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DETERMINATION OF THE TEMPERATURE DEPENDENCES OF THERMOELECTRIC PARAMETERS OF MATERIALS USED IN GENERATOR THERMOELECTRIC MODULES WITH A RISE IN TEMPERATURE DIFFERENCE

A method is proposed for determining the thermoelectric parameters of materials used in generator thermoelectric modules in the case when the cold side of module is thermostated, and the temperature difference across the module gradually increases due to a rise in the hot side temperature with the help of an electric heater. A detailed physical model of this method is considered and the results of estimating possible values of measurement errors are presented.

Key words: measurement, electric conductivity, thermoEMF, thermal conductivity, figure of merit, thermoelectric module.

Introduction

Further progress in thermoelectricity largely depends on the quality of thermoelectric material, which is determined by the figure of merit Z of the material and on which the efficiency of thermoelectric power converters depends, namely the efficiency of generators, the maximum temperature difference and coefficient of performance of coolers, and the heating coefficient of heaters. In this case, the most effective are experimental methods of material optimization, which are reduced to creating a set of samples of materials of different composition and with different concentrations of impurities, measuring their electrical conductivity, thermoEMF, thermal conductivity and determining the figure of merit Z. In this procedure, the correct measurement of these material parameters plays a decisive role. Preliminary studies carried out at the Institute of Thermoelectricity of the National Academy of Sciences and the Ministry of Education and Science of Ukraine made it possible to develop methods and create equipment for accurate determination of the properties of thermoelectric materials by the absolute method, the accuracy of which exceeds the accuracy of world analogues by a factor of 3-5.

The task of creating measuring equipment for studying the parameters of materials used in ready-made thermoelectric power converters remains important. This information is necessary both for optimizing the thermoelectric material for its specific applications, and for improving the design of the thermoelectric converters themselves, improving the technology for creating connecting junctions, and also expanding the possibilities for quality control of the finished product. The most suitable for solving this problem is the absolute method for measuring the parameters of generator thermoelectric modules and equipment ALTEC-10002 based on it [8]. At the Institute of Thermoelectricity, a method for determining the thermoelectric parameters of the module leg material when measuring its parameters by the absolute method is developed, a detailed physical model of this method is considered and the results of estimating possible error values are given. However, practical implementation of this method encounters difficulties due to the fact that for measurements it is required to create a small temperature difference (about 10 °C) at temperatures of both sides of the module up to 500–600 °C.

The purpose of this work is to create a method for determining the thermoelectric parameters of materials used in the generator thermoelectric modules for the case when the cold side of module is thermostated, and the temperature difference on the module gradually increases due to a rise in the hot side temperature.

Description of the method for determining the σ, α, κ, *Z* of the legs material when measuring parameters of a generator thermoelectric module

The method for determining the average values σ, α, κ, Z of the legs material making up the module is as follows:

– determination of electrical conductivity σ by the measured value of the AC resistance of the module and the known design of the module;

– determination of the Seebeck coefficient α by the measured values of module EMF and temperature difference between the heater and the heat sink (with regard to corrections);

– determination of thermal conductivity κ according to the measured values of heat flow through the module (using a heat meter) and the temperature difference between the heater and the heat sink (taking into account corrections and minimizing heat loss).

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

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

$$\alpha = \frac{E/2N}{\left(Tг_0 - Tx_0\right)}, \tag{2}$$

$$\kappa = \frac{Q/2N}{\left(Tг_0 - Tx_0\right)}\frac{h_1}{a_1 \cdot b_1}, \tag{3}$$

$$Z = \frac{\alpha^2\sigma}{\kappa}, \tag{4}$$

where R_M is module resistance measured on alternating current; $a_1 \times b_1$ is the cross-section of legs; h_1 is the height of legs; N is the number of pairs; E is the EMF of module; Th_0 is the temperature on the heat-leveling plate located on the hot side of module; Tc_0 is the temperature on heat meter located on the cold side of module; Q is heat flow through the module measured by heat meter.

