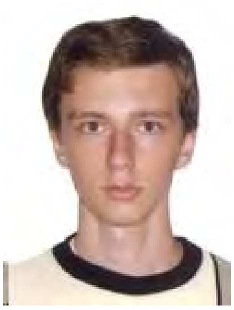
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COMPUTER METHOD OF DESCRIPTION OF THE TECHNOLOGIES AND PROPERTIES OF Bi_2-Te_3-BASED THERMOELECTRIC MATERIALS OBTAINED BY THE PRESSING METHOD

This paper presents the results of the study of literary sources describing the technologies and properties of thermoelectric materials obtained by the pressing method. The results of one of the stages of creating a software product for the description of the production technologies and properties of thermoelectric material based on Bi-Te compounds are given. Bibl. 13, Fig. 2, Table 1.
Key words: hot pressing method, cold pressing method, dynamic elements, bismuth telluride

Introduction

Thermoelectric materials science is an important direction in the development of thermoelectricity, since advances in this area as a whole determine the possibilities and versatility of practical uses of thermoelectric energy conversion [1]. Increasing the efficiency of thermoelectric converters is a rather important and widespread problem. The characteristics of thermoelectric materials can be determined by the formula:

$$Z = \frac{\alpha^2 \sigma}{\kappa}, \quad (1)$$

where α is the Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity.

One of the ways to obtain thermoelectric materials is the pressing method. An important advantage of pressed thermoelectric materials (TEMs) based on Bi_2Te_3 is their high mechanical strength compared to crystallizing materials from a melt. In addition, powder metallurgy contributes to increased productivity and savings. Materials obtained by powder pressing, as a rule, have a lower value of figure of merit Z due to misorientation of grains in the bulk of the material [2].The purpose of this work is to study the thermoelectric characteristics of solid solutions based on bismuth telluride obtained by pressing, as well as application of a modified computer program to study the pressing method and characteristics of thermoelectric materials based on *Bi-Te* compounds.

Dependence of the thermoelectric characteristics of Bi_2-Te_3-based materials obtained by the pressing method

Pressed Bi_2Te_3-based materials are obtained from a powder of a preliminarily synthesized material from a mixture of powders of initial components taken in a stoichiometric ratio [3]. Two pressing methods are used: cold pressing, which consists in briquetting the powder in a cold mold, followed by sintering in vacuum, in an atmosphere of hydrogen, an inert gas, and hot pressing of the powder in a heated mold with additional annealing of the sample. Materials obtained by the pressing methods have increased strength due to grain boundaries that prevent the propagation of cracks along cleavage planes. In addition, this method is relatively inexpensive. One of the important thermoelectric characteristics of pressed materials is the ability to withstand shock loads and thermal stresses. The thermoelectric characteristics of *Bi-Te*-based materials obtained by pressing are indicated in Table 1.

Table 1

Production technologies and properties of thermoelectric materials obtained by the pressing method

Working temperature, K	Z, 10^{-3},K^{-1}	α, mV/K	σ, $Ohm^{-1}cm^{-1}$	κ, W/m·K	Material type	Material composition	Ingot length, mm	Ingot diameter, mm	Pressing pressure, MPa	Pressing temperature, K	Reference:
613-723	1.7	160	-	1.4	*N*	$(Bi_2Te_3)_{0.95}$ $(Bi_2Se_3)_{0.05}$	-	10 ×1	60	-	[1]
450-530	1.4	290	454	1.3	*P*	$Bi_{0.5}Sb_{1.5}Te_3$	-	-	30	480	[2]
100-250	1.4	215	-	1.2	*P*	*BiSbTe*	-	1.25 - 25	-	-	[3]
380, 400, 420	2.69	223	-	0.95 1.09 1.17	*P*	$Bi_{0.5}Sb_{0.5}$ $Te_{0.5}$	-	30	200	-	[4]
700	3	-	-	-	*N*	$Bi_{0.5}Sb_{0.5}$ $Te_{0.5}$	5 × 10	-	30	400-585	[5]
400-500	3	226	780	1.17	*P*	Bi_2Te_3-Bi_2Se_3	-	-	700	450	[6]
25-250	0.45	171	0,25	0.55	*P*	25%Bi_2Te_3+ 75%Sb_2Te_3	-	-	70	-	[7]

Continuation of Table

623-773	1.92	235	533	1.53	*P*	$Bi_{0.5}Sb_{1.5}Te_3$ (120:1)	5 × 5 × 10	-	500	500	[8]
533-693	0.71	180	-	0.61	*N*	$(Bi_{0,25}Sb_{0,75})_2Te_3$	20 × 13	-	-	-	[9]
200-700	2.52	180	900	1.4	*N*	$Bi_2Te_{2,88}Se_{0,12}$ $Bi_{0.52}Sb_{1.48}Te_3$	30× 30×20	-	-	-	[10]
200-700	2.41	180	900	1.4	*P*	$Bi_{0.52}Sb_{1.48}Te_3$	30×30×20	-	-	-	[10]
200-600	1.65	175	890	16.5	*N*	$Bi_2Te_{2,3}Se_{0,7}$	-	-	-	-	[11]
200-600	2.45	182	1250	16.9	*P*	$Bi_{0,56}Te_{2,9}$ $Sb_{1,44}Se_{0,1м}$	-	-	-	-	[11]
300-550	3	-	-	-	*P*	$Bi_{0,4}Sb_{16}$ Te_3+*Pb*	-	-	800	-	[12]
300-550	2	-	-	-	*P*	$Bi_{0.4}Sb_{1.6}Te_3$	-	-	800	-	[12]
100-400	3.12	171	-	-	*P*	$Sb_{1.51}Bi_{0.49}Te_3$	4 × 2 × 2	-	1200	-	[13]

All the data in the table were implemented in the software product to describe the technologies and properties of the thermoelectric *Bi-Te* - based material. Further updating the software product database will be described in future articles.

Further updating the software product to describe the technologies and properties of *Bi-Te*-based thermoelectric material

Currently, the function of adding new records has been implemented into the software product, which contains data on the growing technology and characteristics of the thermoelectric material based on *Bi-Te* compounds. The general algorithm of this function is as follows.

- Calling the add function by the user.
- Creation of a dynamic form and all its components, according to the chosen method of obtaining thermoelectric materials.
- After the user enters all the necessary data about the mode of obtaining thermoelectric material, the program checks the correctness of the data.
- The program switches to data adding mode.
- A new record is created in the database.
- The program switches to working mode.

- Delete the dynamic form and all its components.

The general view of record adding window is presented in Fig. 1.

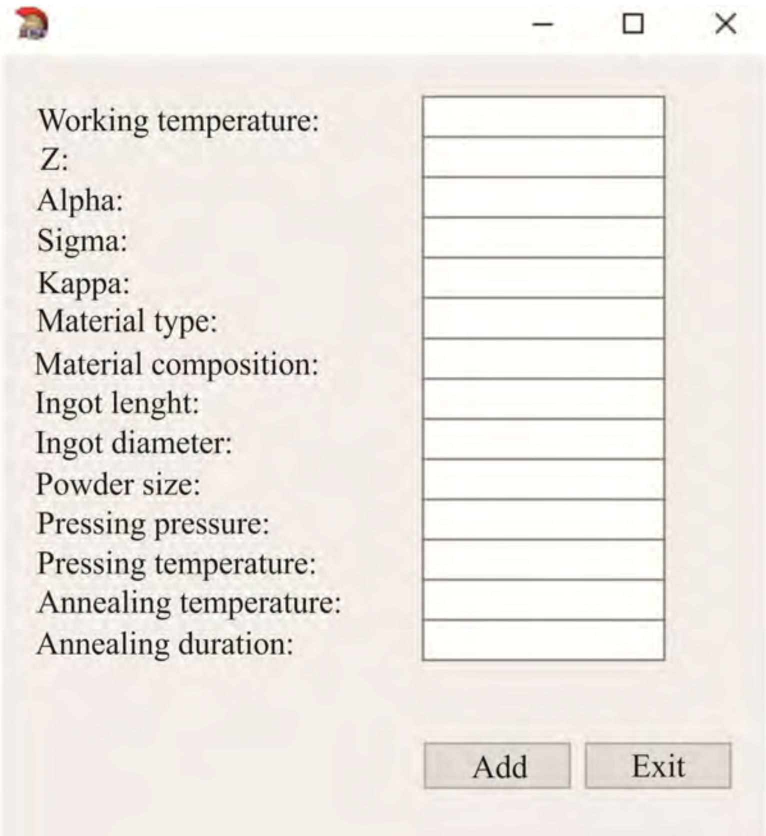

Fig. 1. General view of record adding window.

The function of editing existing records was also implemented. The general algorithm of this function is as follows.

- Calling the editing function by the user.
- Creation of a dynamic form and all its components, according to the chosen method of obtaining thermoelectric materials.
- Transfer of information from the selected record to the editing window.
- After the user makes all the necessary corrections in the thermoelectric material acquisition mode, the program checks the correctness of the data.
- The program switches to data editing mode.
- Editing of the selected record in the database.
- Transition of the program into working mode.
- Delete the dynamic form and all its components.

The general view of record editing window is presented in Fig. 2

It should be noted that depending on the chosen method of obtaining thermoelectric material, a corresponding window for adding and editing records about the mode of obtaining thermoelectric material is created. Further development of the software product will be described in future articles.

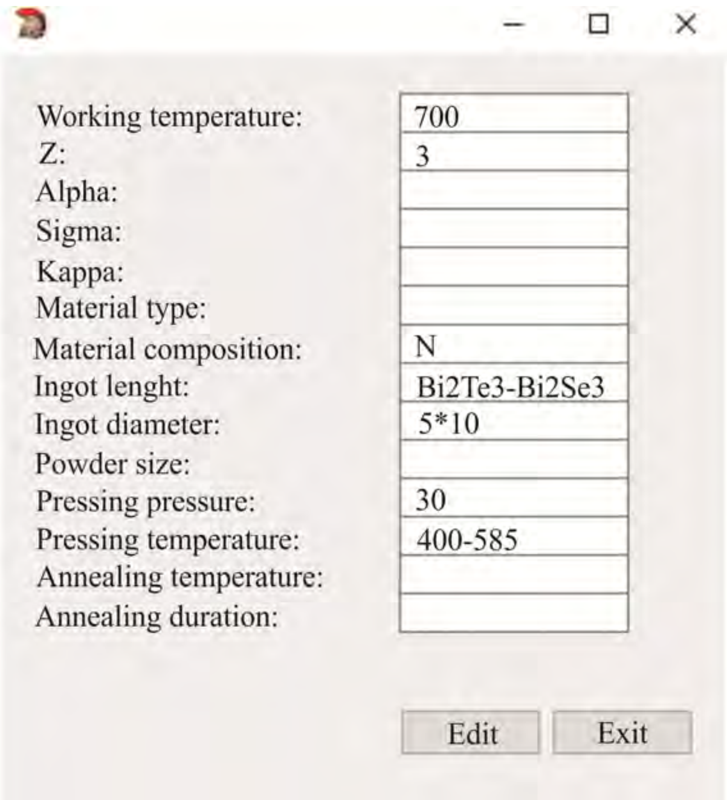

Fig. 2. General view of record editing window.

Conclusions

1. A study of literary sources describing *Bi-Te*-based thermoelectric materials obtained by pressing was carried out.
2. The research data were added to the database of the software product to describe the technologies and properties of obtaining *Bi-Te*-based thermoelectric material.
3. New functions were introduced into the software product to describe the technologies and properties of obtaining *Bi-Te*-based thermoelectric material.
4. Further versions of the software product will be described in the future articles.

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КОМП'ЮТЕРНИЙ МЕТОД ОПИСУ ТЕХНОЛОГІЙ ТА ВЛАСТИВОСТЕЙ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ НА ОСНОВІ Bi_2-Te_3, ОТРИМАНИХ МЕТОДОМ ПРЕСУВАННЯ

У даній роботі наводяться результати дослідження літературних джерел в яких описуються технології та властивості термоелектричних матеріалів отриманих методом пресування. Наводяться результати одного з етапів створення програмного продукту для опису технологій отримання та властивостей термоелектричного матеріалу на основі сполук Bi-Te. Бібл. 13. рис. 2. табл. 1.
Ключові слова: метод гарячого пресування, метод холодного пресування, динамічні елементи, телурид вісмуту.

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КОМПЬЮТЕРНЫЙ МЕТОД ОПИСАНИЯ ТЕХНОЛОГИЙ И СВОЙСТВ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ НА ОСНОВЕ Bi_2-Te_3, ПОЛУЧЕННЫХ МЕТОДОМ ПРЕССОВАНИЯ

В данной работе приводятся результаты исследования литературных источников, в которых описываются технологии и свойства термоэлектрических материалов полученных методом прессования. Приводятся результаты одного из этапов создания программного продукта для описания технологий получения и свойств термоэлектрического материала на основе соединений Bi-Te. Библ. 13. рис. 2. табл. 1.
Ключевые слова: метод горячего прессования, метод холодного прессования, динамические элементы, теллурид висмута.

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THEORETICAL MODELS OF ORDERED ALLOYS OF TERNARY SYSTEMS OF THERMOELECTRIC MATERIALS. 2. CHEMICAL BOND AND STATE DIAGRAMS OF *Bi-Pb-Te*

A comprehensive approach has been developed for the construction of theoretical models of ordered alloys of ternary systems of promising thermoelectric materials. Calculations of effective radii, redistribution of electron density and dissociation energy of non-equivalent hybrid orbitals (NHO) in the Bi-Pb-Te system depending on interatomic distances are presented. Triangulation methods were used to construct the distribution scheme of phase areas and isothermal sections in the Bi-Pb-Te system based on intermediate binary compounds Pb-Te; Bi-Te; Pb-Bi. Bibl. 15, Fig. 4, Table 7.

Key words: theoretical models, chemical bond, non-equivalent hybrid orbitals, effective radii, electron density, dissociation energy, state diagrams.

Introduction

Bismuth telluride is considered to be the most studied thermoelectric material. It has high thermoelectric parameters [1, 2].

However, despite many years of research into its physicochemical properties, many important questions remain unanswered. The question of chemical bonds remains open, and the theoretical understanding of many empirical relationships is associated with a revision of views on the problem of interatomic interactions [3].

In this connection, the study of the problems of synthesis of new materials based on tellurides with programmable properties remain an urgent issue. At the same time, the search for new promising thermoelectric materials is increasingly reduced to the need to study multicomponent systems. The reason is that solid phases of variable composition are formed in such systems, within which a transition is made in both chemical composition and structure with corresponding changes in physical properties [4, 5].

However, it should be noted that when studying complex systems, the classical scheme of dividing them into the sum of one-sided experiments no longer reveals the conditions for the appearance of the desired properties with the prospect of their change in the desired direction, since such systems are nonlinear, and there is still no consistent theory of phase transformations from the standpoint of chemical bond [7].

There is a search for new ways and approaches to solving such problems. The question of how general principles can be fruitfully use d to solve the set nonlinear problems acquires special relevance and significance. The answer to this question is related to the multi-layer structure of theoretical knowledge in various areas dealing with nonlinear systems. Knowledge of them is possible on the paths of interdisciplinary synthesis. The basis of this synthesis, according to [7], is the energy approach. In so doing, energy, as a general measure of various types of interaction, is considered both in terms of its organizational structure and state function. The combination of electronic, vibrational and configurational components of energy made it possible to calculate the ordering processes in alloys by statistical methods [8]; regularities of the formation of short-range order of chemical bonds in melts – by quantum chemical methods [9]; redistribution of electron density and dissociation energy of non-equivalent chemical bonds in ternary systems – by methods of microscopic theory using solutions of inverse problems and molecular models 10].

This work contributes to further comprehensive research [3 – 10] and is devoted to the construction of theoretical models of ordered alloys of the *Bi-Pb-Te* ternary systems. What was new in the study of tellurides was that a method based the geometrical properties of a triangle was used to solve the given problem [11]. This mathematical approach - the method of triangulation - makes it possible to solve a number of problems of physics, chemistry, mathematics. In particular, in chemistry, when studying state diagrams of ternary systems, this approach allows you to divide them into simpler binaries with regard to the laws of chemical interaction (solubility; substitution; exchange; formation of compounds; formation of solid solutions and mechanical mixtures).

This work solves the inverse problem of triangulation: based on the experimentally established and given in [12] state diagrams of binary alloys with regard to chemical interaction between the elements *Bi*, *Pb*, *Te*, located at the vertices of the triangle, a diagram of the distribution of phase regions for different isothermal sections is constructed in the *Bi-Pb-Te* system, and the parameters of phase transformations were calculated theoretically by the methods of quantum chemistry [7].

The availability of such information makes it possible to theoretically describe the processes of melting and crystallization in ternary systems *Bi-Pb-Te* and to optimize the synthesis of new materials based on them with programmable properties.

