Physical model of vertical zone melting process with current

The physical model of the process of growing single crystals based on Bi_2Te_3 by the method of vertical zone melting is shown in Fig.1.

The figure shows an ingot fragment, including polycrystalline material 2, molten zone 6 and single crystal 3. The ingot is placed in quartz ampoule 1. With the help of heater 7 and cooler system 8, molten zone 6 is formed, which, moving with the heater along the sample, provides melting of polycrystal and melt crystallization below boundary 5, which is called the crystallization front.

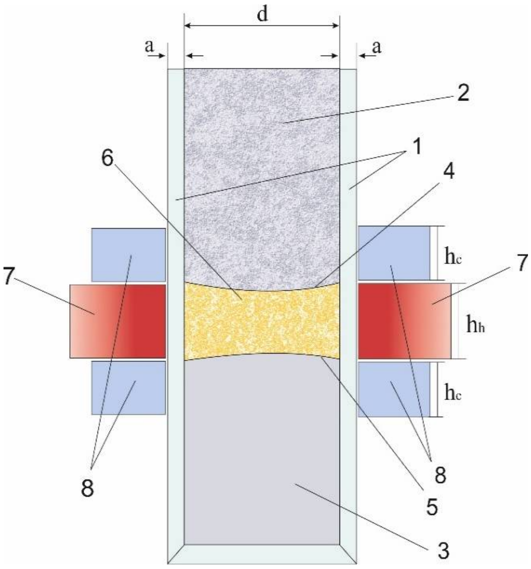

Fig.1. Physical model of installation for growing TEM by vertical zone melting method: 1 – quartz ampoule, 2 – material in solid phase (polycrystal), 3 – material n solid phase (single crystal), 4 – melt front boundary, 5 – crystallization front boundary, 6 – material in liquid phase (melt zone), 7 – heater, 8 – coolers.

When simulating zone growth, the stationary mode was considered, that is, the movement of the heat unit, including heater 7 and coolers 8, was not taken into account. It is known that crystals based on bismuth telluride are grown at a velocity of 1.5-2.5 cm/h. Estimating the time required for the system to achieve thermal equilibrium, which, even with rough calculations, was 40 s, it was determined that during this time the furnace will only move 0.2 mm. The heat loss in this area will be two orders of magnitude less than the heat that is transferred from the thermal unit to the ampoule. Thus, these losses can be neglected in computer simulation, since they will have little effect on the overall temperature distribution.

Mathematical model of TEM growing process by vertical zine melting method with current

When simulating the heat conduction process in a homogeneous medium with a phase transition in the COMSOL Multiphysics software package, the classical system of nonstationary differential heat conduction equations is solved, supplemented by the dependences of the physical properties of the solid under study as a function of the phase state at a given point at a specified temperature with regard to the Joule-Lenz heat and thermoelectric effects:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \nabla T + \nabla q = Q + Q_e \quad (1)$$

$$q = -\kappa \nabla T + Pj, \quad (2)$$

$$Q_e = jE \tag{3}$$

here

$$j = \sigma E + j_e, \tag{4}$$

$$j_e = -\sigma\alpha\nabla T, \tag{5}$$

$$P = \alpha T, \tag{6}$$

$$E = -\nabla U, \tag{7}$$

$$\rho = \theta\rho_{phase1} + (1-\theta)\rho_{phase2}, \tag{8}$$

$$C_p = \frac{1}{2}\left(\theta\rho_{phase1} C_{p_{phase1}} + (1-\theta)\rho_{phase2} C_{p_{phase2}}\right) + L\frac{d\alpha_m}{dT}, \tag{9}$$

$$\alpha_m = \frac{1}{2}\cdot\frac{(1-\theta)\rho_{phase2} - \theta\rho_{phase1}}{\theta\rho_{phase1} + (1-\theta)\rho_{phase2}}, \tag{10}$$

$$\kappa = \theta\kappa_{phase1} + (1-\theta)\kappa_{phase2}. \tag{11}$$

де ρ is the density, kg/m^3; C_p is heat capacity of material at constant pressure, J/(kg·K); κ is thermal conductivity, W/(cm·K), u is medium velocity, m/s, in the investigated problem is zero; T is temperature, K; t is time, s; θ is the phase ratio at a given temperature; α_m is mass ratio between phases; L is the latent heat of phase transition, J/kg; Q is external heat flux, W. The indices phase1 and phase2 indicate to what phase the properties, solid phase or liquid, respectively, are related.