In Fig. 1: Q is heat released by heater 11; Q_1 is heat transferred from heater 11 to the "hot" side of module 5; Q_2 is heat transferred from heat leveling plate 6 to shield 7 by convection; Q_3 is heat transferred from heat leveling plate 6 to shield 7 by radiation; Q_4, Q_{10} is heat transferred from heater 11 to shield 7 through heater wires; Q_5, Q_9 is heat transferred from heater 11 to shield 7 through potential heater wires; Q_6

is heat transferred from heater 11 to shield 7 through the module clamp; Q_7 is heat transferred from heater 11 to shield 7 by convection; Q_8 is heat transferred from heater 11 to shield 7 by radiation; Q_{11} is heat transferred from heat leveling plate 6 to shield 7 through wires of thermocouple 21; Q_{12} is heat transferred from module 5 to shield 7 by convection; Q_{13} is heat transferred from module 5 to shield 7 by radiation; Q_{14}, Q_{19} is heat transferred from module 5 to shield 7 through module wires 4 and 23; Q_{15} is heat transferred from heat meter 2 to shield 7 through wires of thermocouple 25; Q_{16} is heat transferred from the "cold" side of module 5 to heat meter 2; Q_{17} is heat transferred from heat meter 2 to shield 7 by convection; Q_{18} is heat transferred from heat meter 2 to shield 7 by radiation.

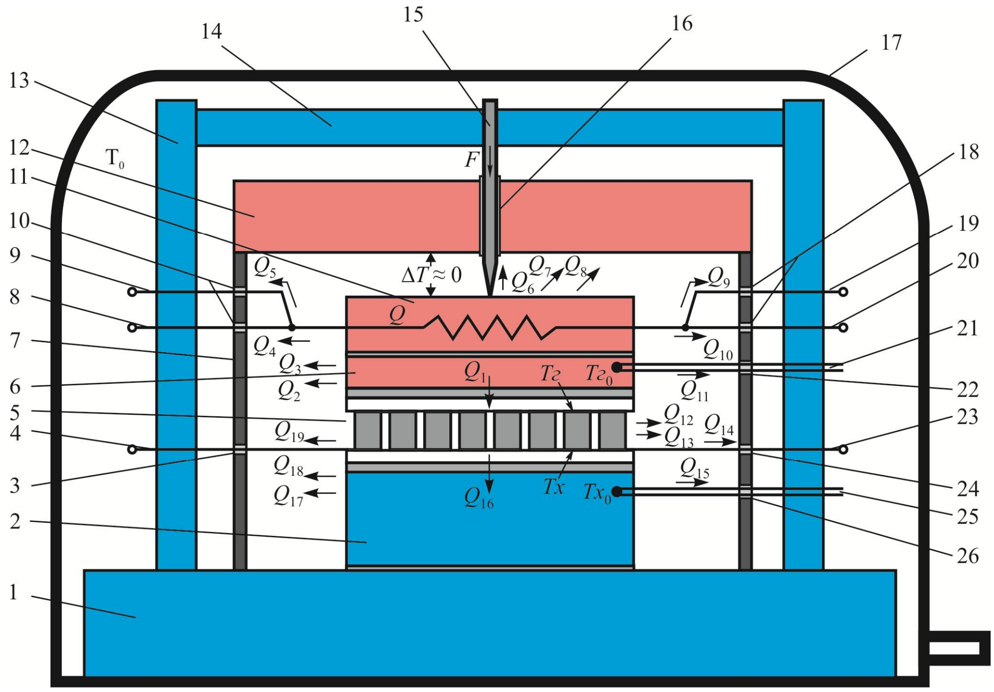

Fig. 1. Schematic for determining the thermoelectric parameters of materials when measuring the parameters of generator thermoelectric modules using thermal switches and radiation shield: 1 – device for providing the required "cold" temperature of module; 2 – heat meter; 3, 10, 16, 18, 22, 24, 26 – thermal switches; 4, 23 – module wires; 5 – module; 6 – heat leveling plate; 7 – gradient radiation shield; 8, 20 – heater wires; 9, 19 – potential heater wires; 11 – module heater; 12 – shield heater; 13 – clamping mechanism racks; 14 – clamping bar; 15 – clamping screw; 17 – bell jar; 21, 25 – thermocouples.

In this case, due to the temperature dependence of the thermoelectric parameters of material, measurements should be carried out at small temperature differences. Therefore, to apply this technique on equipment for measuring generator modules, in which temperatures can be in the range of T_c = 30 - 90 °C, T_h = 30 - 600 °C, additional operations are required to determine the parameters of materials with a rise in temperature difference.

In general, *the method for determining the average values σ, α, κ, Z of the legs material with a rise in temperature difference* will include the following steps.

1. Accurate measurements of σ, α, κ, Z with temperature difference up to 10 K in the temperature range of the cold module side T_c = 30 – 90 °C (for instance: T_c = 30 °C, T_h = 40 °C).

