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Computer Simulation of the Vertical Zone Melting Method for Manufacturing Ingots of Bismuth Telluride-Based Thermoelectric Materials with a Square Cross-Section

It has been shown that losses of thermoelectric material when cutting discs with a circular cross-section into legs for thermoelements are significant – the weight of rejected legs can reach 20 – 30 %, depending on the size of the legs and discs. It can be avoided by producing thermoelectric material in the form of ingots with a square cross-section. The results of computer simulation of vertical zone melting for manufacturing ingots of bismuth telluride-based thermoelectric materials with a square cross-section are presented. The dependence of the shape of the crystallization front on the geometric dimensions of the heater and coolers, their temperatures, movement velocity, and other technological parameters was obtained. These dependences were analyzed for different materials used to manufacture the container in which the material is grown – quartz, ceramics and graphite. Multifactorial computer optimization of the process technological modes and the design of the equipment was carried out. Bibl. 26, Fig. 9.
Key words: simulation, vertical zone melting, thermoelectric material, bismuth telluride.

Introduction

Thermoelectricity is finding more and more practical applications in various industries – military and space technology, medicine, household appliances, etc. [1 – 10]. These applications are implemented in three main areas – thermoelectric cooling devices, generators

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and measuring devices. According to estimates [11], the market for thermoelectric converters today is ~ 1.46 billion US dollars and is growing by approximately 10.6 % annually. About 70 million units of thermoelectric converters are produced.

At the same time, the main materials still in use in these energy converters are bismuth telluride-based alloys, which have the best thermoelectric properties in the temperature range of 200 – 600 K [12 – 15].

One of the main industrial methods for producing thermoelectric materials is vertical zone melting [16]. The quality of this method depends on the crystallization parameters, such as the distribution of impurities, the shape of the crystallization front, the heater temperature, and the velocity of the melting zone. Optimization of these processes allows obtaining a material with high quality and uniformity. For this purpose, computer simulation is successfully used, which significantly speeds up research and reduces its costs.

Thus, in [17, 18], the results of computer simulation of the process of vertical zone melting of thermoelectric material in the form of rods with a circular cross-section are presented; in particular, the influence of the temperature and dimensions of the heater, the growth rate, and other technological parameters on the shape of the crystallization front is investigated. In [19], the possibility of growing single crystals of thermoelectric materials by the method of vertical zone melting in the presence of a direct electric current passing through the ingot is considered.

An interesting possibility is the growth of ingots in the form of flat rods, which not only increases the yield of homogeneous material, but also helps to reduce defects when cutting them and allows more efficient use of the material.

In [20, 21], computer optimization of the process of manufacturing flat ingots of Bi_2Te_3-based thermoelectric materials by the method of vertical zone melting was carried out. The computer model uses a container in the form of a quartz ampoule with inserts that form a flat ingot, also made of quartz. This approach allows increasing the percentage of material yield with an improved structure by 1.2 – 1.3 times compared to circular ingots for the same ampoule diameter.

A further development of this technology is the growth of ingots with a square cross-section, which will further reduce losses when cutting discs of thermoelectric material into thermoelement legs for energy converters.

Since the production and use of quartz inserts encounters significant technological difficulties, it is also advisable to consider options for a container made of other materials, such as graphite or ceramics.

Therefore, *the purpose of this work* is to assess the possibility of reducing the rejects of thermoelectric material in the manufacture of thermoelement legs for thermoelectric energy converters by growing ingots of bismuth telluride-based thermoelectric materials with a square cross-section and conducting computer optimization of technological modes and equipment design for the manufacture of such ingots.

1. Estimation of thermoelectric material losses when cutting discs into legs

To assemble thermoelectric modules, the material is usually cut into legs of square or rectangular cross-section. However, when using circular discs (Fig. 1), a significant amount of thermoelectric material is lost in the form of defective legs.