To simulate the effect of the electrical field on the growing process, the following boundary conditions are set at the upper and lower boundaries of the ingot:

$$U|_{z=0} = U_0\,,\ U|_{z=l} = 0. \tag{11}$$

The condition of thermal insulation was set on all external walls of the heater and coolers:

$$-n\cdot(-\kappa\nabla T) = 0. \tag{12}$$

On the outer wall of the quartz ampoule the boundary condition is set as a function of:

$$-n(-\kappa\nabla T) = h(T_{ext} - T) + \varepsilon\sigma_b(T_{ext}^4 - T^4), \tag{13}$$

where T_{ext} is the ambient temperature, K; T is the temperature of the wall of the quartz ampoule, K; n is vector directed along the normal to the surface of the cylinder (ampoule); ε is quartz emissivity; σ_b is Stephan-Boltzmann constant, Wт/(m^2·K^4); h is the heat transfer coefficient, W/(m^2·K), which is expressed by the formula [4]:

$$h = \begin{cases} \frac{k}{l}\left(0{,}68 + \frac{0{,}67\,Ra_l^{1/4}}{\left(1+\left(\frac{0{,}492\,k}{\mu\,C_p}\right)^{9/16}\right)^{4/9}}\right), \text{якщо } Ra_l \le 10^9 \\ \frac{k}{l}\left(0{,}825 + \frac{0{,}38\,Ra_l^{1/6}}{\left(1+\left(\frac{0{,}492\,k}{\mu\,C_p}\right)^{9/16}\right)^{8/27}}\right), \text{якщо } Ra_l > 10^9 \end{cases},$$

here, Ra_l is the Raleigh number which is defined by the following expression:

$$Ra_l = \frac{g\alpha_p\rho^2 C_p (T - T_{ext}) l^3}{\mu\kappa},$$

where g is the acceleration of gravity, m/s^2; α_p is the temperature coefficient of volumetric expansion, K^{-1}; l is the length of the air layer, m; μ is the dynamic viscosity, (Pa·S).

In order to take into account the features of phase transitions during heating – cooling of Bi_2Te_3, the thermoelectric properties of TEM are set depending on temperature, according to the data obtained in [5]. Convection and mass transfer of molten Bi_2Te_3 were not taken into account in this model.

Computer simulation results

Below are the results of computer simulation of the influence of the Peltier effect on the crystallization of bismuth telluride by vertical zone melting in the presence of electric current, in accordance with the physical model shown in Fig. 1. Table 1 shows some input parameters of the model.

Table 1.

Input data used in simulation

	T, °C	ε	C_p, J/(mole·K)	ρ, g/cm³	*Liquidus and solidus*, °C
Bi_2Te_3	-	-	59.73-126.19	7.74	585-530
Quartz	-	0.9-0.41	-	-	-
Heater	700-820	0.8	-	7.0	-
Cooler	30	-	-	-	-

The diameter d of the grown crystal was taken to be 24 mm, the height of the heater was chosen optimal and, as noted in [6], should be equal to h_h=3d. The height of the coolers h_c=1/2d, the distance between the quartz tube, as well as between the heater and coolers was 2 mm. To simulate the effect of the electric field on the growing process, a potential difference was set at the upper and lower boundaries of the material.