2. Determination of σ, α, κ, Z at temperature differences greater than 10 K.

2.1. Determination of thermal conductivity κ.

To determine the thermal conductivity at each subsequent value of the temperature difference, the value of thermal conductivity obtained from the results of previous measurements is used. It allows dividing the thermal resistance K_T of the leg into two parts (Fig. 2): thermal resistance K_T^{N-1} of the leg section from $x = 0$ to $x = L^{N-1}$, where the temperature difference is equal to the difference of the previous investigated point – $(Th^{N-1} – Tc)$;

- thermal resistance K_T^{N} of the leg section from $x = L^{N-1}$ to $x = L^N = L_{total.}$, where the temperature difference is equal to $(Th^{N} – Th^{N-1}) \approx 10$ K.

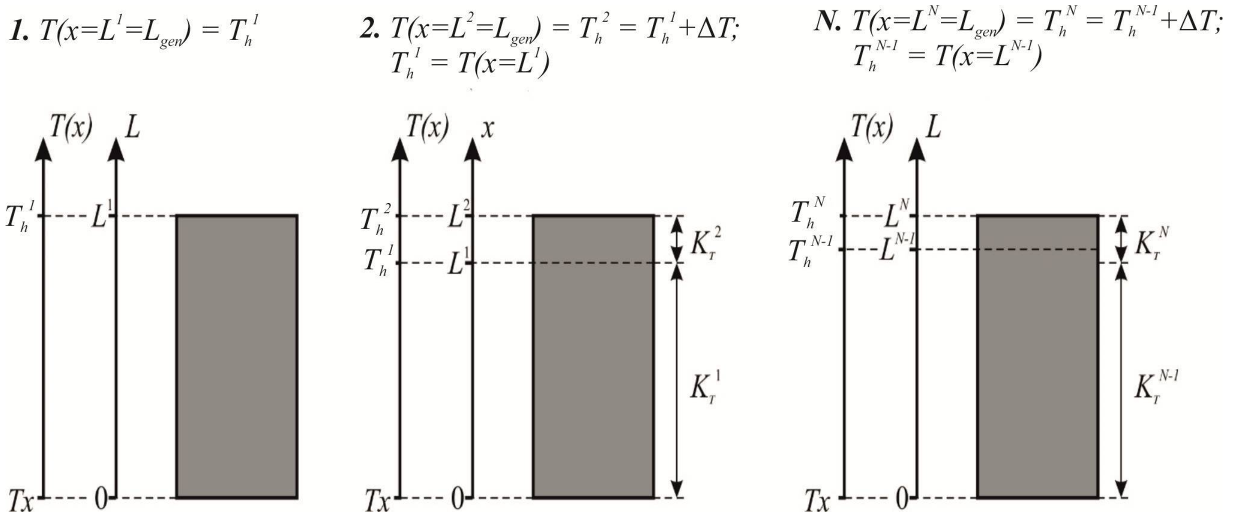

Fig. 2. Procedure for determining the thermal conductivity of the legs material with a rise in temperature difference

Then the value of thermal conductivity at temperature $(Th^{N} + Th^{N-1})/2$ will be determined by the formula

$$\kappa(\frac{Tг^N + Tг^{N-1}}{2}) = \frac{L_{total.}}{a_1 \cdot b_1} \frac{Q^N - Q^{N-1}}{\left(Tг^N - T_0\right) - \left(Tг^{N-1} - T_0\right)}, \tag{5}$$

2.2. Determination of the Seebeck coefficient α.

$$\alpha(\frac{Tг^N + Tг^{N-1}}{2}) = \frac{E^N - E^{N-1}}{\left(Tг^N - T_0\right) - \left(Tг^{N-1} - T_0\right)}, \tag{6}$$

2.3. Determination of electrical conductivity σ.

Electrical conductivity can be determined according to the procedure described in paragraph 2.1 for thermal conductivity, using electric resistance R instead of thermal resistance K_T.

$$\sigma(\frac{Tг^N + Tг^{N-1}}{2}) = \frac{L_{total.}}{a_1 \cdot b_1} \frac{1 - \frac{Q^{N-1}}{Q^N}}{R^N - R^{N-1} \cdot \frac{Q^{N-1}}{Q^N}}, \tag{7}$$

2.4. Determination of the figure of merit Z.

The figure of merit of the leg material is determined by the classical ratio

$$Z(T) = \frac{\alpha^2(T) \cdot \sigma(T)}{\kappa(T)}. \quad (8)$$

where:

$$\alpha(T) = A_0 + A_1 \cdot T + A_2 \cdot T^2 + ... + A_n \cdot T^n, \quad (9)$$

$$\sigma(T) = B_0 + B_1 \cdot T + B_2 \cdot T^2 + ... + B_n \cdot T^n, \quad (10)$$

$$\kappa(T) = C_0 + C_1 \cdot T + C_2 \cdot T^2 + ... + C_n \cdot T^n, \quad (11)$$

where A_i, B_i, C_i, are coefficients of polynomials, n is polynomial degree.