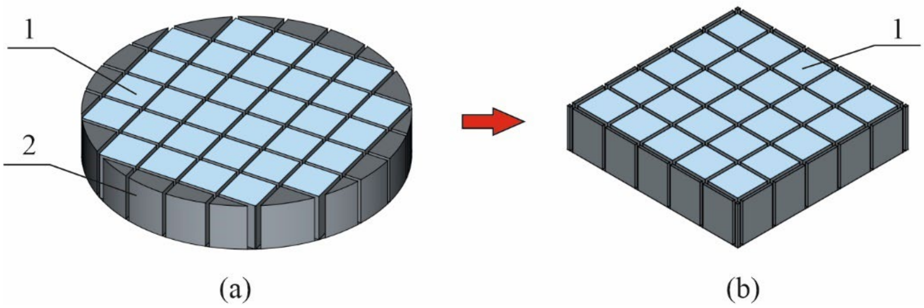

Fig.1. Cutting of thermoelectric material.
1 – conditioned legs, 2 – defective legs

In addition, a certain part of the thermoelectric material is lost as process dust. These losses are an integral part of the cutting process with an abrasive tool. Fig. 2 shows the yield and losses of thermoelectric material when cutting a circular disk into legs of different cross-sections.

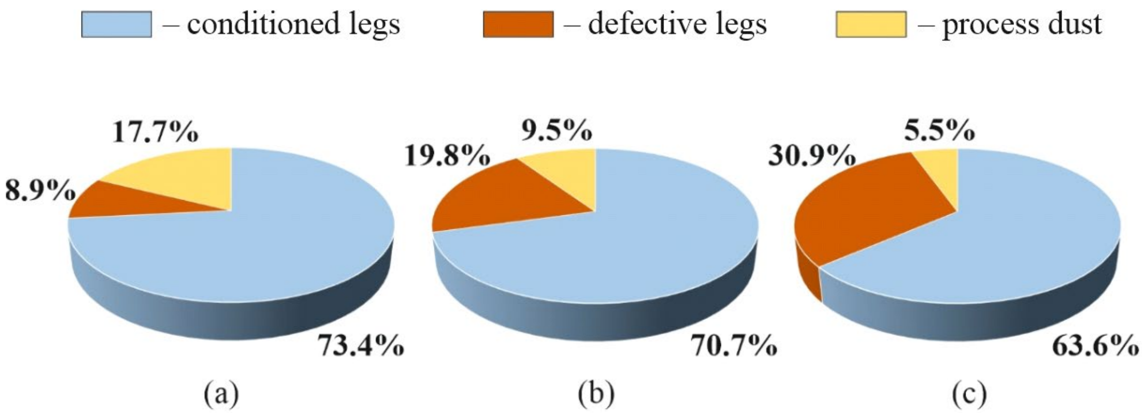

Fig 2. Estimation of TEM losses when cutting a circular disk ⌀24 mm.
a) legs 1 × 1 mm²; b) legs 2×2 mm²; c) legs 3×3 mm²

As can be seen from the diagrams, the losses of thermoelectric material due to the circular shape of the disk can be up to 30 %. Therefore, it is advisable to consider the possibility of manufacturing ingots of square cross-section. Such an approach should ideally leave only losses in the form of technological dust during the cutting process.

2. Physical model

To achieve the stated goals, we will first consider the physical model of the process of manufacturing a square-section thermoelectric material ingot using the vertical zone melting method (Fig. 3).