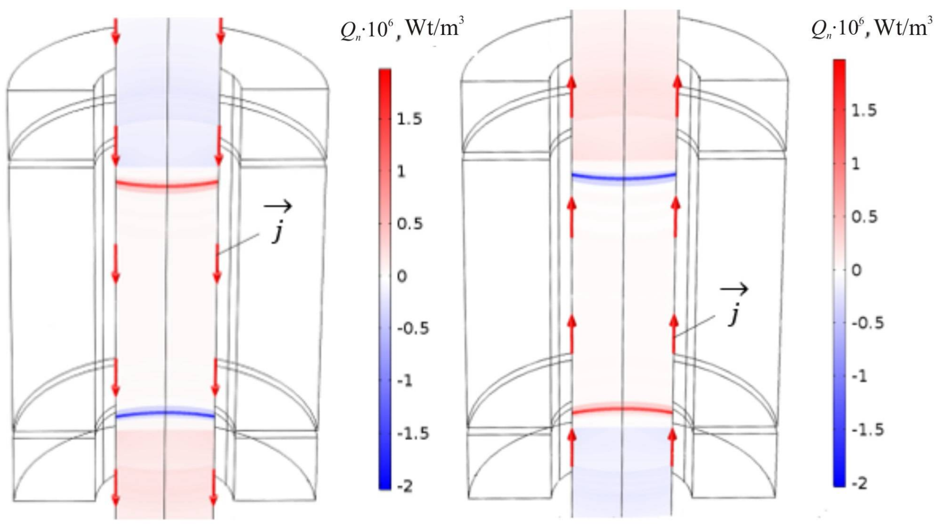

Fig.2. Release and absorption of the Peltier heat at the interfaces between solid and liquid phases depending on the direction of current passage

As can be seen from Fig. 2, the Peltier heat is a positive value, when current passes from the solid to liquid phase and, on the contrary, when current flows from the liquid to solid phase, the Peltier heat is absorbed.

The shape of the crystallization front, which can be concave, flat, or convex, is of great importance for the formation of a structurally homogeneous crystal during growth [6–7]. On a concave surface in the melt, near the walls of the container, parasitic nuclei easily appear. This form of the front contributes to stresses, shrinkage shells and uneven distribution of impurities over the cross section of the grown crystal. The convex interface prevents the growth of random nuclei formed near the walls of the container, but the higher the growth rate, the more likely the formation of parasitic nuclei and the smaller the radius of curvature of the interface. A flat interface minimizes the occurrence of stresses in the crystal and promotes a uniform distribution of impurities over the cross section of the crystal. Therefore, it is important to create a flat crystallization front (Fig. 3, b).

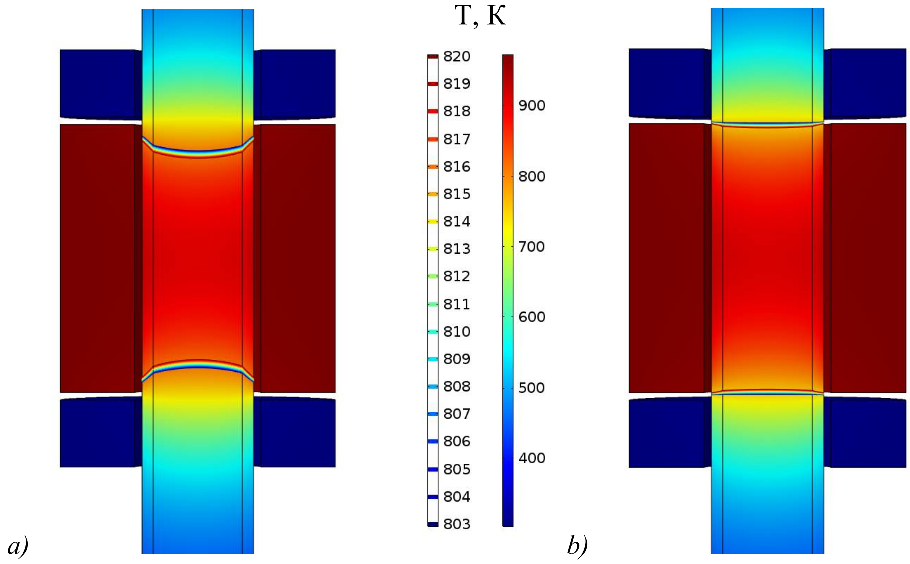

Fig.3. Crystallization front view for different heater temperatures at j=0.5·10^5:
a) T_h=700°C; b) T_h=790°C

Fig.4 shows the dependence of the curvature value *k* of the crystallization front on the heater temperature at different densities of current passed through the molten zone. The curvature was calculated as $k = z_{max} – z_{min}$ along the front.