Results of estimation of possible errors of the proposed method

To test the proposed method for determining the temperature dependences of the thermoelectric parameters of materials used in generator thermoelectric modules with a rise in temperature difference, a computer experiment was carried out in the COMSOL Multiphysics application package. To do this, a computer model of thermoelectric generator module Altec-1061 was created with the following parameters: number of pairs – 56; leg height – 3 mm; leg cross section – 1.8 mm x 4.2 mm; ceramics thickness – 0.65 mm; ceramics area – 40 mm × 40 mm; interconnect thickness – 0.25 mm.

The temperature dependences of the thermoelectric properties of module legs material based on Bi-Te are given by polynomials

$$\alpha(T) = 178.25 + 0.6507 \cdot T - (3.9\times10^{-3}) \cdot T^2 + (5\times10^{-6}) \cdot T^3, \quad (12)$$

$$\sigma(T) = 1356.2 - 6.1067 \cdot T + (1.38\times10^{-2}) \cdot T^2 - (7\times10^{-6}) \cdot T^3, \quad (13)$$

$$\kappa(T) = 1.4987 + (2\times10^{-4}) \cdot T - (8\times10^{-6}) \cdot T^2 + (7\times10^{-8}) \cdot T^3, \quad (14)$$

$$Z(T) = \frac{\alpha^2(T) \cdot \sigma(T)}{\kappa(T)}. \quad (15)$$

The cold side of the module was thermostated at a temperature Tc = 30 °C. The temperature of the hot side gradually increased, starting from Th = 40 °C with a step of 10 °C and at each subsequent step according to the computer simulations of temperature and electric potential distributions found in the module, the average values σ, α, κ, Z of legs material were calculated by formulae (5) - (8) of the procedure described in paragraph 1.