Theoretical models of state diagrams

When constructing the theoretical model of *Bi-Pb-Te*, it was necessary to summarize the results of experimental studies of binary state diagrams of *Pb-Te*; *Bi-Te*; *Pb-Bi* [12]; physicochemical properties and results of studies of quantum regularities of the initial components [9,10]. First, an analysis of binary state diagrams was given and isothermal sections at different temperatures were constructed. Then, by constructing the corresponding conoid triangles, the quantitative ratios of the coexisting phases were determined and the limits of phase equilibrium in the liquid-crystal regions were established. This made it possible to predict cases of congruent and incongruent melting. The obtained results are shown in Figs.1-4, where the following designations are entered:

α – solid phase based on *Bi*;

β – solid phase based on *Te*;

γ – solid phase based on *Pb*;

ε – solid phase based on intermediate *Bi-Te* binary compounds;

ς – solid phase based on intermediate *Pb-Te* binary compounds;

σ – solid phase based on intermediate *Pb-Bi* binary compounds;

δ – solid phase based on intermediate *Bi-Pb-Te* ternary compound;

L – liquid.

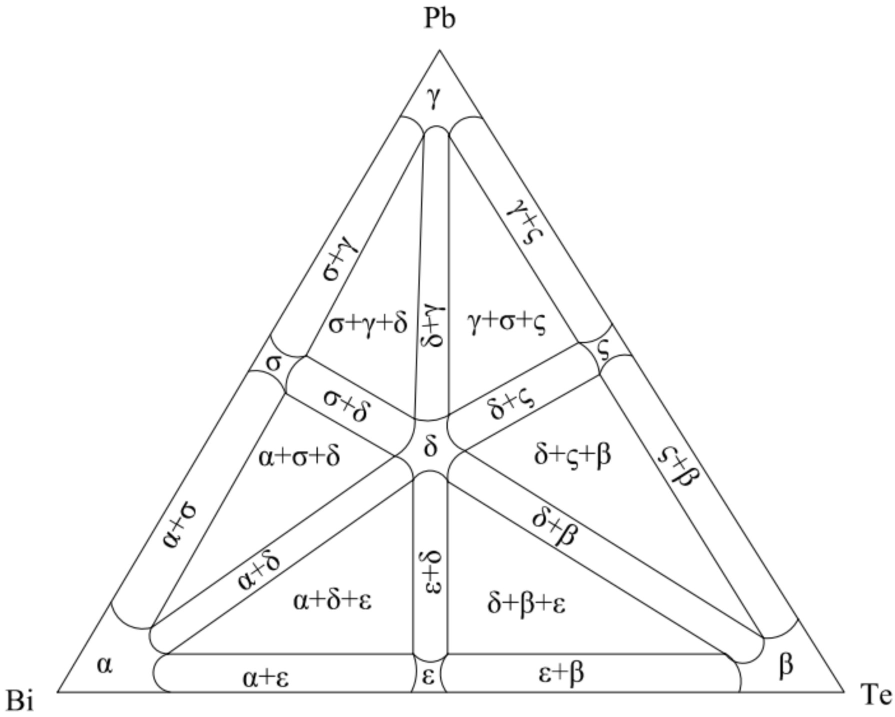

Fig. 1. A diagram of the distribution of
Bi-Pb-Te phase regions for
equilibrium in the solid state

Fig. 1 shows a diagram of the distribution of *Bi-Pb-Te* phase regions in the solid state. The division of the *Bi-Pb-Te* ternary system into six ordered ternary subsystems is clearly observed. This makes it possible to consider the issue of interatomic interaction both from the standpoint of state diagrams and chemical bond. It should be also noted that with the availability of additional experimental data, the number of ordered ternary systems may be larger.

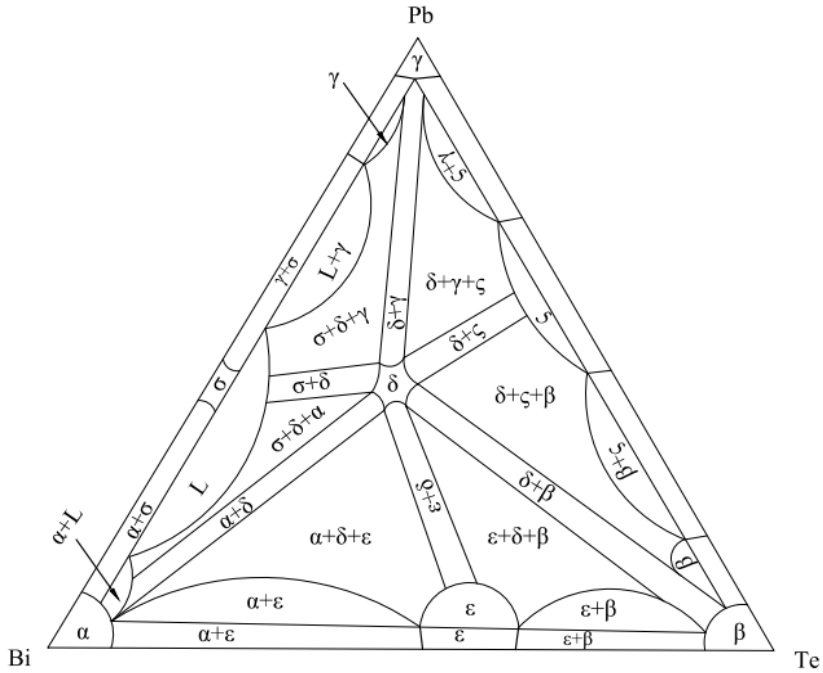

Fig. 2. Bi-Pb-Te isothermal section at t = 200°C

Fig. 2 shows an isothermal section at a temperature of $t = 200$°C, which is lower than the melting temperature of *Bi*, *Pb*, *Te* components and at the same time higher than the temperature of the first eutectic of the *Pb-Bi* system. Most of the *Pb-Bi* section is occupied by liquid L. Two-phase equilibrium (L+α), (L+γ), (L+σ) is realized by primary crystals α and γ, as well as σ- crystals (based on Bi_nPb_m compounds) and liquid.

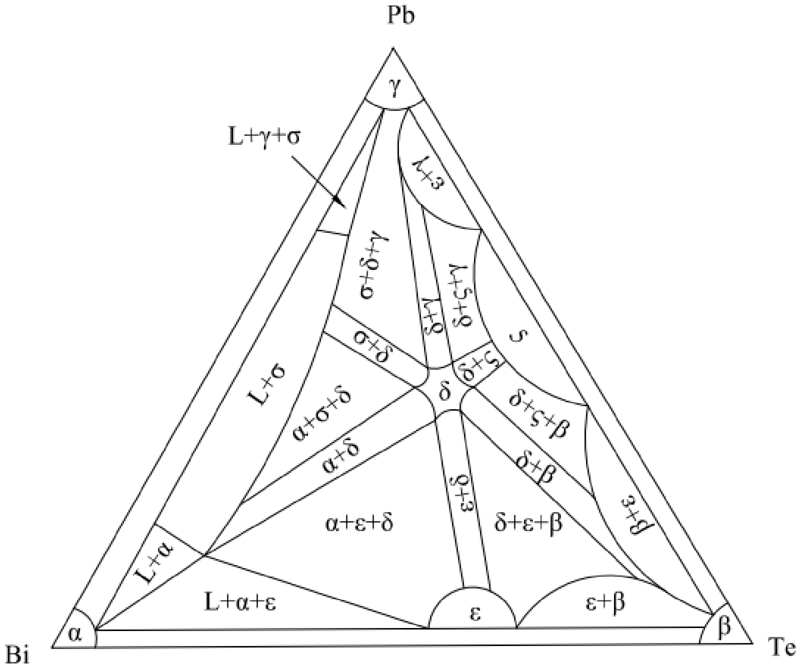

Fig. 3. Bi-Pb-Te isothermal section at t = 300°C

Fig. 3 shows an isothermal section at a temperature of 300°C, which is slightly lower than the melting temperature of *Pb* and *Te* components. As in the previous case, most of the *Pb-Bi* section is occupied by liquid *L,* but unlike the previous case, the cross-section contains conoid triangles with equilibrium phases (*L*+α+ε) and (*L*+γ+σ), which are formed by primary crystals α and γ, as well as ε and σ crystals (based on Bi_nTe_m and Bi_ePb_k) and liquid *L*. Exactly this division of ternary systems into separate sectors of dual state diagrams makes it possible to study the fine structure of cooling and heating of individual elements depending on their environment and the processes of forming the short-range order of chemical bonding.

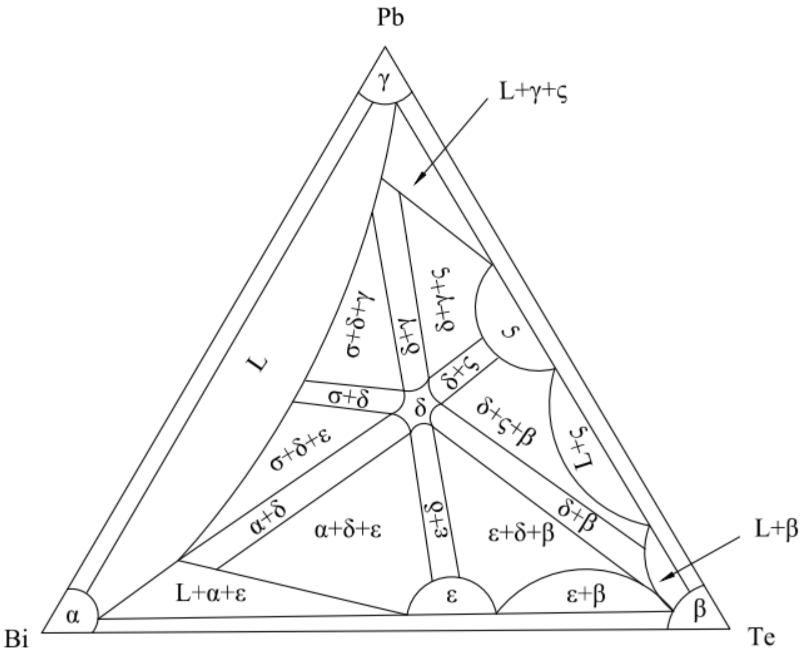

Fig. 4. Bi-Pb-Te isothermal section at t = 400°C.

Fig. 4 shows the isothermal section at t = 400°C, which is higher than the melting temperature of *Bi* and *Pb*. The entire *Bi-Pb* section is occupied by liquid, and in the *Bi-Te* and *Pb-Te* diagrams three-phase equilibria are represented by conoid triangles with phases (*L*+α+ε) and (*L*+γ+ς). Alloys of *Bi-Pb-Te* triangle are in a solid state at this temperature. Thus, the given isothermal sections make it possible to:

1. Determine quantitative ratios of coexisting phases and their concentrations.
2. Establish the limits of phase equilibrium in the liquid-crystal regions and transformations in the solid state.
3. Distinguish state diagrams corresponding to chemical compounds and solid solutions of different concentrations and mechanical mixtures.
4. Separate the boundaries of eutectic and peritectic state diagrams.
5. Predict cases of incongruent melting of chemical compounds, the composition of which differs from the composition of the original compound.

However, it should be also noted that isothermal sections alone do not yet indicate the temperature points of phase transitions of multicomponent systems. In such cases, additional methods are used that combine analytical and topological approaches with calculations of the interaction energy in both phases and increase the role of theoretical calculations in the construction of the state diagram of ternary systems.

Theoretical models of chemical bonding of ordered *Bi-Pb-Te* alloys

The theoretical analysis of empirical dependences of crystallization processes is related to the revision of views on the problem of interatomic interaction and the emergence of new ideas which are not always the result of the development of existing theories, but mostly deny some of them.

Analytical relations reflecting the quantum patterns of interatomic interaction in tellurium were given in [9, 10]. However, there is still no single quantitative method for calculating the electronic structure of tellurium compounds and alloys based on both the quantum mechanical and empirical approaches.

Thus, for instance, the calculation of electron density distribution between interacting atoms by the methods of quantum mechanics does not take into consideration the fact that different types of their hybrid orbitals affect the strength of the electron-nucleus bond, and the electron density distribution around an isolated atom (ion), according to the calculation method, has spherical symmetry. This contradicts the fact that the formation of a chemical bond is accompanied by a rearrangement of the valence electron shells of the interacting atoms, and a redistribution of the electron density along the chemical bonds.

On the other hand, allowance for statistical regularities made it possible to obtain the dependence of electrons n on the outer shell of an atom on the Fermi radius r_F. Establishing the relationship between r_F and n can be considered the beginning of a quantitative theory of chemical bonding [13].

Empirical information on the properties of atoms and ions based on the experience and traditions of the crystal-chemical approach can be combined by introducing the concept of unpolarized $R_{ин}$ ionic radii [13]. Since both the functions that include the Fermi radii $r_F = f(n)$ and the equations that include $R_{ин}$ determine the electronic configurations of the interacting atoms depending on the length and number of bonds formed by them, all this gives reason to consider the concepts of the Fermi radius and unpolarized radius identical and denote by one symbol R_u – effective ionic radii.

Despite the imperfection, from a theoretical point of view, of the concepts of the crystal chemical radius of ions, electronegativity, polarizability and other empirical criteria, their positive role in the systematization of experimental data and the development of ideas about the nature of interatomic interaction does not raise doubts, since the numerical values of these criteria are determined on the basis of the generalization of experimental data in combination with their interpretation from the standpoint of quantum mechanics, which contain important information about the nature of interatomic interactions.

Numerical values of electronegativity turned out to be most useful when searching for the form of a graphical solution to the problem of the connection of R_u to n. The relationship between

$\tan\alpha = \dfrac{\Delta \log R_u}{\Delta n}$ and electronegativity does not make it possible to change the compared values arbitrarily, fixing the position of the lines in the coordinates $\log R_u = f(n)$. A good agreement of the complex of experimental data on various physicochemical properties of atoms and their ions with the values of R_u and $\tan\alpha$ gives the postulated dependence

$$\log R_{uA}^{x} = \log R_{uA}^{0} - x\tan\alpha, \qquad (1)$$

Where R_{uA}^{0} is the radius of the atoms in the unexcited state, and *x* is the valence which allows us to state that the derivation of equations for ionic radii is based on the generalization of the main empirical material of physics and chemistry, and their usefulness is determined by the extent to which their use allows overcoming the difficulties of the modern theory of chemical bonding and obtaining quite accurate and physically justified result of interatomic interaction.

As already noted, the formation of a chemical bond is accompanied by a rearrangement of valence electron shells of interacting atoms. The possibility of using the system of ionic radii for their description follows from the basic principles of quantum mechanics. Since the equations of the system of ionic radii describe the change in R_u of atoms *A* and *B* when the number of electrons in the orbitals changes, assuming the equality of the absolute values of the charges of interacting atoms, dependence (1) takes the form of a system of equations [13]:

$$\lg R_{uA}^{+x} = \lg R_{uA}^{o} - x\tan\alpha_A, \qquad (2)$$

$$\lg R_{uB}^{-x} = \lg R_{uB}^{o} + x\tan\alpha_B, \qquad (3)$$

$$d_1^0 = \log R_{uA}^{+x} + \log R_{uB}^{-1}, \qquad (4)$$

The presence of d_{min} and two possible values of $z_{eф}$ for $d_1 > d_{min}$ from the standpoint of crystal chemical approach is justified by the increase in the internuclear distance with a change in the ionicity and covalency between the same partners.

The main drawback of this approach is that in many cases the internuclear distances *A-B* in molecular and crystalline compounds are smaller than the $d_{\min}$ value, and it is impossible to calculate the charge of ions using $z_{eф} = f(d)$ diagrams. Therefore, difficulties can be overcome only by abandoning the attempt to interpret the solution of system (2)-(4) in terms of crystal-chemical approach. The reason is that in the system (2)-(4) the ideas of the theory of polarization and the concept of electronegativity (EN) are combined, as it describes the mutual change of the polarization of anion and cation depending on tan α. From the standpoint of a quantum mechanical approach to solving the problem of chemical bonding, system (2)-(4) formally considers the geometrical conditions of contact of spherical electron shells with different density at the boundary. In this case, the single quantum system is replaced by an arithmetic sum of parts that retain their individuality, and the complex process of rebuilding the electronic shells of interacting atoms comes down to a simple transfer of electrons from the orbitals of one to the orbitals of the other. Thus, additional criteria are necessary to translate the crystal chemical system (2)-(4) into the language of quantum chemistry. It should be taken into consideration that in the zone of binding localized orbitals, the spherical symmetry of the electron density is broken and for $d_1 > d_{min},$ the formation of *A-B* bonds is accompanied by the transition of electrons to other directions of interatomic interaction, and this bond becomes a donor.