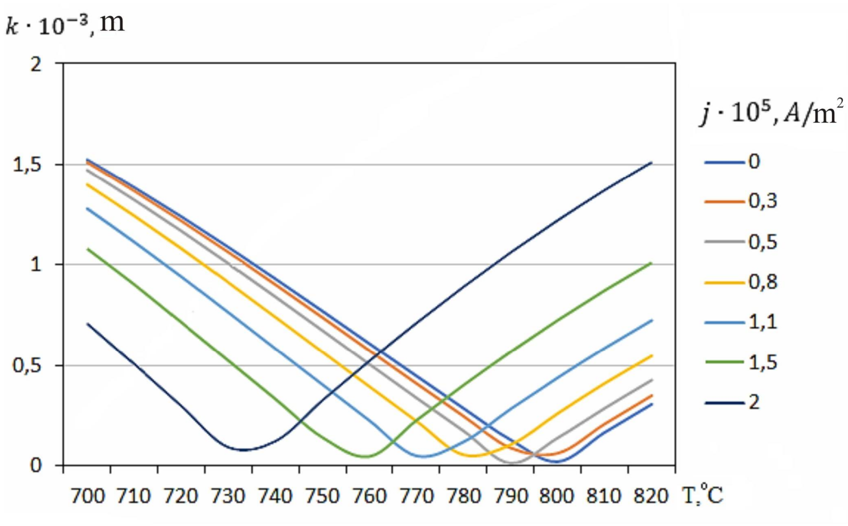

Fig.4. Dependence of the curvature value k of the crystallization front on the heater temperature at different densities of current

As can be seen from Fig. 4, for a given installation configuration, without passing an electric current, a flat crystallization front was achieved at temperatures of 790-800 ° C. By varying the current density from *0.3* до $2\cdot10^5$ A/m^2, a flat front can be achieved at lower heater temperatures.

The dependence of the temperature gradient along the crystallization front on the direction of current passage is shown in Fig.5. In this case the temperature of the heater is $T_h=785^oC$, the current density $j=0.5\cdot10^5$ A/m^2.

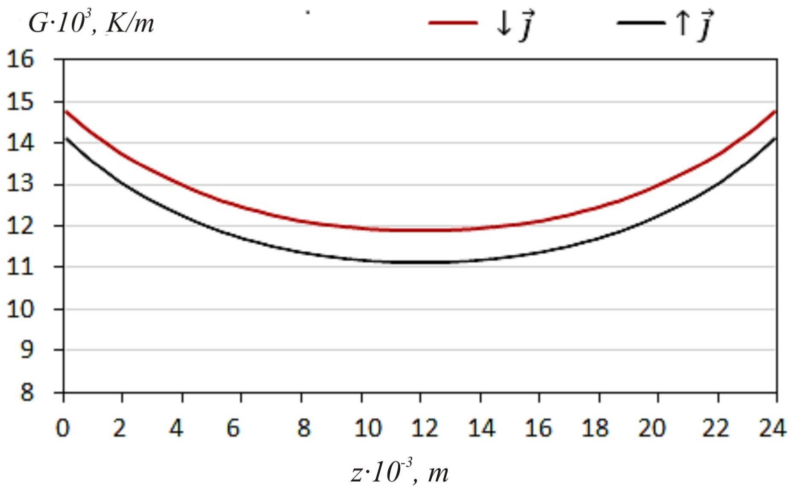

Fig.5. Dependence if the radial temperature gradient G on the direction of current passage

The use of the Peltier effect for zone growing with the passage of direct electric current is complicated by the fact that the Joule-Lenz heat is simultaneously released in the solid and liquid phases, which enhances the Peltier effect at the melt front and weakens it at the crystallization front.

Fig.6. shows the dependence of the radial temperature gradient G on the heater temperatures for different densities of current which is passed through the molten zone.

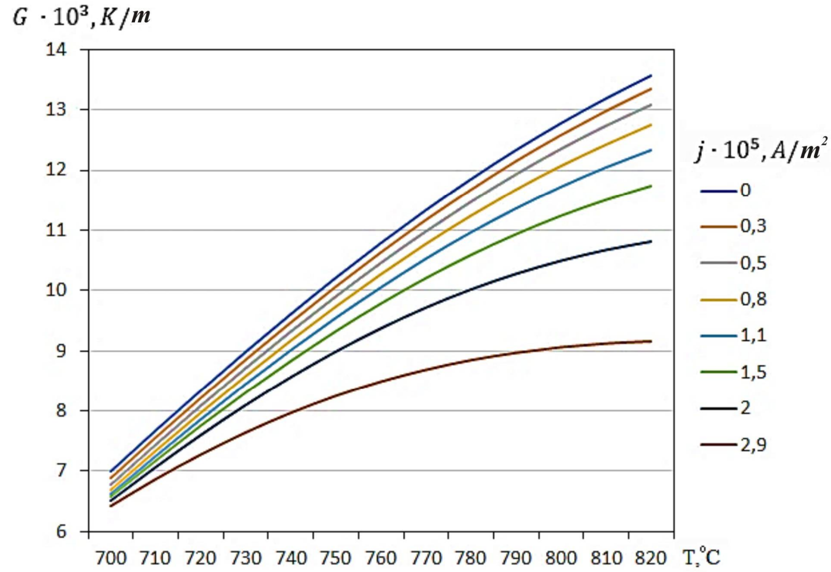

Fig.5. Dependence of the radial temperature gradient G on the heater temperatures for different current densities