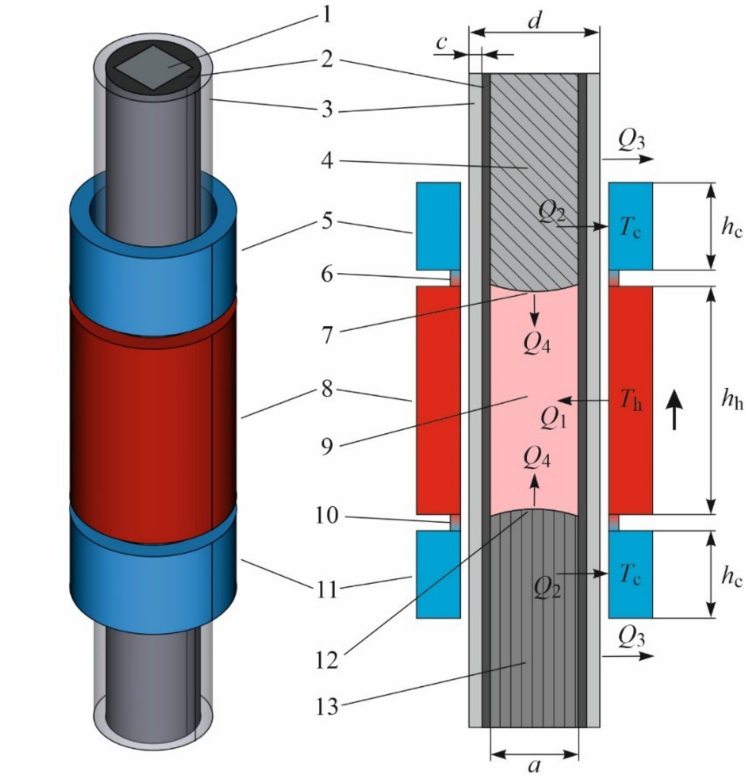

Fig.3. Physical model of the process of growing thermoelectric material by vertical zone melting:
1 – thermoelectric material, 2 – container, 3 – quartz ampoule,
4, 13 – solid-phase thermoelectric material, 5, 11 – coolers,
6, 10 – fasteners, 7, 12 – melt/crystallization fronts
8 – heater, 9 – melt zone

Thermoelectric material 1 is located in a container 2, which forms its geometric configuration. Elements 1, 2 are placed in a classic quartz ampoule 3. The polycrystalline material 4 melts in zone 9 and crystallizes into a single crystal 13. Melting occurs due to heat Q_1, which is transferred from the heater 8 at a temperature T_h. Heat Q_2 is removed by coolers 5 and 11 at temperature T_c. At the melt front 7 and crystallization front 12, additional absorption and release of heat Q_4, occurs, caused by phase transitions from the solid to the liquid phase and vice versa. The model also takes into account heat losses Q_3 from the ampoule to the environment. The task is to optimize the technological regime to achieve the most flat crystallization front 12. This will make possible obtaining a high-quality single crystal 13.

3. Mathematical and computer description of the model

Computer simulation of the process of obtaining thermoelectric material by vertical zone melting was implemented in the COMSOL Multiphysics environment [24].

The multiphysics environment module “**Heat Transfer with Surface-to-Surface Radiation**” was used to describe the model, which combines “Heat Transfer in Solids” and “Surface-to-Surface Radiation” modules. It can be used to simulate the known methods of heat transfer – thermal conduction, convection, and radiation.

The general equation of heat conduction in differential form is given below

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \nabla T - \kappa \nabla T = Q, \tag{1}$$

where ρ is density, C_p is heat capacity of material, κ is thermal conductivity, **u** is the velocity of the medium, T is temperature, t is time, Q are external heat sources.

In this paper, the stationary case was considered, since, as was shown earlier [20, 21], zone movement can be neglected. The velocity of the medium is zero. Then equation (1) takes the form

$$-\kappa \nabla T = Q. \tag{2}$$

To describe the phase transition, it is sufficient to supplement the stationary equation (2) with equations that take into account the change in the properties of the thermoelectric material in different phases, as well as the additional heat of the phase transition:

$$\kappa = \theta \kappa_{\text{solid}} + (1-\theta)\kappa_{\text{liquid}}, \tag{3}$$

$$q_{\text{ph}} = \lambda \delta (T - T_m). \tag{4}$$

where θ is the phase ratio at a given temperature, q_{ph} is the phase transition heat, λ is the specific heat of fusion, T_{m} is the melting point, δ is the delta function. The subscripts 'solid' and 'liquid' indicate which phase the properties belong to – solid or liquid.

The following boundary conditions to equation (2) complete the description of the model.

To take into account the process of heat transfer by radiation in the model, the following condition must be met on all surfaces.

$$-\mathbf{n} \cdot \mathbf{q} = \varepsilon \left(G - e_b(T) \right), \tag{5}$$

where **n** is the normal vector, **q** is the heat flux through the surface, ε is the emissivity of the surface, G is the total irradiance of the surface, $e_b(T)$ is the radiation of a completely black body at temperature T.

$$e_b(T) = n^2 \sigma T^4, \tag{6}$$

where n is the refractive index of the medium, σ is the Stefan-Boltzmann constant.