Thus, at $d_1 \neq d_{min}$, the change in the values of $z_{eф}$ of atoms should be such as to ensure the equality of the density of states at the boundary of the corresponding ions. This condition is fulfilled if the extraction ($+\Delta e$) of electrons or their localization ($-\Delta e$), in the given bond direction equally change the value of charges that this pair has at $d_1 = d_{min}$, i.e. $z_{eф}A(B) = z_{min}\, A(B) + (\Delta e/z)$. The thus calculated $z_{eф}$ and R_u characterize for arbitrary d_1 the conditions for preserving the continuity of the wave function in the zone of interacting atoms. These conditions are described by a system of equations:

$$d_1 = R_{uA}^{zA} + R_{uB}^{zB} \tag{5}$$

$$\log R_{uA}^{zA} = \log R_{uA}^{0} - \left(z_{\min A} + \frac{\Delta e}{r} \right) \tan \alpha, \tag{6}$$

$$\log R_{uB}^{zB} = \log R_{uB}^{0} - \left(z_{\min B} + \frac{\Delta e}{r} \right) \tan \beta, \tag{7}$$

Externally, Eqs. (2)-(4) and (5)-(7) are similar, but in reality, replacing x with $\left(z_{\min} + \frac{\Delta e}{r} \right)$ changes their physical content. The function $d_1 = f(z_{eф})$ is calculated in accordance with the traditions of the crystal chemical approach ($Z_A = -Z_B$), is correct from the quantum molecular point of view only at $d = d_{min}$, but this turns out to be sufficient for system (5)-(7) to be solved for known d_1. With this approach, the system (5)-(7) allows to reconcile the theoretical part with the experimental one and was solved for all possible values of d_i in the considered compounds. Thus, as a result of taking into consideration quantum interpretation of empirical material, the expression for the energy of chemical bonds acquires the form:

$$D_{A-B}^{(i)} = \frac{c_1 \left(R_{uA}^{o} + R_{uB}^{o} \right)}{\left(\tan \alpha_A + \tan \alpha_B \right)} \left(\frac{c_2 d_i}{d_1^2 - R_{uA} R_{uB}} - \frac{1}{d_i} \right) \tag{8}$$

where $R_{uA(B)}^{o}$ and $\tan \alpha_{A(B)}$ are coefficients of equations (2)-(4) for atoms *A* and *B*, and R_{UA} and R_{UB} are the effective radii of their ions, in *A-B* bonds of length d_i, i is the number of non-equivalent interatomic distances in the considered compounds; C_1 is a coefficient reflecting the relationship between dimensional and energy characteristics of interatomic interaction (measured in electric volts);

C_2 is a coefficient which depends on the type of crystal structure and chemical bond and is chosen dimensionless.

The given equations were used in the calculations of effective charges, effective radii and dissociation energies of non-equivalent chemical bonds of compounds and alloys that are part of the ternary system *Bi-Pb-Te*. The result of calculating the coefficients of equations (2)-(4) $R_u^{(0)}$ and $\tan\alpha$ of initial components are given in Table 1.

Table 1

Coefficients of equations of initial components

Z	Element	$R_u^{(0)}(A)$	$\tan\alpha$
52	*Te*	1.57	0.076
82	*Pb*	1.53	0.0675
83	*Bi*	1.63	0.068

Effective charges Δq_i, effective radii R_{ui} and dissociation energies for nearest neighbours at different interatomic distances d_i ($1 \le i \le 8$) of structural modifications of bismuth are given in Table 2.

Table 2

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at different interatomic distances d_i of various structural modifications of bismuth.

Parameters	*Bi*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.805	2.9033	3.009	3.1008	3.3036	3.5034	3.7008	4.7024
$R_u(A)$	1.4025	1.45165	1.5045	1.5504	1.651	1.7517	1.8504	2.3512
Δq_i	0.13	0.10064	0.06936	0.0435	-0.111	-0.0625	-0.11	-0.318
$D_i(ev)$	2.8536	2.75524	2.6634	2.577	2.421	2.2829	2.1595	1.700

Results of calculations for tellurium and lead are given in Tables 3 and 4.

<u>*Table 3*</u>

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at different interatomic distances d_i of various structural modifications of tellurium.

Parameters	*Te*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.024	2.9046	3.00558	3.1018	3.30056	3.4998	3.7014	4.7042
$R_u(A)$	1.4012	1.4523	1.50279	1.5509	1.65028	1.7499	1.8507	2.3521
Δq_i	0.0988	0.06764	0.038	0.0106 4	-0.04332	-0.09424	-0.143	-0.35112
$D_i(ev)$	2.45927	2.37447	2.29533	2.2213	2.0866	1.9674	1.86107	1.465097

<u>*Table 4*</u>

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at different interatomic distances d_i of various structural modifications of Pb.

Parameters	*Pb*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.80057	2.90024	3.00345	3.1006	3.302	3.50032	3.7016	4.699
$R_u(A)$	1.400285	1.45012	1.50428	1.5503	1.651	1.75016	1.8508	2.3495
Δq_i	0.07695	0.046575	0.0162	0.011475	-0.06615	-0.1168	-0.1654	-0.3726
$D_i(ev)$	2.6984	2.5272	2.5185	2.43729	2.289562	2.15873	2.04204	1.60756

As regards the above parameters for *Bi-Te*, *Pb-Te* and *Pb-Bi* compounds, they are given in Tables 5, 6, 7.

Table 5

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at non-equivalent interatomic distances d_i of various structural modifications of Bi-Te.

Parameters	*Bi-Te*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.803	2.906	3.0048	3.106	3.303	3.502	3.702	4,707
$R_{ui}^{Bi}(A)$	1.438	1.488	1.536	1.584	1.681	1.775	1.871	2.347
$R_{ui}^{Te}(A)$	1.365	1.418	1.468	1.522	1.622	1.727	1.831	2.36
Δq_i	0.1152	0.08352	0.05472	0.02736	-0.0288	-0.0785	-0.126	-0.3355
$D_i(ev)$	2.6429	2.5664	2.4672	2.38814	2.24367	2.115826	2.00169	1.576

Table 6

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at non-equivalent interatomic distances d_i of various structural modifications of Pb-Te.

Parameters	*Pb-Te*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.804	2.904	2.998	3.104	3.302	3.504	3.7062	4.7037
$R_{ui}^{Pb}(A)$	1.392	1.4378	1.4827	1.531	1.6231	1.7163	1.8096	2.2635
$R_{ui}^{Te}(A)$	1.412	1.4662	1.5153	1.573	1.6771	1.7877	1.8966	2.4402
Δq_i	0.0868	0.0574	0.0290	-	-0.05455	-0.106	-0.1549	-0.36162
$D_i(ev)$	2.5718	2.4828	2.40	2.344	2.18132	2.05638	1.945	1.5291

Table 7

Effective charges Δq_i, effective radii R_{ui}, dissociation energies D_i of chemical bonds φ_i for nearest neighbours at non-equivalent interatomic distances d_i of various structural modifications of Pb-Bi.

Parameters	*Pb-Bi*							
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7	φ_8
$d_i^{екс}(A)$	2.8	2.9	3.0	3.1	3.3	3.5	3.7	4.7
$d_i^{теор}(A)$	2.8028	2.90014	3.0014	3.11	3.306	3.5027	3.7051	4.704
$R_{ui}^{Pb}(A)$	1.3574	1.40464	1.4535	1.506	1.601	1.6952	1.7928	2.273
$R_{ui}^{Bi}(A)$	1.4454	1.4955	1.5479	1.604	1.705	1.8075	1.9123	2.451
Δq_i	0.104	0.0745	0.0447	0.01355	-0.0393	-0.0894	-0.1382	-0.3455
$D_i(ev)$	2.773	2.677	2.588	2.504	2.3528	2.2181	2.098	1.65148

In the above tables, the values of the coefficients C_1 and C_2 when calculating in the first approximation are chosen to be equal to unity.

Discussion of results

As follows from the results presented in Table 2, with increasing interatomic distances, the dissociation energy of the corresponding chemical bonds decreases, the redistribution of the electron density in the interval of interatomic distances $3.1 \le d_i \le 3.3$ changes its sign. This means that chemical bonds can be donors and acceptors in certain conditions. In turn, this confirms the experimentally established fact [14] that in compounds bismuth has different oxidation states, which can take values from -3 to +5 and can exhibit electronic properties in semiconductor melts as metallizing liquids, semimetallic liquids and semiconductors withy one and bilateral arrangement [15].

Thus, the use of the obtained results of the electronic properties of bismuth makes it possible to predict the shape of the liquidus, and hence the type of melting of the resulting material.

As for tellurium, with increasing interatomic distances, the dissociation energy of chemical bonds decreases, and the redistribution of electron density changes sign, just like bismuth. Tellurium can also have different oxidation states +4, +6 and -2, and has semiconducting properties. In melts with bismuth and lead, it behaves as a semi-metallic liquid.

The results of calculations of effective charges, effective radii and dissociation energies obtained in this work are in good agreement with the results of thermal rearrangement of atoms, during the formation of short-range order of chemical bonds in the *Bi-Te*, *Pb-Te* and *Pb-Bi* systems, which expands the technological possibilities when considering phase transformations, which are affected by such factors as the destruction of existing connections and the formation of new ones. This makes it possible to calculate the influence of the composition on the formation of the nuclei of a new phase, the influence of the distribution of phase components on the physical properties of the obtained materials.

Conclusions

1. A method of constructing theoretical models of ordered *Pb-Bi-Te* alloys using the geometric properties of a triangle is proposed.
2. The diagram of the distribution of phase regions and isothermal sections in the *Bi-Pb-Te* ternary systems has been constructed.
3. Calculations of effective radii, effective charges, dissociation energies in the *Bi-Pb-Te* ternary systems have been carried out.
4. The results obtained are consistent with the results of calculations of chemical bond parameters by the methods of microscopic theory [3 – 5], [7] and can be used in the development of technological modes for obtaining new materials based on *Bi-Pb-Te*.

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ТЕОРЕТИЧНІ МОДЕЛІ ВПОРЯДКОВУВАНИХ СПЛАВІВ ПОТРІЙНИХ СИСТЕМ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ. 2. ХІМІЧНИЙ ЗВ'ЯЗОК ТА ДІАГРАМИ СТАНУ *Bi-Pb-Te*

Розроблено комплексний підхід для побудови теоретичних моделей упорядкованих сплавів потрійних систем перспективних термоелектричних матеріалів.
Представлено розрахунки ефективних радіусів, перерозподілу електронної густини та енергії дисоціації нееквівалентних гібридних орбіталей (нго) в системі Bi-Pb-Te в залежності від міжатомних віддалей.
Методами триангуляції побудовано схему розподілу фазових областей та ізотермічні перерізи в системі Bi-Pb-Te. На основі проміжних бінарних сполук Pb-Te; Bi-Te; Pb-Bi. Бібл. 15, рис.4, табл. 7.

Ключові слова: теоретичні моделі, хімічний зв'язок, нееквівалентні гібридні орбіталі, ефективні радіуси, електронна густина, енергія дисоціації, діаграми стану.

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ТЕОРЕТИЧЕСКИЕ МОДЕЛИ УПРАВЛЯЕМЫХ СПЛАВОВ ТРОЙНЫХ СИСТЕМ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ. 1. ХИМИЧЕСКАЯ СВЯЗЬ И ДИАГРАММЫ СОСТОЯНИЯ *Bi-Pb-Te*

Разработан комплексный подход для построения теоретических моделей упорядоченных сплавов тройных систем перспективных термоэлектрических материалов. Представлены расчеты эффективных радиусов, перераспределения электронной плотности и энергии диссоциации неэквивалентных гибридных орбиталей (нго) в системе Bi-Pb-Te в зависимости от межатомных расстояний. Методами триангуляции построена схема распределения фазовых областей и изотермические сечения в системе Bi-Pb-Te. На основе промежуточных бинарных соединений Pb-Te; Bi-Te; Pb-Bi. Библ. 15, рис.4, табл. 7.

Ключевые слова: теоретические модели, химическая связь, неэквивалентные гибридные орбитали, эффективные радиусы, электронная плотность, энергия диссоциации, диаграммы состояния.

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COMPUTER SIMULATION OF A PERMEABLE GENERATOR THERMOELEMENT

The paper presents the results of computer studies of a 3D model of a permeable generator thermoelement. A physical model and design of a permeable thermoelement are given, and its mathematical description is presented. A method for calculating a thermoelement based on the Comsol Multiphysics software package has been developed. The dependences of the energy characteristics of a thermoelement made of Bi-Te-Se-Sb based materials on the height of the thermoelement leg are calculated. Bibl.11, Fig. 4.

Key words: permeable thermoelement, computer simulation, electric energy generation, energy characteristics.

Introduction

The widest application of thermoelectric energy converters is based on the use of a thermocouple element [1, 2]. Its energy conversion efficiency is determined by the figure of merit Z of materials used. Therefore, the search for materials with the maximum value of the figure of merit becomes the main task of thermoelectric materials science. However, despite intensive research, no significant increase in the figure of merit has been observed in this direction over the past 20–30 years [3, 4]. The maximum values of the dimensionless figure of merit of thermoelectric materials for industrial use remain at the level of 1 ÷ 1.2. Therefore, to improve efficiency, it is necessary to use new, unconventional approaches, which consist in the use of other non-traditional variants of physical models of thermoelements, which are the main component of a thermoelectric power converter.

One of them is the use of thermoelements with a developed internal heat exchange surface, i.e. permeable thermoelements. In such thermoelements, heat exchange with the heat source and heat sink occurs not only at the junctions, but also in the legs. Already the first theoretical [5] and experimental

[6] studies for cooling gas flows showed their promise. They point to the possibility of improving the energy conversion efficiency by a factor of 1.3 ÷ 1.4.

However, such studies were carried out for a model that is difficult to implement in practice. Therefore, it is necessary to create and study a more realistic 3D model of a permeable thermoelement, which is the purpose of this work.

Physical model and its mathematical description

The physical model of a permeable thermoelement, in which heat exchange with the heat carrier occurs not only through the interconnect plates, but also with the side surfaces of the leg, is shown in Fig. 1.

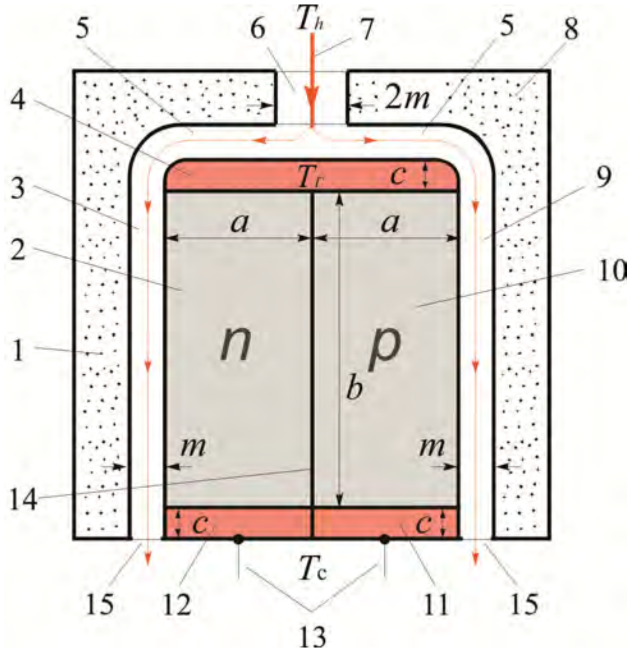


Fig. 1. Physical model of a permeable thermoelement:
1 – adiabatic isolation, 2 – n-type legs, 3 – channels,
4 – interconnect plate, 5 – channel, 6 – channel,
7 – heat carrier, 8 – adiabatic isolation, 9 – channel,
10 – p-type leg, 11, 12 – interconnect plates, 13 – electric contacts,
14 – layer between n- and p-type legs, 15 – channel outlets.

It includes n - and p - type legs (2, 10), covered by adiabatic isolation 1 and 8, which together form channels 5, 6, 9. Heat carrier 7 with temperature T_h flowing through channels 3, 5 and 5, 9 is supplied through channel 6. The legs are made of a homogeneous material based on *Bi-Te* with a maximum value of figure of merit Z in the temperature range 20 ÷ 320 °C. The temperature dependence of the material parameters should be taken into account. Interconnect plates c are made of copper, interconnect resistance is 10^{-6} Ohm·cm^2. The temperature T_0 of the lower interconnect plates is thermostatically controlled. The n - and p - type legs are interconnected by a thin layer 14, the thermal conductivity, electrical conductivity and thickness of which are neglected. The material of the legs is homogeneous and isotropic with known temperature dependences: electrical conductivity $\sigma(T)$, thermoelectric coefficient $\alpha(T)$, thermal conductivity $\kappa(T)$. In the thermoelectric medium, the volumetric effects of Thomson, Joule-Lenz and the near-contact Peltier effect are taken into account. The temperature of the heat carrier at the inlet to the thermoelement was assumed to be equal to the temperature of the hot junctions. The size of the thermoelement in the direction perpendicular to the plane of the figure is *d*, the value of *d = a*. The planes *d = 0* and *d = a* are the adiabatic isolations forming channels 5, 6, 9. There is no friction between the heat carrier and the adiabatic isolations 1, 8.

On the side surface of the legs 2 of the interconnect 4, which are in thermal contact with the heat carrier 7, heat transfer is described by the Newton-Richmann law:

$$q_0 = \alpha_T (t - T)\,, \tag{1}$$

where α_T is the heat transfer coefficient, T is the temperature of the thermoelement leg, t is the heat carrier temperature.

The system of equations describing the distribution of temperature and potential in the thermoelectric medium is described by the fundamental laws of conservation of energy and current carriers [7]:

$$\vec{\nabla}\vec{W} = 0 \tag{2}$$

$$\vec{\nabla}\vec{i} = 0 \tag{3}$$

where $\vec{W} = \vec{q} + U\vec{i}$ is energy flow density.