From these results it follows that due to an increase in the Joule-Lenz heat, the temperature gradient at the crystallization front decreases with increasing current.

Conclusions

1. A technique was developed for computer simulation of the process of growing TEM based on Bi_2Te_3 by the method of vertical zone recrystallization with the passage of electric current through the sample.
2. The possibility of controlling the temperature distribution in the ingot during TEM growth by vertical zone melting method by passing electric current through the molten zone and the origination of the Peltier effect at the interface between the solid and liquid phases was confirmed.

The optimal values of the heater temperatures and current values were determined which ensure the formation of a flat crystallization front.

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КОМП'ЮТЕРНЕ ДОСЛІДЖЕННЯ ВПЛИВУ ЕФЕКТУ ПЕЛЬТЬЄ НА ПРОЦЕС КРИСТАЛІЗАЦІЇ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ НА ОСНОВІ Bi_2Te_3

У статті наведено результати комп'ютерного моделювання процесу вирощування термоелектричних матеріалів на основі Bi2Te3 методом вертикальної зонної плавки з врахуванням ефекту Пельтьє, що виникає на межі розділу твердої та рідкої фаз вирощуваного матеріалу при пропусканні через злиток електричного струму. . Бібл. 7, рис. 5, табл. 1.
Ключові слова: моделювання, вертикальна зонна плавка, термоелектричний матеріал, вирощування в електричному полі.

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КОМПЬЮТЕРНОЕ ИССЛЕДОВАНИЕ ВЛИЯНИЯ ЭФФЕКТА ПЕЛЬТЬЕ НА ПРОЦЕСС КРИСТАЛЛИЗАЦИИ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ НА ОСНОВЕ Bi_2Te_3

В статье приведены результаты компьютерного моделирования процесса выращивания термоэлектрических материалов на основе Bi_2Te_3 методом вертикальной зонной плавки с учетом эффекта Пельтье, который возникает на границе раздела твердой и жидкой фаз выращиваемого материала при пропускании через слиток электрического тока. Библ. 7, рис. 6, табл. 1.
Ключевые слова: моделирование, вертикальная зонная плавка, термоэлектрический материал, выращивание в электрическом поле.

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EXPERIMENTAL STUDIES OF A THERMOELECTRIC CURRENT SOURCE WITH AN ANNULAR THERMOPILE

The results of studies of a single-acting thermoelectric current source with an annular thermopile are presented. The research results confirmed the efficiency of current source breadboard models with an annular thermopile and the compliance of their electrical parameters with the requirements of the Performance Specification under Contract 3/2019. Bibl. 2, Fig. 6, Tabl. 1.
Key words: thermoelectric battery, current source, voltage, output power.

Introduction

In conformity with the Performance Specification under Contract 3/2019 of 16.04.2019, a thermoelectric current source with an annular thermopile shall be made and investigated. A thermoelectric converter for the current source shall be structurally made in the form of a toroidal ring with the outer and inner diameters of 50 and 39 mm, respectively, and a width of 16.5 mm. In this case, the current source shall provide an output power of not less than 20 W at a voltage of 5 V. The operating temperature difference ΔT, in this case, shall not exceed 300 K.

Studies of elementary thermopiles for an annular thermopile

At each stage of manufacturing a component part of an annular thermopile for current source, i.e. elementary single-row thermopiles, a step-by-step visual inspection of thermoelement legs was carried out with the rejection of defective elements according to geometric dimensions, and a sorting was carried out by the resistance of thermoelement legs.

Each thermopile assembled from those that passed step-by-step inspection (Fig. 1), which is a component part of an annular thermopile for current source, was tested and selected after measuring its main parameters at the "Altec-10002" installation specially created at the Institute of Thermoelectricity, the appearance of which is shown in Fig. 2.