Full surface irradiation

$$G = G_{\text{m}} + G_{\text{amb}} + G_{\text{ext}} \tag{7}$$

includes G_{m} – radiation from other bodies of the model, G_{ext} – radiation from external sources, G_{amb} – radiation from the environment

$$G_{\text{amb}} = F_{\text{amb}} e_b(T_{\text{amb}}), \tag{8}$$

where F_{amb} is the visibility coefficient of the environment.

Heat transfer by *external free convection* is described by the boundary condition

$$-\mathbf{n} \cdot \mathbf{q} = h(T_{\text{ext}} - T), \tag{10}$$

where h is the heat transfer coefficient, T_{ext} is the external temperature.

Under free convection conditions, the heat transfer coefficient

$$h = \frac{k}{L} Nu \,, \tag{11}$$

where k is the thermal conductivity of the medium, L is the characteristic length of the surface, Nu is the Nusselt number.

In the "Heat Transfer in Solids" module, the Nusselt number is entered empirically as follows:

$$Nu = 0.68 + \frac{0.67 \cdot Ra_L^{1/4}}{\left[1 + \left(0.492 \dfrac{k}{\mu C_p}\right)^{9/16}\right]^{4/9}} \text{ at } Ra_L \le 10^9 \,, \tag{12}$$

$$Nu = \left[0.825 + \frac{0.387 \cdot Ra_L^{1/6}}{\left(1 + \left(0.492 \dfrac{k}{\mu C_p}\right)^{9/16}\right)^{8/27}}\right]^2 \text{ at } Ra_L > 10^9 \,, \tag{13}$$

$$Ra_L = \frac{g\beta(T - T_{\text{amb}})L^3}{\nu\alpha} \,, \tag{14}$$

where μ is the dynamic viscosity of the medium, Ra_L is the Rayleigh number, g is the acceleration of gravity, β is the coefficient of volumetric thermal expansion of the medium, ν is the kinematic viscosity, α is the thermal diffusivity of the medium.

The description of the model is completed by the boundary conditions for thermostatting the outer surfaces of the heater and coolers, respectively:

$$T = T_{\text{h}}, \tag{15}$$

$$T = T_{\text{c}}. \tag{16}$$

4. Simulation results

The following input data were used in the simulation. The inner diameter of the ampoule $d = 24$ mm, the height of the ampoule – 300 mm, the thickness of its walls $c = 3$ mm. The heights of the heater $h_{\text{h}} = 3d = 72$ mm and the coolers $h_{\text{c}} = d = 24$ mm. The cross-section of the container with the thermoelectric material was 16×16 mm^2. The coolers temperature was set at $T_{\text{c}} = 30$ °C. The heater temperature was varied in the range $T_{\text{h}} = 840$–920 °C to determine its effect on the shape of the crystallization front.

The properties of the thermoelectric material necessary for simulation were obtained using equipment developed at the Institute of Thermoelectricity [22, 23].

Fig. 4 shows an example of the calculated temperature distribution in the structural elements and the thermoelectric material itself during the zone melting process. Fig. 5 shows the deviation Δz of the crystallization front from flatness.

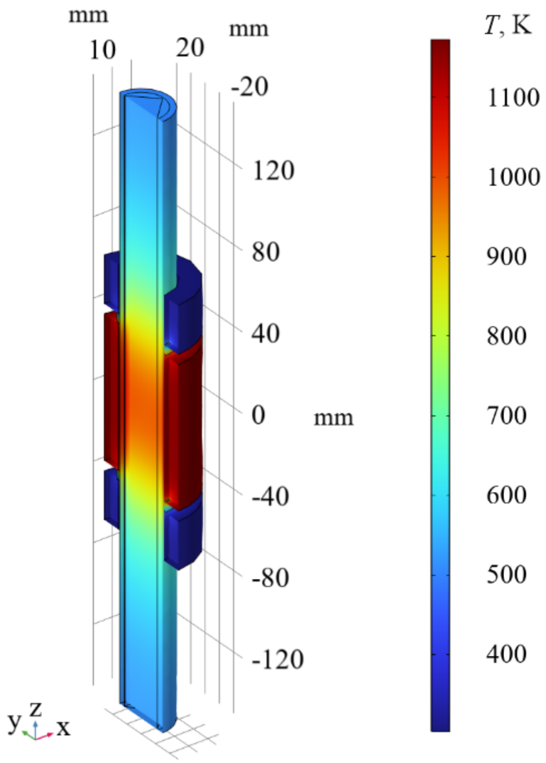

Fig.4. Temperature distribution in the zone melting process.
Container material – graphite, heater temperature – 900 °C