Using the generalized Fourier and Ohm’s laws for a thermoelectric medium:

$$\vec{q} = -\kappa\vec{\nabla}T + \alpha\vec{i}\,T \tag{4}$$

$$\vec{i} = -\sigma(\vec{\nabla}U + \alpha\vec{\nabla}T) \tag{5}$$

where U is the potential, κ is the thermal conductivity, α is the thermoelectric coefficient, σ is the electric conductivity, it is possible to obtain a system of differential equations for finding the distribution of temperatures and potentials:

$$\left.\begin{array}{l} \vec{\nabla}\kappa\vec{\nabla}T + \dfrac{i^2}{\sigma} - T\vec{i}\,\vec{\nabla}\alpha = 0; \\ \vec{\nabla}(-\sigma(\vec{\nabla}U + \alpha\vec{\nabla}T)) = 0. \end{array}\right\} \tag{6}$$

The Navier-Stokes equation and the continuity equation can be written as [8]:

$$\left.\begin{array}{l} \rho\dfrac{d\vec{\vartheta}}{dt} = \rho\vec{F} - \vec{\nabla}P + \mu\vec{\nabla}^2\vec{\vartheta} + \dfrac{1}{3}\mu\vec{\nabla}(div\vec{\vartheta}), \\ div\rho\vec{\vartheta} = 0. \end{array}\right\} \tag{7}$$

The left side of (7) represents the fluid inertia force. The first term on the right side of (7) is the mass force, the second is the action of surface pressure forces (normal stresses), and the last two terms are the action of the contiguous components of surface forces (internal friction forces).

Heat transfer in a liquid is described by thermal conductivity equation [9]:

$$\rho C_p\left(\frac{\partial T}{\partial t}+(\vec{\vartheta}\vec{\nabla})T\right)=-(\vec{\nabla}\vec{q})+\sum_{i,j}\tau_{ij}S_{ij}-\frac{T}{\rho}\frac{\partial\rho}{\partial T}\bigg|_P\left(\frac{\partial\rho}{\partial t}+(\vec{\vartheta}\vec{\nabla})P\right)+Q \tag{8}$$

where ρ is the density, C_p is the heat capacity, T is the temperature, $\vec{\vartheta}$ is the heat flux density, q is the heat flux density, P is the pressure, τ_{ij} is the viscous stress tensor, η is the viscosity, I is the unit tensor, $\vec{S}_{ij}$ is the strain rate tensor.

Since this problem is considered for a steady-state case, the left side of the first equation of system (7) is equal to zero. The influence of mass forces is also neglected, so the first term in the left part of the same equation is also equal to zero. Equation (8) must also be written for the steady-state case, and heating of the liquid due to internal friction, compression of the liquid, and heating of the liquid due to internal heat sources are neglected. Then the system of Navier-Stokes, continuity and heat conduction equations for this problem will be written in the form:

$$\left.\begin{array}{l}-\vec{\nabla}P+\mu\vec{\nabla}^2\vec{\vartheta}+\frac{1}{3}\mu\vec{\nabla}(div\vec{\vartheta})=0,\\ div\rho\vec{\vartheta}=0,\\ \rho C_p(\vec{\vartheta}\vec{\nabla})T+\vec{\nabla}\vec{q}=0.\end{array}\right\} \tag{9}$$

Boundary conditions describing the conjugate problem used in this task have the following form:

– for thermoelectric medium:

$$\text{temperature - }\begin{array}{l}T|_0=300K\\ T|_{z_h}=\alpha_T(T_h-T)\end{array}, \tag{10}$$

$$\text{potential - }\begin{array}{l}U|_0=0\\ U|_{x_3}=U_0\end{array}, \tag{11}$$

– for heat carrier:

$$\text{velocity - }\begin{array}{l}\vartheta|_0=\vartheta_0\\ \vartheta|_{z_h}=P_0=0\\ \vartheta|_{S\delta}=0\end{array}, \tag{12}$$

$$\text{inlet temperature - } t|_{z_h}=T_h \tag{13}$$

where ϑ_0 is the initial velocity of heat carrier, U_0 is a fixed potential value, S_0 is the side surface of thermoelement.

Implementation of given problem in the Comsol Multiphysics software package

To calculate the problem, the Comsol Multiphysics software package was chosen, namely, the equation in partial derivatives (PDE modes), where one of the ways to represent the equation is the coefficient form:

$$e_a \frac{\partial^2 \vec{u}}{\partial t^2} + d_a \frac{\partial \vec{u}}{\partial t} + \vec{\nabla}(-c\vec{\nabla}\vec{u} - \alpha\vec{u} + \gamma) + \beta\vec{\nabla}u + a\vec{u} = f \tag{14}$$

This equation is used for a thermoelectric medium and reduced to the form of $\vec{\nabla}(-c\vec{\nabla}\vec{u}) = 0$. For this, e_a, d_a, α, γ, β, a are set to zero, and the value c is written in the form of a matrix:

$$c = \begin{pmatrix} \kappa + \alpha^2\sigma T + \sigma U\alpha & \alpha T\sigma + \sigma U \\ \alpha\sigma & \sigma \end{pmatrix}. \tag{15}$$

Moreover, the vector $\vec{u}$ also has the form of a matrix:

$$\vec{u} = \begin{pmatrix} T \\ U \end{pmatrix}. \tag{16}$$

The Comsol Multiphysics – Non-Isothermal Flow module [11] is used to describe the motion and heat transfer of a fluid. The module includes a system of Navier-Stokes equations, a continuity equation and a heat transfer equation for a fluid, in a time-varying or steady-state mode. The calculation of the given model, in the steady-state mode, was carried out according to the relations:

$$\left.\begin{array}{l} \rho(\vec{\vartheta}\vec{\nabla})\vec{u}_2 = \vec{\nabla}\left[-PI + \mu(\vec{\nabla}\vec{\vartheta} + (\vec{\nabla}\vec{\vartheta})^T) - \frac{2}{3}\mu(\vec{\nabla}\vec{\vartheta})I\right], \\ \vec{\nabla}(\rho\vec{\vartheta}) = 0, \\ \rho C_p\vec{\vartheta}\vec{\nabla}T + \vec{\nabla}(\kappa\vec{\nabla}T) = 0. \end{array}\right\} \tag{17}$$

The value of the electric current was calculated through the integral over the cross-sectional area S_V::

$$I = \iint_{S_V} I_n dS_V\ , \tag{19}$$

where $I_n = n_x I_x + n_y I_y + n_z I_z$ is electric current density vector. The values of I_x I_y I_z were determined by the relations:

$$I_x = -\sigma \frac{\partial U}{\partial x} - \sigma\alpha \frac{\partial T}{\partial x}, \tag{20}$$

$$I_y = -\sigma \frac{\partial U}{\partial y} - \sigma\alpha \frac{\partial T}{\partial y}, \tag{21}$$

$$I_z = -\sigma \frac{\partial U}{\partial z} - \sigma\alpha \frac{\partial T}{\partial z}. \tag{22}$$

The heat carrier flow rate was determined by integrating the velocity υ over the cross-sectional area of the channel S_{V1}:

$$G = \iint_{S_{V1}} \vartheta dS_{V1} \tag{23}$$

Electrical power of the thermoelement $W = I \cdot U$, heat flux entering the thermoelement $Q_h = GC_p \Delta t$

The main parameter characterizing the efficiency of the thermoelement in the electric power generation mode is the efficiency factor, determined by the relation:

$$\eta = \frac{W}{Q_h}. \tag{24}$$

Results of computer research on the characteristics of a permeable thermoelement based on *Bi-Te-Se –Sb* materials

Calculation was made for materials based on *Bi-Te-Se-Sb* with functional dependences of material parameters, i.e. the Seebeck coefficient α, thermal conductivity κ and electric conductivity σ on temperature [3].

The simulation of the permeable thermoelement was carried out in the Comsol Multiphysics program for the following basic design (Fig. 1): height b = 10 *mm*, length 10 *mm*, width a = 10 mm. Dimensions of the lower interconnect: height c = 1 *mm*, length 10 *mm*, width a =10 mm; of the upper interconnect: height d = 1 mm, length c = 10 *mm*, width a = 10 *mm*. The interconnect material is copper. The slots in interconnects, together with the legs, form a system of channels for pumping the heat carrier. The design takes into account the presence of a transient layer of solder with a thickness of 0.3 mm. Fig. 2 shows the partition of such a design into finite elements.

At the inlet gas temperature of 600K, the temperature distributions in the heat carrier in Fig. 3 and the thermoelement material in Fig. 4 were obtained.

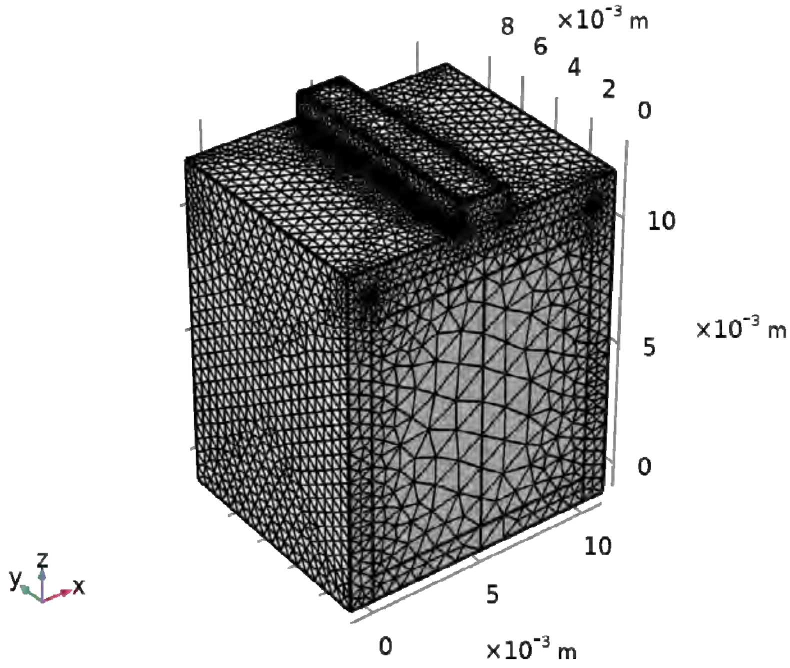
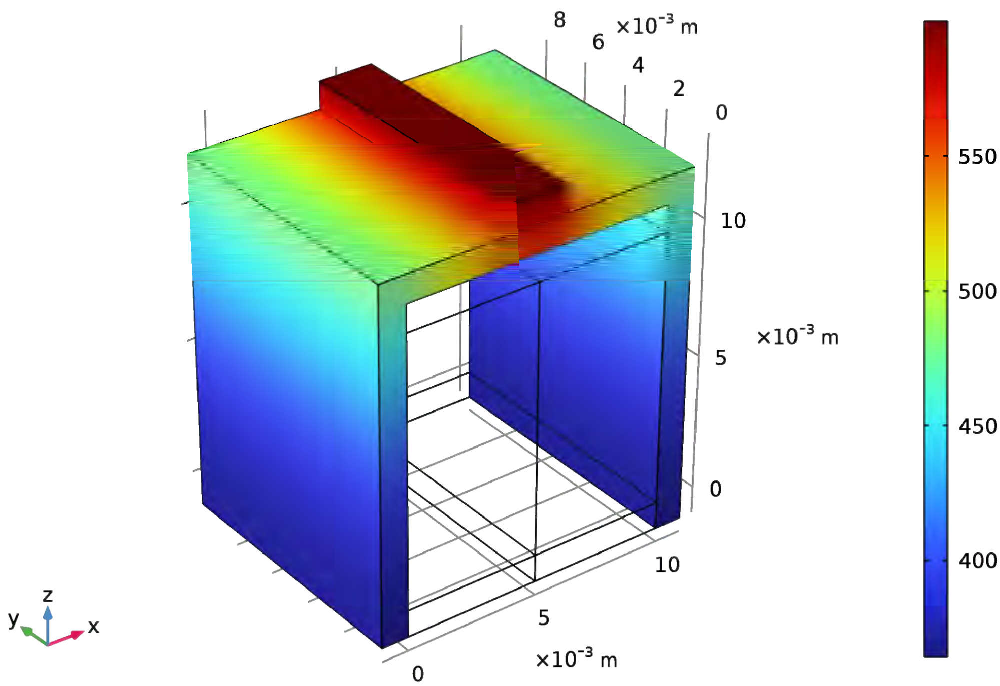
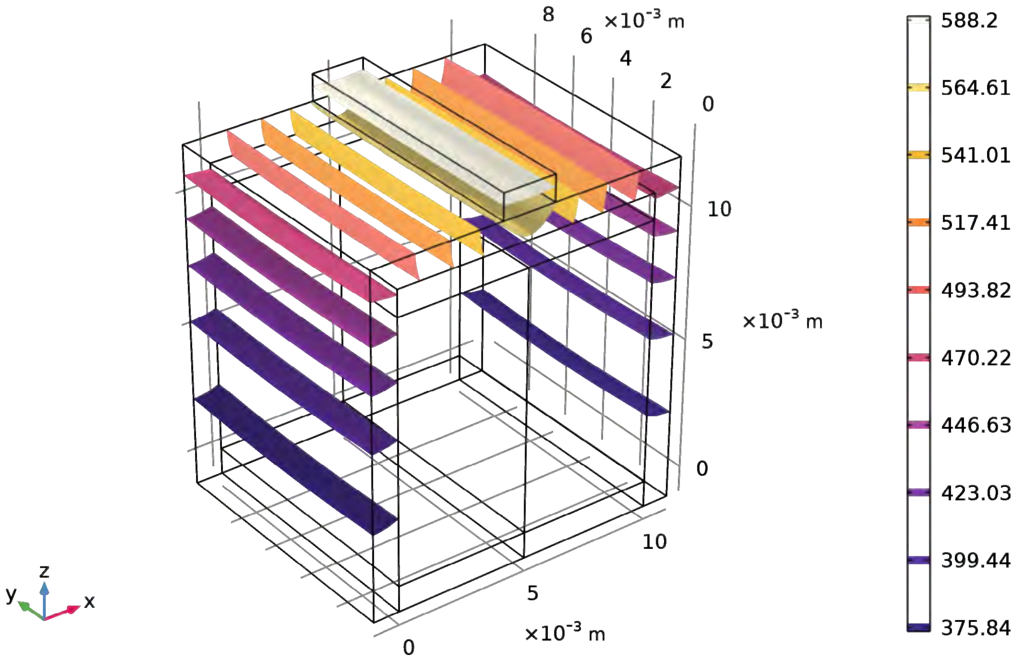


Fig. 2. Geometric grid.

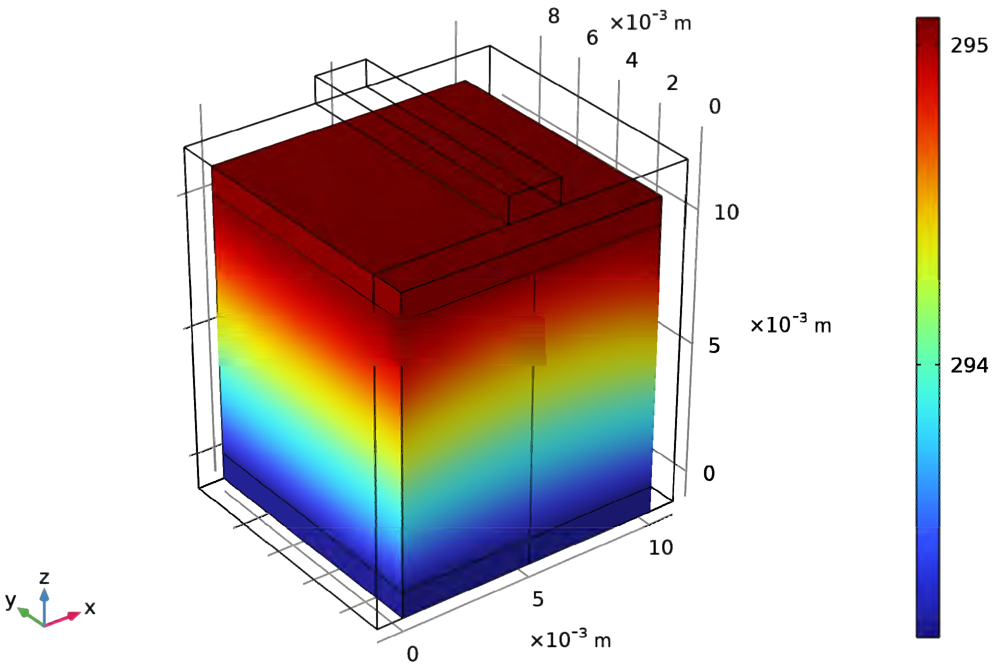


a)

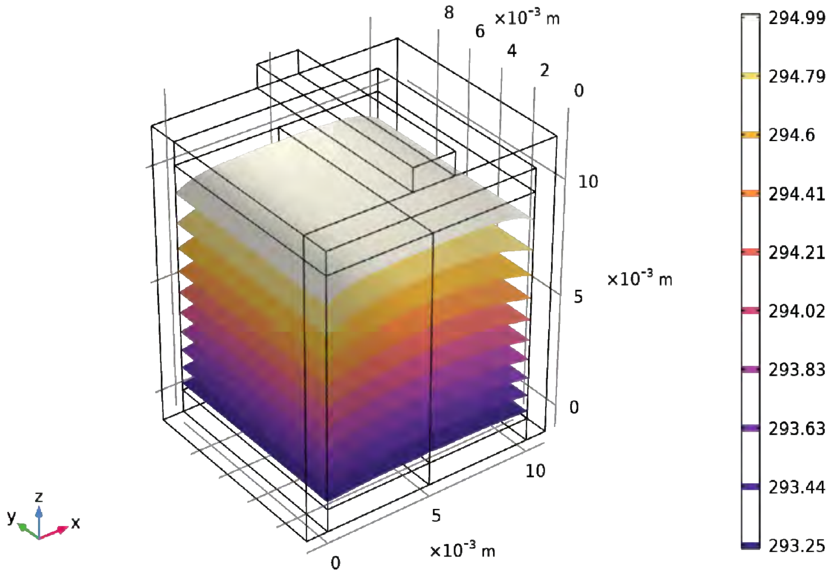


b)

Fig. 3. a) temperature distribution;
b) isothermal surfaces



a)



b)

Fig.4. a) temperature distribution;
b) isothermal surfaces

The height of the thermoelement legs was set equal to 1mm, 5 mm, 10 mm, 15 mm, 20 mm. The coefficient of heat exchange between water and thermoelement - α_T, in the Newton-Richmann law, was 1000 $W/(m^2 \cdot K)$.