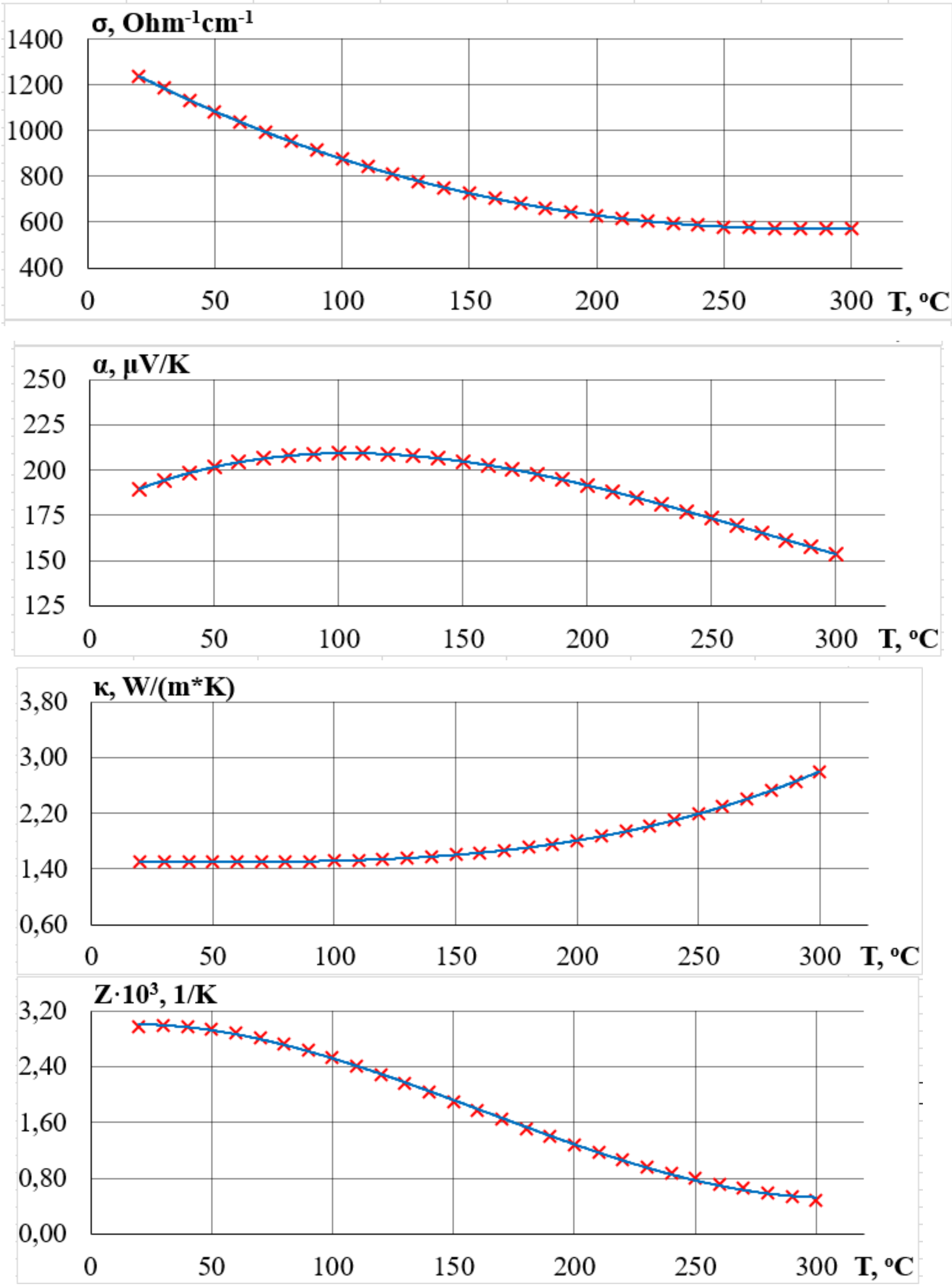

Fig. 3. Temperature dependences of the thermoelectric properties of Bi-Te based material (the lines indicate the dependences constructed using polynomials (5)-(8), the marks "x" are the results obtained by a computer experiment using the proposed measurement technique).

Fig. 3 compares the temperature dependences of the thermoelectric properties of module legs material obtained by a computer experiment in COMSOL Multiphysics using the proposed measurement method and given by polynomials (12) - (15). According to the results of computer simulations, the errors in determining the σ, α, κ, Z of legs material with a rise in temperature difference by the proposed method do not exceed 2-3%. The proposed method is easier to implement and is the basis for the modernization of "ALTEC-10002" equipment for measuring the parameters of thermoelectric generator modules.

Conclusions

1. A method is proposed for determining the temperature dependences of the thermoelectric properties of the legs material of generator thermoelectric module when measuring its parameters by the absolute method. A detailed physical model of this method is considered and an estimate of possible errors is made.
2. Computer experiment has been used to confirm the possibility of determining the thermoelectric parameters of materials used in generator thermoelectric modules in the case when the cold module side is thermostated, and the temperature difference on the module gradually increases due to a rise in its hot side temperature. In so doing, the errors in determining the σ, α, κ, Z of legs material do not exceed 2-3%.

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ВИЗНАЧЕННЯ ТЕМПЕРАТУРНИХ ЗАЛЕЖНОСТЕЙ ТЕРМОЕЛЕКТРИЧНИХ ПАРАМЕТРІВ МАТЕРІАЛІВ У СКЛАДІ ГЕНЕРАТОРНИХТЕРМОЕЛЕКТРИЧНИХ МОДУЛІВ ПРИ ЗРОСТАЮЧОМУ ПЕРЕПАДІ ТЕМПЕРАТУР

Запропоновано методику визначення термоелектричних параметрів матеріалів у складі

генераторних термоелектричних модулів у випадку, коли холодна сторона модуля є термостатованою, а перепад температури на модулі поступово зростає за рахунок підвищення температури гарячої сторони за допомогою електричного нагрівника. Розглянуто детальну фізичну модель цієї методики та наведено результати оцінки можливих величин похибок при вимірюваннях. Бібл. 8, рис. 3.
Ключові слова: вимірювання, електропровідність, термоЕРС, теплопровідність, добротність, термоелектричний модуль.

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МЕТОДИКА ОПРЕДЕЛЕНИЯ ТЕРМОЭЛЕКТРИЧЕСКИХ ПАРАМЕТРОВ МАТЕРИАЛОВ В СОСТАВЕ ТЕРМОЭЛЕКТРИЧЕСКИХ МОДУЛЕЙ ОХЛАЖДЕНИЯ

Предложена методика определения термоэлектрических параметров материалов в составе термоэлектрических модулей охлаждения. Рассмотрена подробная физическая модель этой методики и приведены результаты оценки возможных величин погрешностей. Исследована эффективность применения различных методов снижения погрешностей. Библ. 8, рис. 2, табл. 1.
Ключевые слова: измерение, электропроводность, термоЭДС, теплопроводность, добротность, термоэлектрический модуль.

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