For these parameters, the mean integral characteristics of the thermoelement were determined: air temperature at the thermoelement outlet - t_{out}; thermoelement electromotive force - EMF; the value of electric current *I*, *A*; air consumption - *G*; electric power *W*; efficiency η . The dependences of these parameters on the leg height *l*, for the case when the air temperature at the inlet to the thermoelement was 600K, are presented in the table.

Table

l, mm	t_{out} , K	EMF, V	*I*, A	*G*, m^3/s	*W* , 10^{-8} W	η (%)
1	473.60	0.00003	0.0004782	0.00047	1.43	1.57
5	414.13	0.00017	0.0001539	0.00680	2.62	1.84
10	365.01	0.00038	0.0001355	0.00599	5.13	2.87
15	335.62	0.00062	0.0000822	0.00582	5.09	1.56
20	299.98	0.00243	0.0000215	0.00480	5.22	0.83

Thus, there are such rational heights of the thermoelement legs whereby the efficiency has maximum values. To reveal the extreme possibilities of a permeable thermoelement, it is necessary to carry out multi-parameter optimization of its structural and thermophysical parameters.

Conclusions

1. A 3*D* model of a permeable thermoelement for cooling liquid and gas flows has been developed in the Comsol Multiphysics software package.
2. Temperature distributions in the material of the thermoelement legs and heat carrier, potentials in the thermoelement, air velocities and energy characteristics of a permeable thermoelement made of *Bi-Te-Se-Sb* based materials are determined.
3. It is necessary to carry out multi-parametric optimization of the structural and thermophysical parameters of a permeable thermoelement, which will make it possible to determine the maximum characteristics

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КОМП'ЮТЕРНЕ МОДЕЛЮВАННЯ ПРОНИКНОГО ГЕНЕРАТОРНОГО ТЕРМОЕЛЕМЕНТА

В роботі представлені результати комп'ютерних досліджень 3D моделі проникного генераторного термоелемента. Приведено фізичну модель та конструкцію проникного термоелемента, представлено її математичний опис. Створено метод розрахунку термоелемента на основі пакета прикладних комп'ютерних програм Comsol Multiphysics. Розраховано залежності енергетичних характеристик термоелемента з матеріалів на основі Bi-Te-Se-Sb від висоти вітки термоелемента. Бібл. 11, рис.4, табл.1.
Ключові слова: проникний термоелемент, комп'ютерне моделювання, генерація електричної енергії, енергетичні характеристики.

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КОМПЬЮТЕРНОЕ МОДЕЛИРОВАНИЕ ПРОНИЦАЕМОГО ГЕНЕРАТОРНОГО ТЕРМОЭЛЕМЕНТА

В работе представлены результаты компьютерных исследований 3D модели *проницаемого генераторного термоэлемента. Описаны физическая модель и конструкция проницаемого термоэлемента, представлено ее математическое описание. Создан метод расчета термоэлемента на основе пакета прикладных компьютерных программ Comsol Multiphysics. Рассчитаны зависимости энергетических характеристик термоэлемента из материалов на основе Bi-Te-Se-Sb от высоты ветки термоэлемента. Библ. 11, рис.4, табл.1.*

Ключевые слова: проницаемый термоэлемент, компьютерное моделирование, генерация электроэнергии, энергетические характеристики.

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EXPERIMENTAL BENCH STUDIES OF THERMOELECTRIC SOURCE OF HEAT AND ELECTRICITY FOR HEAVY DUTY VEHICLES

The design of a thermoelectric generator with an electrical power of up to 350 W for supplying electrical energy and ensuring autonomous operation of pre-start sources of heat and electricity with a thermal power of up to 40 kW for high duty vehicles is considered. A description of the bench for studying the characteristics of the developed thermoelectric generator and the results of experimental investigations of the generator model sample are presented. Bibl. 8, Fig. 4, Table 1.

Key words: starting pre-heater, thermoelectric generator, bench studies.

Introduction

The operation of vehicles in conditions of low ambient temperatures requires the use of methods for preliminary thermal preparation of engines for start-up. To do this, starting pre-heaters are increasingly used, powered by the fuel of vehicles and using the heating of the engine coolant [1, 2].

Preheating of the engine is also important for large-scale civil and military equipment. The main reasons that make it difficult to start such equipment at low ambient temperatures are: increasing the viscosity of the engine oil on the parts of the connecting rod-piston group of the internal combustion engine (ICE); increasing the viscosity of the lubricant in the transmission units; solidification of fuel in fuel lines, fuel filter and other parts of the fuel system; deterioration of fuel ignition conditions in the engine cylinders, which is due to the reduction of its evaporation and low temperatures of the air entering the cylinders of the internal combustion engine from the environment; freezing of the coolant in the engine cooling system; reduction of power of the starter-generator due to reduction of capacity of rechargeable batteries; overuse of fuel at cold start of the internal combustion engine. The influence of these factors at low temperatures is manifested simultaneously, which leads to a reduction in engine life and premature failure of equipment. This significantly increases the likelihood of sudden violations and failures of the equipment.

The determining factor limiting the possibility of mass use of starting pre-heaters is the discharge of the battery during the operation of pre-start equipment [3]. An effective method of solving this problem is the use of a thermoelectric generator, which works from the heat of the heater and provides autonomous power to its components [4 – 6]. In addition, the excess electricity of the heat generator can be used to recharge the battery and power other equipment.

In [7, 8] the possibility of using thermoelectric sources of heat and electricity to improve the performance of high-power vehicles is shown and the results of development and optimization of thermoelectric generator design for such sources are presented.

The purpose of this work is to conduct experimental studies of the developed model sample of a thermoelectric generator to confirm its expected characteristics.

Description of the thermoelectric generator design

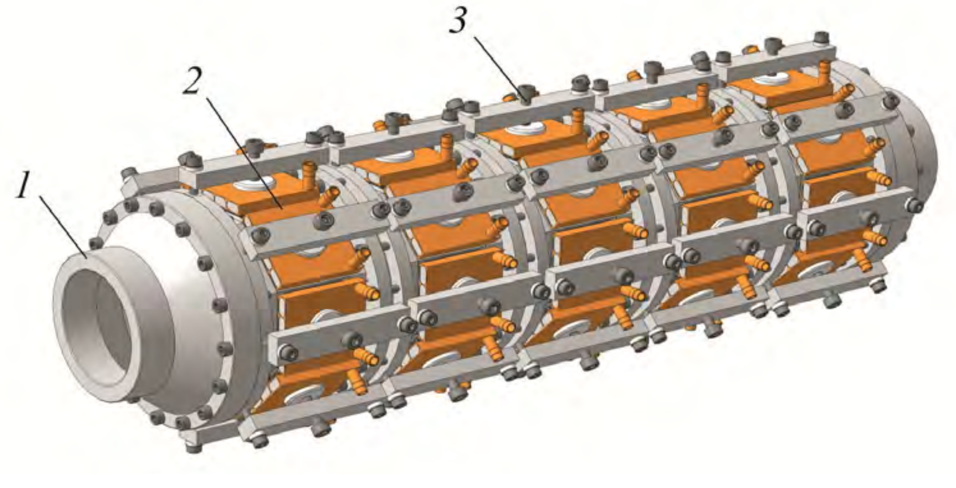
The main unit of the pre-start source of heat and electricity for high duty vehicles, which provides autonomous operation of the system without discharging the vehicle battery is a thermoelectric generator, the general design and appearance of which is shown in Fig. 1. The computer-aided design [8] made it possible to optimize the design of such a generator.

The thermoelectric generator contains a five-section system of hot heat exchangers, which is supplied with hot air from a heat source by a fan, which together with the fuel pump is part of the heat source (not shown).

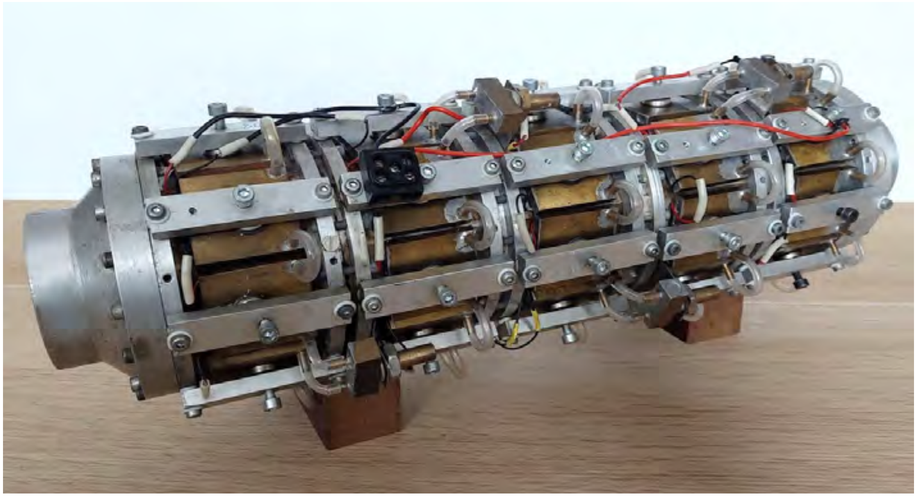
On the outer surface of the heat exchangers are thermoelectric modules, the heat from which is removed by a system of liquid heat exchangers. Thermal contact between thermoelectric modules and heat exchangers is provided by clamping devices. The free space between hot and cold heat exchangers is filled with thermal insulation.

The design of hot heat exchangers (Fig. 2) of each section (diameter and number of channels) is selected so as to ensure optimal operation of thermoelectric modules. The thermoelectric module 10 is clamped between the seat 9 on the hot heat exchanger and the cold heat exchanger 11 by means of a clamp. The clamp consists of a clamping bar 4, a clamping screw 5 and a disk 6 and is attached to the hot heat exchanger by means of screws 7 with fluoroplastic washers 3. Between the surface of the module and the hot heat exchanger is an electrical insulator - mica gasket 8.

Cold heat exchangers consist of a housing made of a material with high thermal conductivity (copper), in which through channels are made, connected in series with a system of plugs. All cold heat exchangers are connected in series in two parallel circuits and are connected to the hydraulic circuit of the vehicle's engine cooling system. The circulation of the liquid heat carrier in the "heater-motor" circuit is carried out by a pump. An overheating sensor is located on one of the cold heat exchangers to control the temperature of the heat carrier.



a)



b)

Fig. 1. Design (a) and appearance (b) of thermoelectric generator for pre-start source of heat and electricity for high duty vehicles:
1– system of hot heat exchangers;
2– system of cold heat exchangers; 3 – clamping devices

The generator contains 40 Altec-1061 generator modules, which are best suited for use in pre-start heat sources. The modules are electrically connected. Interconnect of the modules is selected so that the output voltage of the heater corresponds to the voltage on the vehicle battery.

The thermoelectric generator system has an electric power of up to 350 W, which will be enough to power the preheaters type PROHEAT M90 24V (with a useful thermal power of 26 kW and electric power consumption up to 230 W) or OZhD30.8106010 (with a useful thermal power of 30 kW and electric power consumption up to 140 W). Such a system, taking into account the thermal energy of a thermoelectric generator (about 10 kW), will be equivalent in terms of thermal power – 36 - 40 kW (but autonomous) and will allow replacing the PZhD-44Sh type pre-heater (with a useful thermal output of 37 kW and a consumed electric power of up to 340 V), which is widely used in heavy duty civil and military equipment.

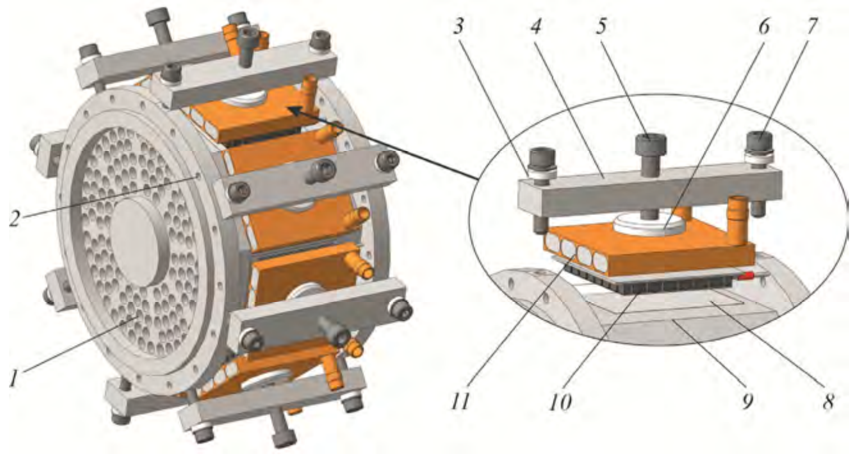


Fig. 2. Design of the hot heat exchanger of thermoelectric generator:1– channels for passing hot gas; 2 – holes for fastening the sections of the hot heat exchanger to each other; 3 – fluoroplastic washers; 4 – clamping bar; 5 – clamping screw; 6 – clamping disc; 7 – screws for attaching the clamp to the heat exchanger; 8 – mica plate; 9 – the seat of thermoelectric module; 10 – thermoelectric module; 11 – cold heat exchanger

Description of a bench for studying characteristics of the developed thermoelectric generator and the results of experimental studies

The layout of the bench for experimental studies of a model sample of a thermoelectric generator is shown in Fig. 3. The thermoelectric generator 1 is connected to the heat source 7 on diesel fuel. In the system of liquid cold heat exchangers 3 by means of the pump 4 the heat carrier was pumped, the flow rate of which was measured by the flow meter 9. The liquid circuit also contained a radiator 8 to transfer heat from the generator to the environment and maintain the desired temperature of the coolant.

The temperatures of hot heat exchangers T_1 – T_5 of sections 1-5 of the thermoelectric generator, as well as the temperature of the coolant at the inlet T_6 and outlet T_7 from the cold heat exchanger system were measured using chromel-alumel thermocouples, the cold junctions of which were immersed in Dewar vessel 6.

As a result of experimental studies (Table 1) of the developed model sample of the thermoelectric generator of heat and electricity for high duty vehicles, it was found that at full power of the heat source the developed generator has an electric power of about 350 watts.

In Table 1: T_1 – T_5 are the temperatures of the hot heat exchangers of sections 1-5 of thermoelectric generator, respectively; T_6 is coolant temperature at the inlet to the system of cold heat exchangers; T_7 is coolant temperature at the outlet of the system of cold heat exchangers; G_T is coolant consumption in the system of cold heat exchangers; E is the EMF of thermoelectric generator; U is the voltage of thermoelectric generator in the mode of matched load; I is the current of thermoelectric generator in the mode of matched load; W is the electrical power of thermoelectric generator in the mode of matched load.

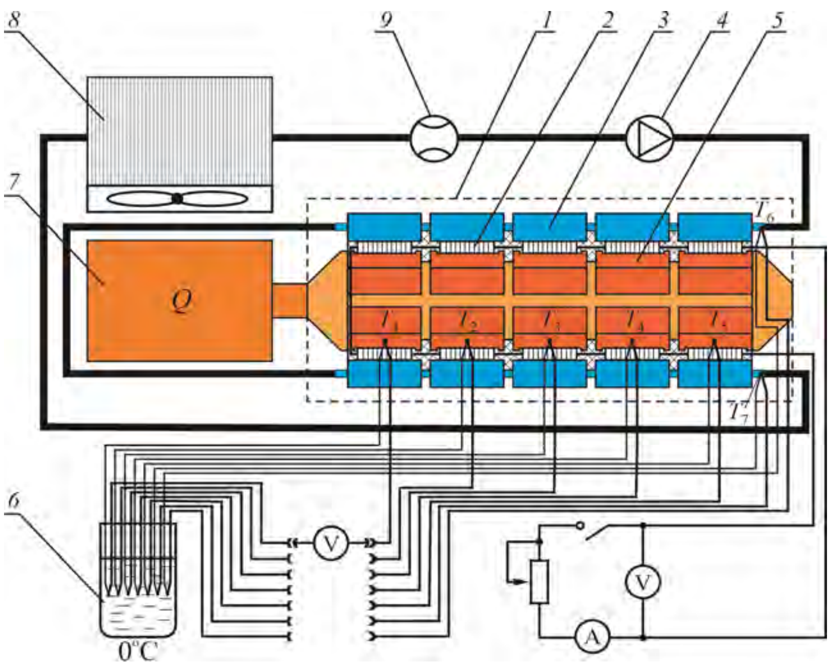


Fig. 3. Layout of the bench for experimental studies of characteristics of the developed model sample of thermoelectric generator: 1 –thermoelectric generator; 2 – thermoelectric modules;3 – cold heat exchangers; 4 – circulation pump; 5 – hot heat exchangers; 6 – Dewar vessel; 7 – heat source on diesel fuel; 8 – radiator

Table 1.

Results of bench studies of thermoelectric generator

T_1, °C	T_2, °C	T_3, °C	T_4, °C	T_5, °C	T_6, °C	T_7, °C	G_T, m³/h	E, V	U, V	I, A	W, W
Thermal power of the heat source ~ 5 kW											
183.2	181.3	175.8	170.0	164.2	19.8	25.5	0.7	20.77	10.39	13.75	142.8
Thermal power of the heat source ~ 10 kW											
294.9	293.8	284.8	275.3	263.3	20.1	30.9	0.7	35.06	17.53	20.07	351.8

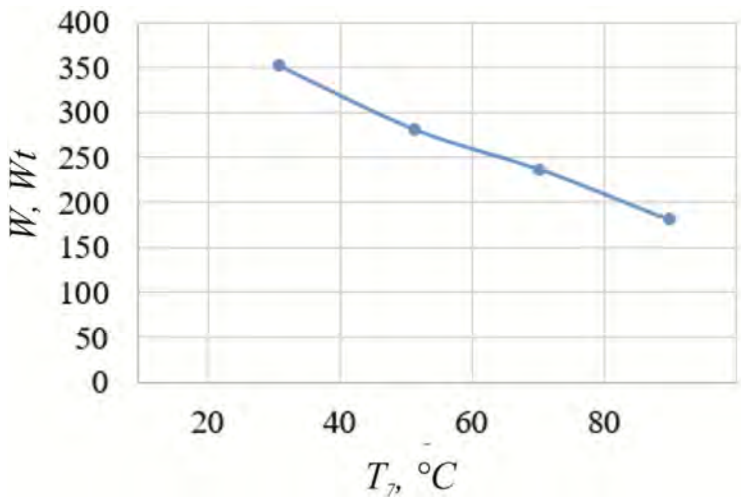


Fig. 4. Dependence of generator power W on coolant temperature T_7 in the system of liquid heat exchangers

The dependence of generator power *W* on coolant temperature T_7 in the system of liquid heat exchangers (heat removal from thermoelectric modules) is presented in Fig. 4. As is seen from the figure, with a rise in coolant temperature (T_7 – from 30 to 90 °C), the generator power is reduced from 350 W to 180 W.

The results obtained, taking into account possible experimental errors, correspond to the expected results of computer design.

Conclusions

1. The design of a thermoelectric generator with electric power up to 350 W and heat power up to 10 kW is described. In combination with a pre-heater with a thermal power of 25-30 kW, the generator will form an autonomous preheating system with a thermal power of up to 40 kW.
2. A bench was set up to study the characteristics of the developed thermoelectric generator for the pre-start source of heat and electricity for high duty vehicles.
3. Bench experimental studies of the model sample of the developed thermoelectric generator were carried out. It has been established that at a coolant temperature in the thermoelectric generator cooling system in the range from 30 to 90 °C, the power of the thermoelectric generator is from 180 to 350 W, which fully corresponds to the expected values.

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СТЕНДОВІ ЕКСПЕРИМЕНТАЛЬНІ ДОСЛІДЖЕННЯ ТЕРМОЕЛЕКТРИЧНОГО ДЖЕРЕЛА ТЕПЛА ТА ЕЛЕКТРИКИ ДЛЯ ТРАНСПОРТНИХ ЗАСОБІВ ВЕЛИКОЇ ПОТУЖНОСТІ

Розглянуто конструкцію термоелектричного генератора електричною потужністю до 350 Вт для живлення електричною енергією та забезпечення автономної роботи передпускових джерел тепла та електрики з тепловою потужністю до 40 кВт для транспортних засобів великої потужності. Наведено опис стенду для дослідження характеристик розробленого термоелектричного генератора та результати експериментальних досліджень макетного зразка генератора. Бібл. 8, рис. 4, табл. 1.

Ключові слова: передпусковий нагрівник, термоелектричний генератор, стендові дослідження.

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СТЕНДОВЫЕ ЭКСПЕРИМЕНТАЛЬНЫЕ ИССЛЕДОВАНИЯ ТЕРМОЭЛЕКТРИЧЕСКОГО ИСТОЧНИКА ТЕПЛА И ЭЛЕКТРИКИ ДЛЯ ТРАНСПОРТНЫХ СРЕДСТВ БОЛЬШОЙ МОЩНОСТИ

Рассмотрена конструкция термоэлектрического генератора электрической мощностью до 350 Вт для питания электрической энергией и автономной работы предпусковых источников тепла и электричества с тепловой мощностью до 40 кВт для транспортных средств большой мощности. Представлено описание стенда для исследования характеристик разработанного термоэлектрического генератора и результаты экспериментальных исследований макетного образца генератора. Библ. 8, рис. 4, табл. 1.

Ключевые слова: предпусковой отопитель, термоэлектрический генератор, стендовые исследования.

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EQUIPMENT FOR DETERMINING THE PARAMETERS OF GENERATOR THERMOELECTRIC MODULES

The results of development of the design of automated equipment for determining the parameters of generator thermoelectric modules are presented. The equipment was created on the basis of the absolute method, which allows measuring the parameters of the modules in real conditions of their operation, instrumentally minimizing the main sources of measurement errors, as well as determining the thermoelectric properties of the materials in the composition of these modules. The measurement control unit is built on the basis of a multi-channel analog-to-digital converter. Processing and display of measurement results are carried out using a computer, the results are displayed in the form of graphs and tables.

Key words: thermoelectric module, generation of electrical energy, electrical conductivity, thermoEMF, thermal conductivity, thermoelectric material, automation, computerization.

Introduction

General characterization of the problem.

Quality control of thermoelectric generator modules plays an important role in the development of these modules and the creation of thermoelectric generators based on them. This control is carried out by measuring the parameters of the modules - electric power and efficiency, as well as their dependence on temperature [1]. One of the best measurement methods in this case is the absolute method [2, 3], which allows measurements to be made in real conditions of module operation and provides the possibility of instrumental minimization of the main sources of measurement errors.

In addition, the absolute method makes it possible to obtain additional information about the properties of the material in the module - thermoEMF, electrical conductivity and thermal conductivity of a pair of thermoelectric circuits [4, 5]. This information is useful for optimizing the material for specific module applications in thermoelectric generators of various types, as well as for improving the design of the modules themselves.

The purpose of this work is to develop the design of equipment for determining the parameters of generator thermoelectric modules, as well as the properties of the thermoelectric material in the composition of these modules.

1. Description of the measurement technique

The diagram of the absolute method for determining the parameters of generator thermoelectric modules is shown in Fig. 1. The module is placed between two heat-levelling plates, which in turn are located between the electric heater and the heat meter. The heat meter contacts the thermostat with its other side.

Using an electric heater, a given temperature difference is created on the module and the EMF E_{TEM}, which occurs at the module terminals, is measured. After this, a matched electrical load is connected to the module terminals, at which the voltage at the module terminals becomes equal to half the EMF. The values of the electric current I_{TEM} passing through the module, the voltage at its terminals U_{TEM} are measured, and the heat flow Q_1 removed from the cold side of the module to the thermostat is determined using a heat meter. The electric power of the module P and its efficiency η are determined using the formulae

$$P = I_{TEM} \cdot U_{TEM}\,, \tag{1}$$

$$\eta = \frac{P}{Q_1 + P_{TEM}}\,. \tag{2}$$

where I_{TEM} and U_{TEM} are current and voltage of module, Q_1 is heat flow removed from the cold side of module and determined with the aid of a heat meter.

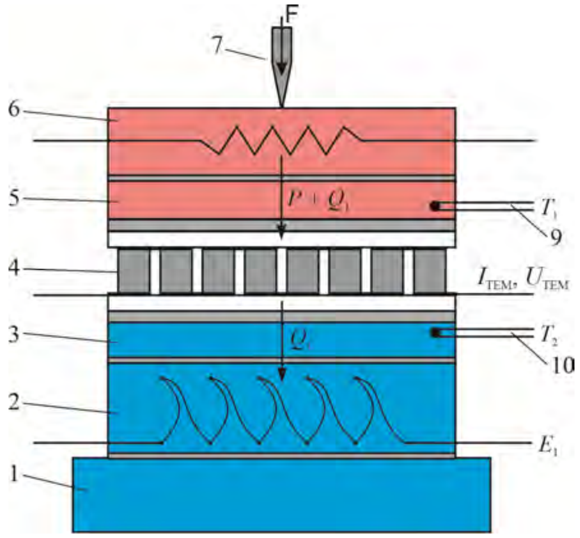

Fig. 1 – Absolute method of measuring the parameters of thermoelectric generator modules: 1 – thermostat; 2 – heat meter, 3, 5 – heat levelling plates; 4 – module under study; 6 – heater; 8 – clamp; 10, 11 –thermocouples.

To find the properties of the thermoelectric material in the modules, the method described in detail in [5] was used. The average values of electrical conductivity, thermoEMF, thermal conductivity and the figure of merit of the material of the legs of the thermoelectric module are determined by the formulae

$$\sigma = \frac{1}{R_M/2N}\frac{h_1}{a_1 \cdot b_1} \cdot K_1\,, \tag{6}$$

$$\alpha = \frac{E/2N}{\Delta T} \cdot K_2\,, \tag{7}$$

$$\kappa = \frac{Q/2N}{\Delta T}\frac{h_1}{a_1 \cdot b_1} \cdot K_3\,, \tag{8}$$

$$Z = \frac{\alpha^2\sigma}{\kappa}\,, \tag{9}$$

where R_M is module resistance measured with alternating current; a_1 x b_1 is cross-section of legs; h_1 is leg height; N is the number of pairs; E is module EMF; ΔT is temperature difference between the thermocouples located on the heat-levelling plates between which the module under study is located; Q is heat flow through the module; K_1 - K_3 are correction factors for reducing the magnitude of measurement errors, calculated for a given module design and measuring equipment or determined experimentally.

2. Description of the design of measuring equipment

The equipment for determining the parameters of the generator thermoelectric module consists of a module holder, an electronic measuring unit and a thermoregulation unit, an electric power supply unit, and hydraulic armature for connecting the holder to water cooling line.

The equipment is computerized to eliminate possible subjective errors and increase the accuracy and speed of measurements. The measurement automation system is built on the basis of a 4-channel analog-to-digital converter (ADC) with differential inputs, the range of measured voltages of which is ± (5 μV – 2.5 V). The differential inputs of the ADC make it possible to carry out high-precision measurements of voltages in electrical circuits of various units, which may have different power sources.

The appearance of the measurement automation system is shown in Fig. 2.

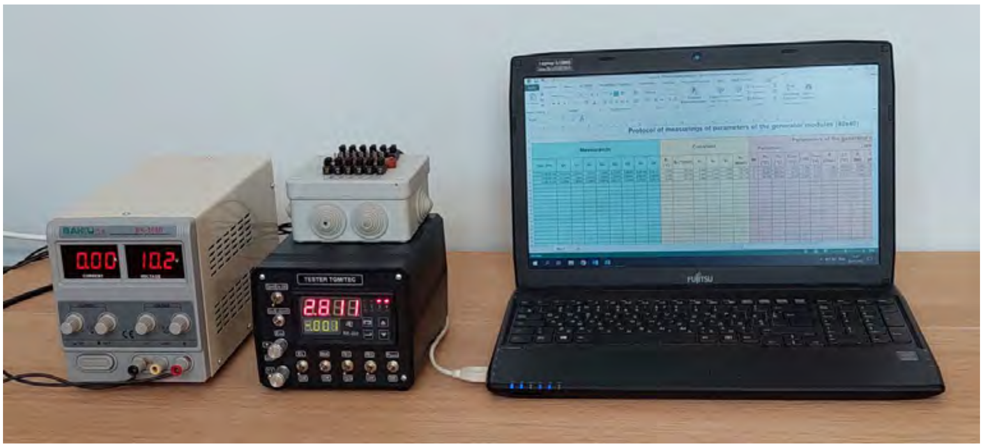

Fig. 2. Appearance of the automation system for measuring parameters of thermoelectric generator modules.

The developed control system is universal. Depending on the selected measurement algorithm, the heat flow can be determined both by the heat meter and by the power of the reference heater, with compensation for heat losses by the screen heater. This allows implementing different algorithms for measuring module parameters.

The generator module holder is a mechanical structure in which the generator module under study is placed. The holder ensures the transfer of thermal power through the module and the removal of the generated electric voltage from the module. The transfer of thermal energy through the module is performed using two heat exchange units: a heating unit and a heat removal unit. The appearance of the generator module holder is shown in Fig. 3.

The heating unit has the main reference heater of the hot side of the generator module and temperature and heat flow control elements: thermocouples, protective and screen auxiliary heaters and an air cooler.

The heat removal unit on the cold side of the module has a main water heat exchanger and temperature and heat flow control elements: thermocouples, heat meter, auxiliary heaters and air cooler.

To increase measurement accuracy and versatility, heat exchange units have replaceable elements that are designed for specific module sizes and can be easily changed.

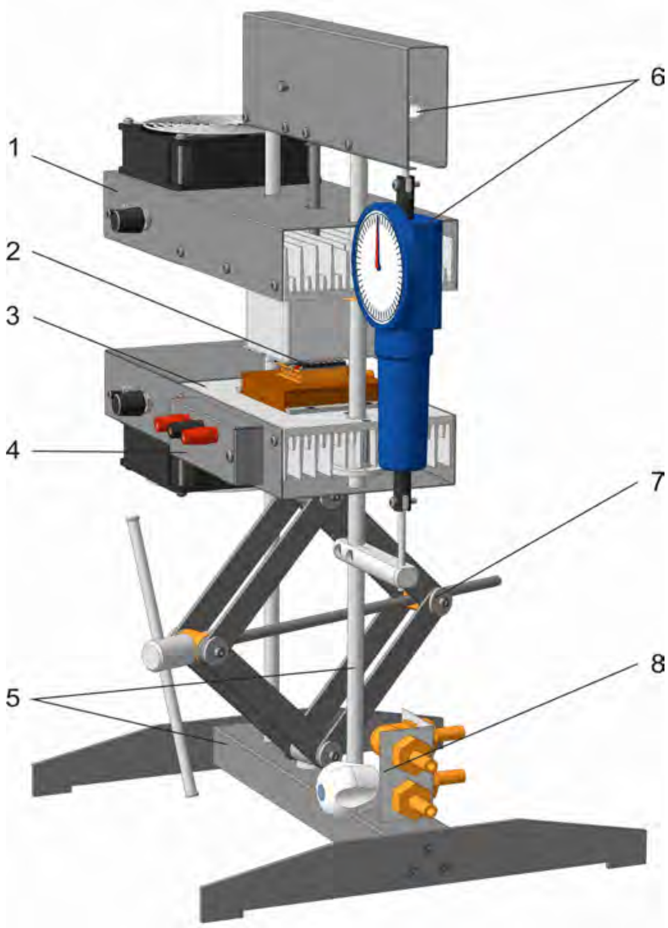

Fig. 3. Design of the generator module holder: 1 – heating unit; 2 – generator module; 3 – heat removal unit; 4 – electrical terminal block; 5 – supporting steel frame; 6 – lever-spring clamping mechanism; 7 – jack-screw mechanism for moving the heat exchanger; 8 – hydraulic armature.

The heat exchange units have sliding bearings, with the help of which they can move up and down along two steel racks fixed on the base of the steel frame. The heat exchange units have working platforms between which the generator module is clamped during measurement. The centers of the working platforms are coaxial.

The heating unit is fixed in the upper part of the racks of the frame, and the heat removal unit on the same racks is located below and can be moved up and down with the help of a jack-type screw mechanism. Even higher, above the heating block on the racks, a generator module clamping device is fixed between the working platforms of the heat exchange blocks. The clamping force is fixed using a lever-spring method, and is set using a jack mechanism. A standard dynamometer is used as a spring.

An electrical terminal block is attached to the heat sink unit for connecting the outputs of the generator module. The terminal block is electrically connected to the electronic load unit with a cable.

The source of thermal power for the generator module in the device is a heating block. The basis of the design of the heating block is an aluminum finned radiator, to which all its components are attached:

moving elements, clamping elements and a replaceable heater unit. For different sizes of generator modules, proportionate heating elements are provided. The structure of the heating block is shown in Fig. 4.

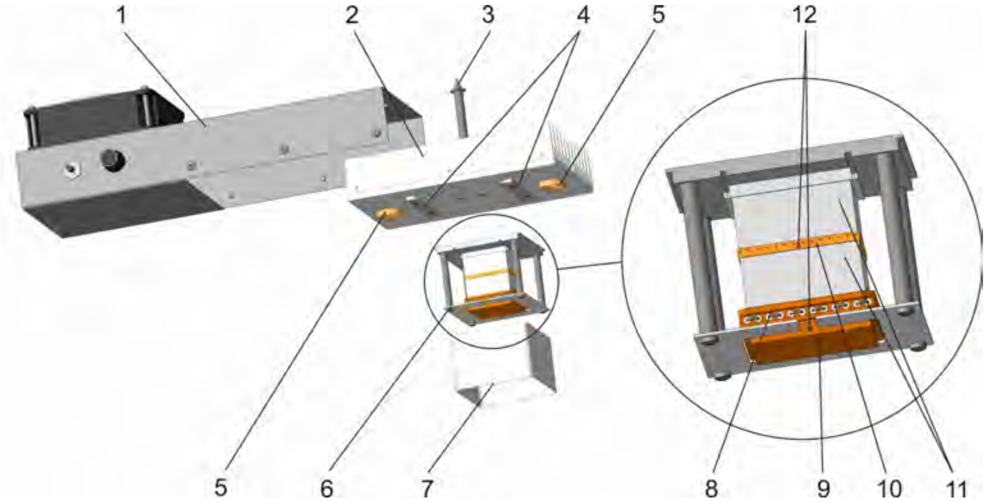

Fig. 4. Structure of the heating unit: 1 – casing with a fan; 2 – ribbed radiator; 3 – rod of the clamping unit; 4 – fastening unit for replaceable heaters, 5 – sliding bearings of the unit for moving heat exchange units; 6 – unit of heaters; 7 – casing of the unit of heaters; 8 – reference heater; 9 – heat levelling plate; 10 – screen heater; 11 – thermal insulation gaskets; 12 – holes for installation of thermocouples.

Thermal energy that flows through the working surfaces of the generator module is partially converted into electrical energy, and the rest is taken by the heat removal unit and dispersed into the environment. The basis of the design of the heat removal unit is also an aluminum finned radiator, to which all its components are attached: moving elements, clamping elements and a replaceable unit of a water heat exchanger, a heat meter and an additional corrective heater (Fig. 5).

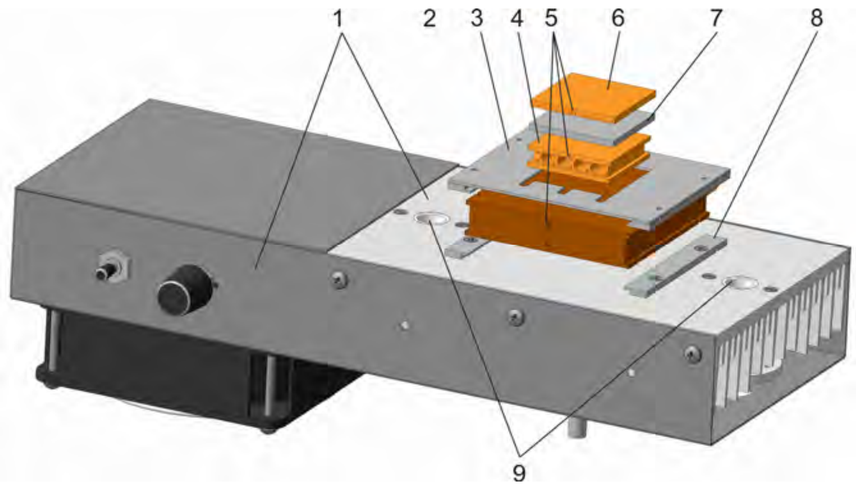

Fig. 5 – Structure of the heat removal unit: 1 – ribbed radiator with blower fan; 2 – water heat exchanger; 3 – centering plate for the thermometer; 4 – thermometer; 5 - holes for installing thermocouples; 6 - corrective heater, 7 - thermal shunt; 8 – fastening unit for replaceable heat exchangers. 9 – sliding bearings of the unit for moving the heat exchange units.

For different types of generator modules, removable, commensurate heat meters and heaters are provided. With the help of the correcting heater, it is possible to change the temperature range of measuring parameters of the generator modules within wide limits. A bracket is attached to the central part of the ribbed radiator below, which is connected to the upper movable platform of the jack. With the help of this jack, the heat removal unit is moved up and down.

The clamping device is important. To improve thermal contacts, thermal drivers are used that can work at elevated temperatures, within the range of maximum operating temperatures for the generator module.

When measuring the parameters of the module, the thermal power from the electric heater, which passes through the module, generates an electrical voltage at its terminals. By the moment the temperatures on the heat-levelling plates reach the set levels, the electronic load is turned off and the thermal emf of the module is measured using an ADC. After reaching the specified temperature difference, the electronic load is switched on at the command of the processor and the current of the module is measured. At the same time, the thermoregulators of the thermostat and the heating heat exchanger automatically compensate for the thermal disturbance caused by the Peltier effect from the action of the module current. The values of electric voltages, currents and temperatures are displayed on a digital indicator, and are also sent to a personal computer for calculations and plotting in a given temperature range. The sequence of measurements and the time intervals between them are specified in the cyclogram, which is formed by the operator before starting the measurements.

The developed equipment allows measuring the parameters of generator thermoelectric modules with sizes from 10x10 to 72x72 mm in the temperature range from 30°C to 600°C, as well as determining the properties of thermoelectric materials in the composition of these modules.

Conclusions

1. The design of measuring equipment has been developed, which allows measuring the parameters of generator thermoelectric modules by the absolute method, as well as determining the properties of thermoelectric materials in the composition of these modules. The created equipment allows measuring the parameters of modules with sizes from 10x10 to 72x72 mm in the temperature range from 30°C to 600°C.
2. The created equipment is computerized, allowing measurements to be taken according to a given algorithm, their results to be processed in real time, the results of measurements to be displayed on the screen in the form of graphs and tables, stored on the computer, and the passport of the module studied to be printed out.

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ОБЛАДНАННЯ ДЛЯ ВИЗНАЧЕННЯ ПАРАМЕТРІВ ГЕНЕРАТОРНИХ ТЕРМОЕЛЕКТРИЧНИХ МОДУЛІВ

Представлено результати розробки конструкції автоматизованого обладнання для визначення параметрів генераторних термоелектричних модулів. Обладнання створено на основі абсолютного методу, що дозволяє проводити вимірювання параметрів модулів у реальних умовах їх експлуатації, інструментально мінімізувати основні джерел похибок вимірювань, а також визначати термоелектричні властивості матеріалів у складі цих модулів. Блок керування вимірюваннями побудовано на основі багатоканального аналогово-цифрового перетворювача. Обробка та відображення результатів вимірювань проводяться за допомогою комп'ютера, результати відображаються у вигляді графіків і таблиць.

Ключові слова: термоелектричний модуль, генерація електричної енергії, електропровідність, термоЕРС, теплопровідність, термоелектричний матеріал, автоматизація, комп'ютеризація.

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ОБОРУДОВАНИЕ ДЛЯ ОПРЕДЕЛЕНИЯ ПАРАМЕТРОВ ГЕНЕРАТОРНЫХ ТЕРМОЭЛЕКТРИЧЕСКИХ МОДУЛЕЙ

Представлены результаты разработки конструкции автоматизированного оборудования для определения параметров генераторных термоэлектрических модулей. Оборудование создано на основе абсолютного метода, позволяющего производить измерение параметров модулей в реальных условиях их эксплуатации, инструментально минимизировать основные источники погрешностей измерений, а также определять термоэлектрические свойства материалов в составе этих модулей. Блок управления измерениями построен на основе многоканального аналогово-цифрового преобразователя. Обработка и отображение результатов измерений производятся с помощью компьютера, результаты отображаются в виде графиков и таблиц.

Ключевые слова: термоэлектрический модуль, генерация электрической энергии, электропроводность, термоЭДС, теплопроводность, термоэлектрический материал, автоматизация, компьютеризация.

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EQUIPMENT FOR DETERMINING THE PARAMETERS OF THERMOELECTRIC COOLING MODULES

The results of the development of the design of equipment for measuring the parameters of thermoelectric cooling modules, as well as determining the thermoelectric properties of materials in these modules, are presented. The equipment was created on the basis of the absolute method, which makes it possible to determine the parameters of modules in real conditions of their operation and allows instrumental minimization of the main sources of measurement errors. The measurement control unit is built on the basis of a multichannel analog-to-digital converter. Processing and display of measurement results are carried out using a computer; the results are displayed through graphs and tables. Bibl. 5, Fig. 6.
Key words: thermoelectric module, cooling, electrical conductivity, thermoEMF, thermal conductivity, thermoelectric material, automation, computerization.

Introduction

General characterization of the problem.

It is known that the quality control of thermoelectric energy converters (modules) plays an important role both in their development and in the creation on the basis of these modules of thermoelectric cooling devices. Such control is carried out by measuring the parameters of thermoelectric modules, namely cooling capacity, coefficient of performance and temperature difference on the module, as well as their temperature dependence [1]. One of the best measurement methods in this case is the absolute method. The main advantages of this method are the determination of module parameters in real operating conditions and the possibility of instrumental minimization of the main sources of measurement errors [4].

Moreover, the absolute method makes it possible to obtain additional information about the properties of the material forming part of the module, namely thermoEMF, electrical conductivity and thermal conductivity of a pair of thermoelectric legs [5]. This information is useful both for optimizing thermoelectric material for its specific applications and for improving the design of modules.

The purpose of this work is to develop the design of equipment for determining the parameters of thermoelectric cooling modules, as well as the properties of thermoelectric material in these modules.

Description of measurement method

The schematic of the absolute method, taken as a basis for the creation of automated equipment for determining the parameters of thermoelectric cooling modules, is shown in Fig.1. To determine the parameters of the thermoelectric module, the latter is placed between two heat equalizing plates, which in turn are located between the electrical heater and the thermostat. Additionally, a protective heater is used, the temperature of which is maintained equal to the temperature of the reference heater, which prevents heat loss from the heater through the clamping mechanism. The electrical current is passed through the module and its value is selected at which the temperature difference between the cold and hot surfaces of the module will reach the maximum value ΔT_{max}. After that, the electrical current through the heater is turned on and gradually increases to a value at which the temperature difference across the module becomes equal to zero.

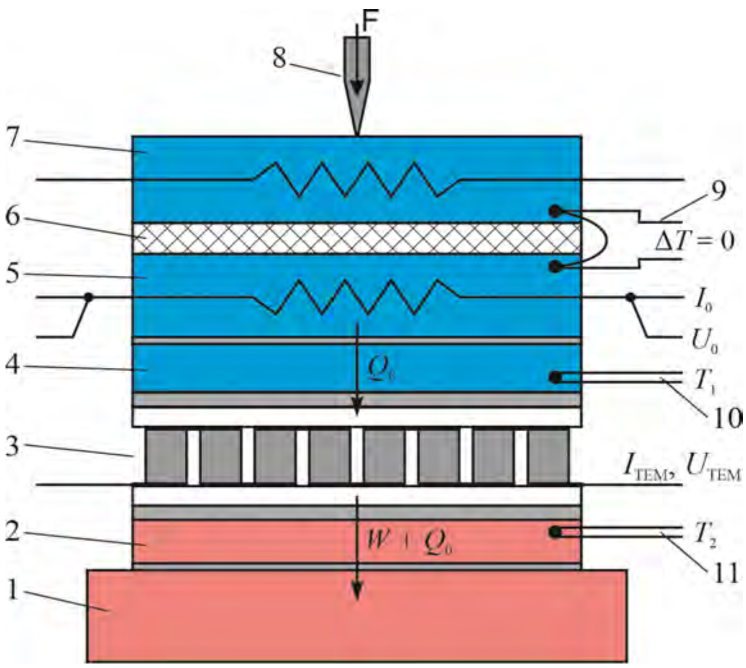

Fig. 1. Absolute method of measuring the parameters of thermoelectric cooling modules:
1 – thermostat; 2, 4 –heat equalizing plates; 3 – module under study; 5 – reference heater;
6 – thermal insulation; 7 – protective heater; 8 – clamp; 9 – zero thermocouple; 10, 11 – thermocouples

The maximum cooling capacity of the module is considered to be equal to the electrical power, which is released by the electrical heater.

The values of cooling capacity Q_0, temperature difference ΔT and coefficient of performance ε are determined by the formulae

$$Q_0 = I_0 \cdot U_0\,, \tag{3}$$

$$\Delta T = T_1 - T_2\,, \tag{4}$$

$$\varepsilon = \frac{Q_0}{W}\,, \tag{5}$$

where I_0 and U_0 is current through the heater and voltage drop thereupon, T_1 is the cold side temperature of module, T_2 is the hot side temperature of module, W is the electrical power consumed by the module.

To find the properties of the thermoelectric material forming part of the modules, the technique described in detail in [5] was used. It is as follows:

- determination of the electrical conductivity σ by the measured module resistance on the alternating current and the known module design;
- creation on the module of temperature difference by means of the electrical heater (with current through the module switched off);
- determination of the Seebeck coefficient α by the measured values of module EMF and temperature difference on the module;
- determination of the thermal conductivity κ by the measured values of heat flux through the module (electrical heater power) and temperature difference on the module.

The average values of the electrical conductivity, thermoEMF, thermal conductivity and figure of merit of the material of thermoelectric module legs are determined by the formulae

$$\sigma = \frac{1}{R_M/2N}\frac{h_1}{a_1 \cdot b_1} \cdot K_1\,, \tag{6}$$

$$\alpha = \frac{E/2N}{\Delta T} \cdot K_2\,, \tag{7}$$

$$\kappa = \frac{Q/2N}{\Delta T}\frac{h_1}{a_1 \cdot b_1} \cdot K_3\,, \tag{8}$$

$$Z = \frac{\alpha^2 \sigma}{\kappa}\,, \tag{9}$$

where R_M is module resistance measured on the alternating current; a_1 x b_1 is cross-section of legs; h_1 is the height of legs; N is the number of pairs; E is module EMF; ΔT is temperature difference between thermocouples placed on heat equalizing plates with a module under study arranged between them; Q is heat flux through the module; K_1 - K_3 are correction factors to reduce the magnitude of measurement errors, calculated for a given design of the module and measuring equipment or determined experimentally.

Description of measuring equipment design

The equipment for determining the parameters of a thermoelectric cooling module consists of a thermoelectric module holder, an electronic measuring unit and a thermal control unit, an electrical power supply unit, hydraulic fittings for connecting the holder to the water cooling line. The measuring unit has an interface for connection to a PC for measurements and processing of their results. The holder of the cooling module is a mechanical design in which the investigated module is placed. The design of the holder is shown in Fig. 2.

The holder provides the supply of current and heat load through the module and the removal of information from the module about the created temperature differences and heat energy transfers. The transfer of thermal energy through the module is carried out by means of supply current between two heat exchange units - from the heating unit to the heat removal unit.

The heating unit has a main reference heater for the cold side of the cooling module and temperature and heat flux control elements: thermocouples, shield thermoelectric heater/cooler, and an air cooler.

The heat removal unit on the hot side of the module has a main water heat exchanger, temperature control elements: thermocouples, an auxiliary thermoelectric table, heaters and an air cooler.

To increase measurement accuracy and for versatility, the heat exchange units have replaceable elements designed for specific cooling module sizes and which can be easily changed as needed.

The heat exchange units have slide bearings, with which they can move up and down along two steel racks fixed on a steel frame. The heat exchange units have working platforms between which the studied module is clamped during the measurement. The centers of the working platforms are coaxial.

The heating unit is fixed in the upper part of the racks of the frame, and the heat removal unit on the same racks is located below and can be moved up and down using a jack-type screw mechanism. Even higher, above the heating block on the racks, a device for pressing the studied cooling module between the working platforms of the heat exchange blocks is fixed. The clamping force is fixed by a lever-spring method, and is set using a jacking mechanism. A standard dynamometer is used as a spring.

An electrical terminal block is attached to the heat removal unit for connecting the wires of the cooling module. The terminal block is connected to the electronic units with a cable.

The source of thermal power for the cooling module in the device is the heating unit, from which it is transferred to the heat removal unit. If there is no inflow of heat from the heating unit - the module operates in the mode of the maximum temperature difference. When a thermal load occurs, the resulting temperature difference will be less and the module will operate in cooling capacity mode. The basis of the design of the heating block is an aluminum finned radiator, to which all its components are attached: moving elements, clamping elements and a replaceable heater unit - a working platform for thermal contact with the surface of the module and heat load heaters. For different standard sizes of cooling modules, elements proportionate to them are provided – work platforms and heaters. The structure of the heating unit is shown in Fig. 3.

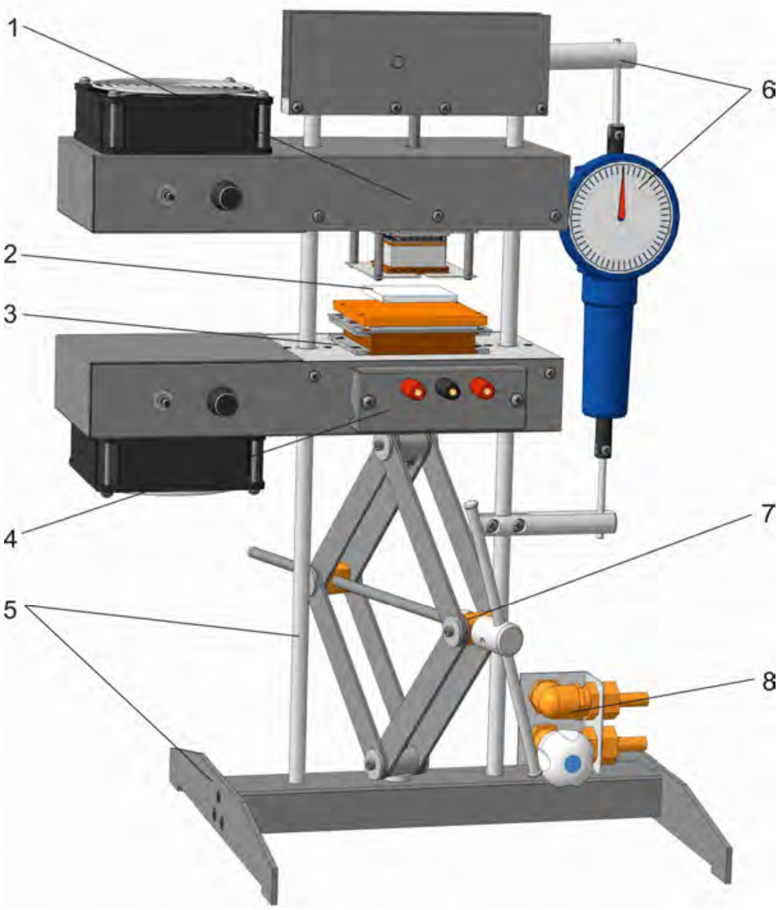

Fig. 2. The design of the module holder for measuring the parameters of thermoelectric cooling modules: 1 – heating unit; 2 – module under study; 3 – heat removal unit; 4 – electrical terminal block; 5 – load-bearing steel frame; 6 – lever-spring clamping mechanism; 7 – jack-screw mechanism for moving the heat exchanger; 8 – hydraulic fittings

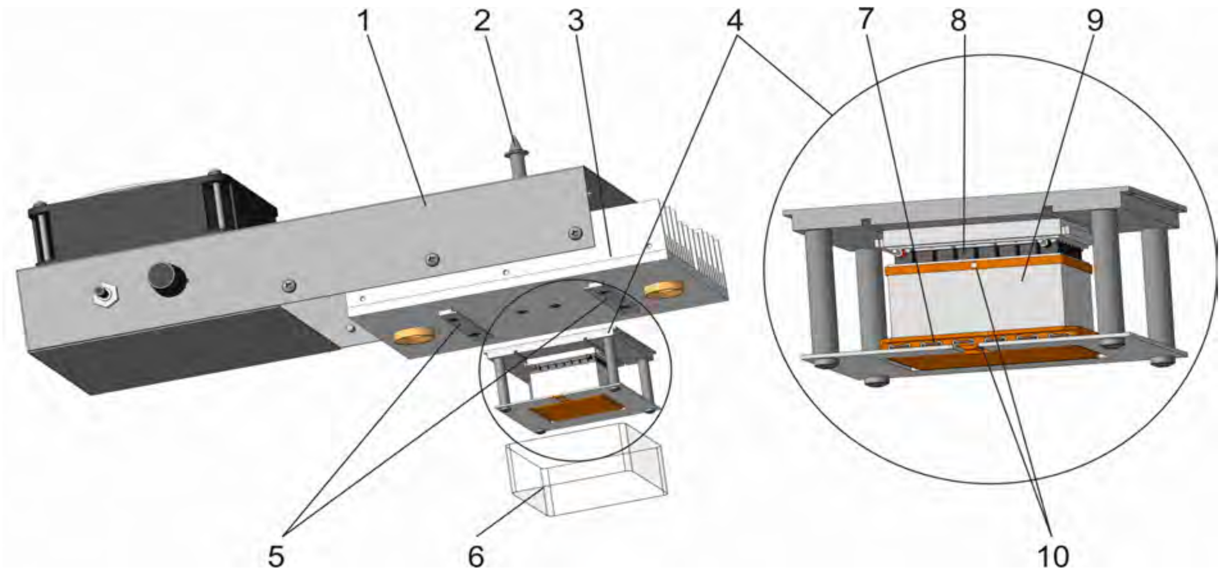

Fig. 3. The structure of the measuring equipment heating unit:
1 – casing with fan; 2 – clamping assembly rod; 3 – finned radiator;
4 – heating unit and the receiving work platform for cooling module;
5 – fixing assembly for replaceable heating units; 6 – heater assembly cover;
7 – reference heater with receiving platform; 8 – shield heater/cooler;
9 – thermal insulation gasket; 9 – holes for mounting thermocouples

The electrical supply current flowing through the cooling module creates a temperature difference on its working surfaces and in the presence of thermal contact between the module and the working platforms of the heat exchange units, a heat flux will appear in the direction from the heater unit to the heat removal unit. External heat can be generated both by the reference heater and absorbed from the environment. To cut off heat from the external environment, passive thermal insulation of the working platform and the use of a shield heater/cooler are used, the operation of which is controlled by electronic units.

The structure of the heat removal unit is shown in Fig. 4. The basis of the design of the unit is also an aluminum finned radiator, to which all its components are attached: elements of movement, clamps and a replaceable unit of water heat exchanger and additional corrective thermotable - heater or cooler, as needed.

For different types of cooling modules, removable, proportionate water heat exchangers are provided with working platforms or thermotables placed on them. With the help of corrective heaters or thermoelectric modules of the thermotable, it is possible to change the temperature range for measuring the parameters of the cooling modules over a wide range.

Attached to the center of the finned radiator, at the bottom, is a bracket that is connected to the upper movable jack pad. With this jack, the heat sink moves up and down.

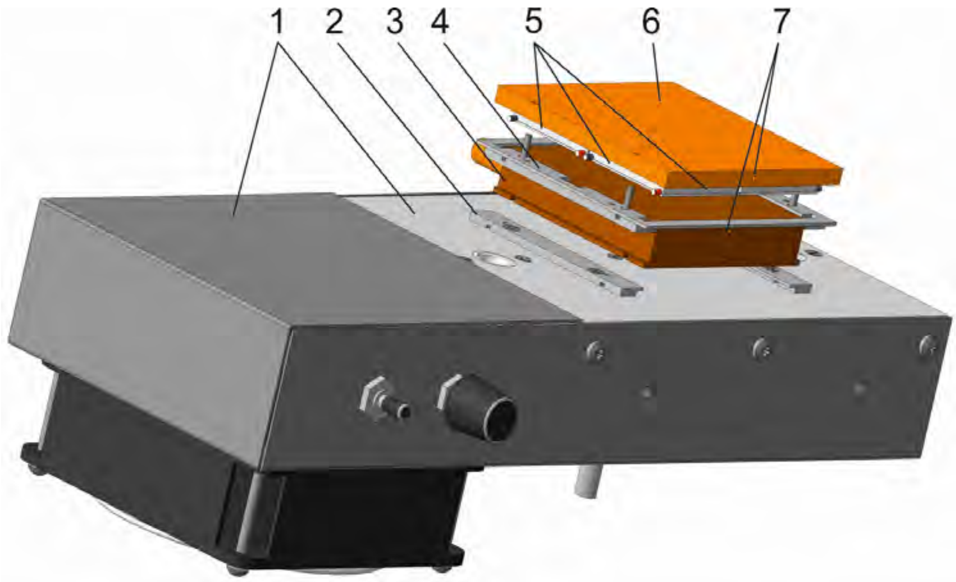

Fig.4. Design of unit for heat removal from cooling module:
1 – finned radiator with a blower fan; 2 – fixing assembly for replaceable heat exchangers; 3 – water heat exchanger; 4 – centering plate for thermotable; 5 – thermoelectric modules of thermotable; 6 – working platform for installation of cooling nodule; 7 – holes for installation of thermocouples

To increase the accuracy of measuring the parameters of a thermoelectric cooling module, it is necessary that the heat generated by the upper heat exchanger and removed through the module by the lower heat exchanger passed with the least losses. The imperfection of the working surfaces of the heat exchangers and the cooling module, which is measured, leads to the fact that the temperatures on the surfaces of the heat exchangers differ from the temperatures on the working surfaces of the module. The actual difference on the module will be less than the measured difference between the heat exchangers, but it is in the heat exchangers that the temperature sensors are located for technological and design reasons.

To improve thermal contact, thermal drivers are also used - liquid substances with a fairly high (relative to air) coefficient of thermal conductivity. These can be various heat-conducting pastes, oils, etc. When using such substances, they fill the air gap between the unevenness of the surfaces of the module and heat exchangers. To improve the thermal contact, the module surfaces between the heat exchangers should be pressed with such force that the excess material of the thermal driver is displaced from the interlayer, and the solid surfaces of the heat exchangers and the module rest against each other only by the nearest protrusions. The holder design makes it possible to apply a compression force from 0 to 200 kg to the module (for example, a standard ALTEC-22 thermoelectric module with a total area of about 10 cm^2 of legs must be compressed between heat exchangers with a force of about 80 kg).

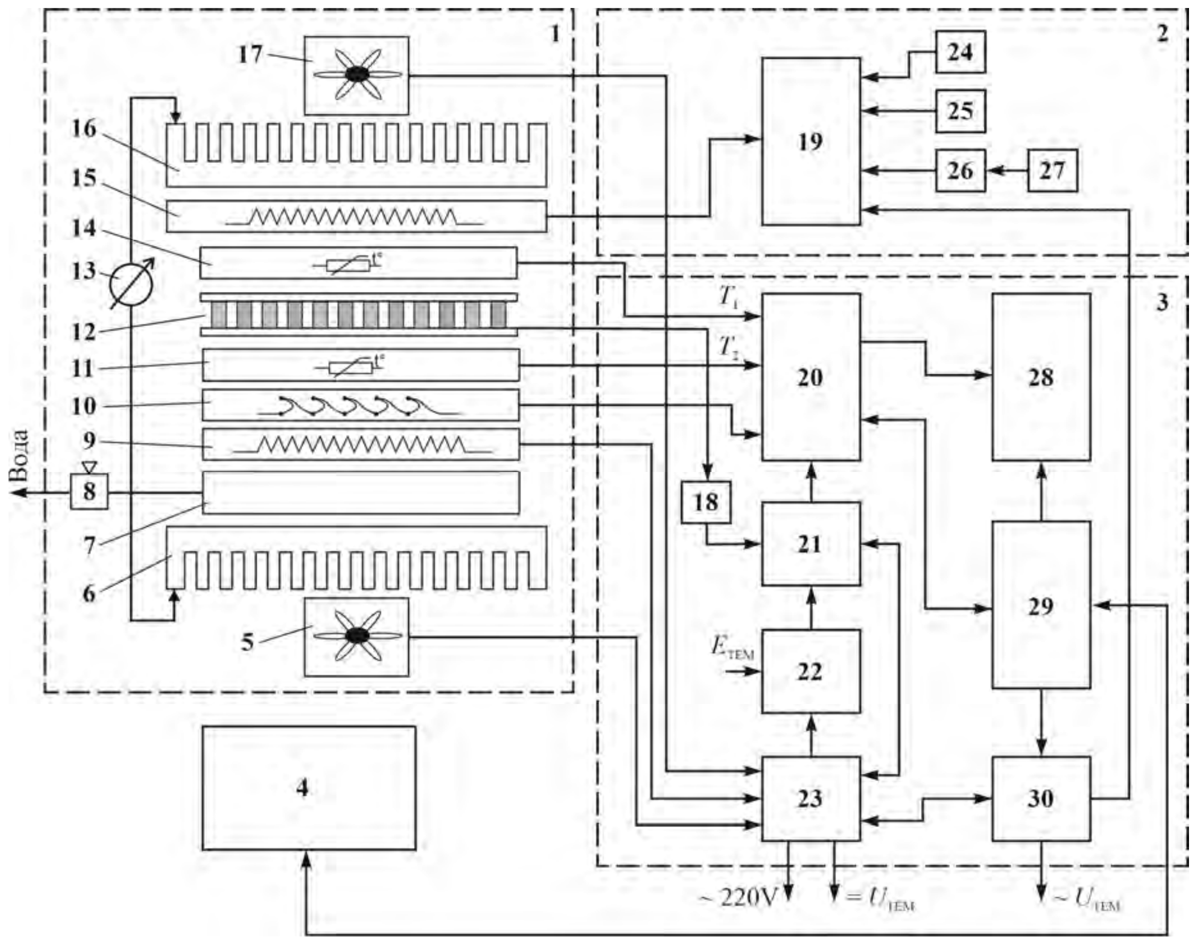

Fig. 5 – Block diagram of the automation system for measuring the parameters of thermoelectric modules by the absolute method:
1 – thermoelectric module holder; 2 – power unit; 3 – control unit; 4 – personal computer; 5, 17 – fans; 6, 16 – air heat exchangers; 7 – water heat exchanger; 8 –tap; 9 –thermostat electric heater; 10 – heat meter; 11, 14 – heat equalizing plates with embedded temperature sensors; 12 – thermoelectric module under study; 13 – dynamometer; 15 – module heater; 18 – electronic load; 19 – heater connection block; 20 – 4- channel precision ADC; 21 – electronic load current/voltage converter; 22 – electronic load control unit; 23 – thermostat power supply; 24 –shield heater power unit; 25 – zero node; 26 – reference heater current/voltage meter; 27 – reference heater power unit; 28 – digital indicator; 29 – control processor; 30 – triac heater control key

The equipment is computerized to eliminate possible human errors and increase the accuracy and speed of measurements. The block diagram of the automation system for measuring the characteristics of thermoelectric modules is shown in Fig.5. It is based on a 4-channel analog-to-digital converter (ADC) with differential inputs, the measured voltage range of which is ±(5 μV - 2.5 V). Differential ADC inputs allow high precision voltage measurements in electrical circuits of different units, which may have different power sources.

Fig. 6. Appearance of equipment for measuring the parameters of thermoelectric cooling modules

The developed control system is universal. Depending on the chosen measurement algorithm, the heat flux can be determined by both the heat meter and the power of the reference heater, provided that the heat loss is compensated by the shield heater. This makes it possible to implement different algorithms for measuring the parameters of both cooling modules and generator modules. All measured signals are sent to the controller, where they are normalized to certain physical values. The values of electrical voltages, currents and temperatures are displayed on a digital indicator 28, and also supplied to a personal computer 4 for calculations and plotting in a given temperature range. The sequence of measurements and the time between them are set in the cyclogram, which is formed by the operator before the start of measurements.

The appearance of the developed equipment is shown in Fig. 6. The equipment makes it possible to measure the parameters of thermoelectric modules with dimensions from 10x10 to 72x72 mm in the range of temperatures from -50°C to 100°C, as well as to determine the properties of thermoelectric materials forming part of these modules.

Conclusions

1. The design of measuring equipment has been developed which makes it possible to measure the parameters of thermoelectric cooling modules by the absolute method, as well as to determine the properties of thermoelectric materials forming part of these modules. The equipment allows measuring the parameters of modules with dimensions from 10 × 10 to 72 × 72 mm in the range of temperatures from -50 °C to 100 °C.
2. Computerized equipment has been created that allows measurements to be made according to a given algorithm, real-time processing of their results, displaying the measurement results on the screen in the form of graphs and tables, storing them on a computer, and printing out a passport of the studied module.

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ОБЛАДНАННЯ ДЛЯ ВИЗНАЧЕННЯ ПАРАМЕТРІВ ТЕРМОЕЛЕКТРИЧНИХ МОДУЛІВ ОХОЛОДЖЕННЯ

Представлено результати розробки конструкції обладнання для вимірювання параметрів термоелектричних модулів охолодження, а також визначення термоелектричних властивостей матеріалів у складі цих модулів. Обладнання створено на основі абсолютного методу, що дозволяє визначати параметри модулів у реальних умовах їх експлуатації та дає можливість інструментально мінімізувати основні джерел похибок вимірювань. Блок керування вимірюваннями побудовано на основі багатоканального аналогово-цифрового перетворювача. Обробка та відображення результатів вимірювань проводяться за допомогою комп'ютера, результати відображаються у вигляді графіків і таблиць. Бібл. 5, рис.6.

Ключові слова: термоелектричний модуль, охолодження, електропровідність, термоЕРС, теплопровідність, термоелектричний матеріал, автоматизація, комп'ютеризація.

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ОБОРУДОВАНИЕ ДЛЯ ОПРЕДЕЛЕНИЯ ПАРАМЕТРОВ ТЕРМОЭЛЕКТРИЧЕСКИХ МОДУЛЕЙ ОХЛАЖДЕНИЯ

Представлены результаты разработки конструкции оборудования для измерения параметров термоэлектрических модулей охлаждения, а также определения термоэлектрических свойств материалов в составе этих модулей. Оборудование создано на основе абсолютного метода, позволяющего определять параметры модулей в реальных условиях их эксплуатации и позволяет инструментально минимизировать основные источники погрешностей измерений. Блок управления измерениями построен на основе многоканального аналогово-цифрового преобразователя. Обработка и отображение результатов измерений производятся с помощью компьютера, результаты отображаются посредством графиков и таблиц. Библ. 5, рис.6.

Ключевые слова: термоэлектрический модуль, охлаждение, электропроводность, термоЭДС, теплопроводность, термоэлектрический материал, автоматизация, компьютеризация.

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