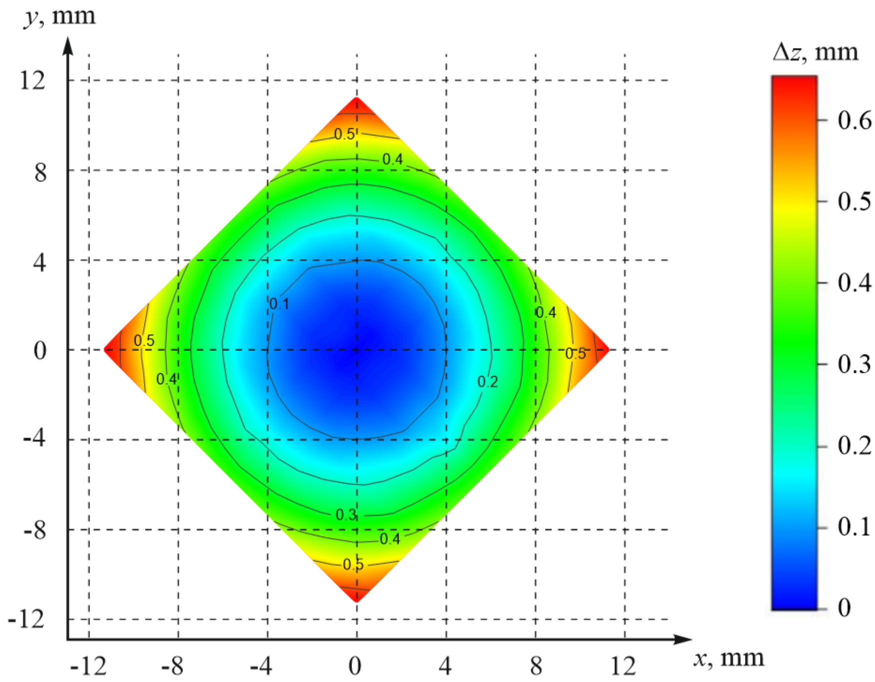

Fig. 5. Example of crystallization front curvature.
Container material – graphite, heater temperature – 840 °C

Figs. 6–8 show the appearance of the crystallization front in the *xz* plane at $y = 0$ for different heater temperatures and container materials. The lower part corresponds to the liquid phase.

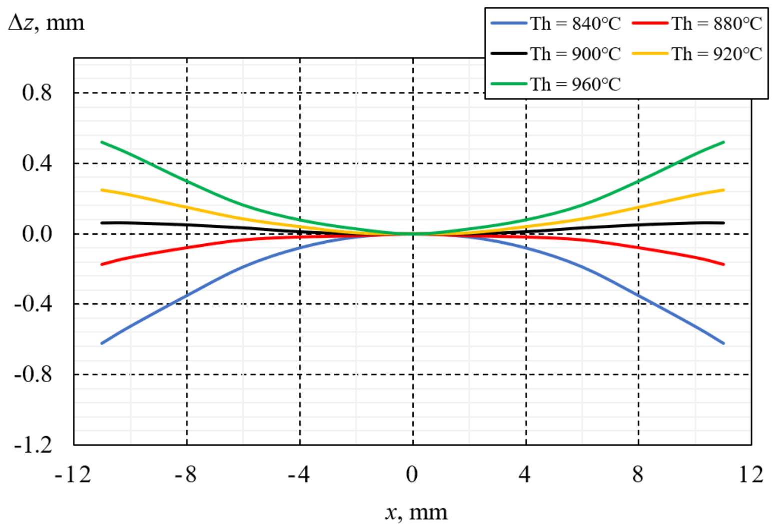

Fig.6. Crystallization front for graphite container at different heater temperatures

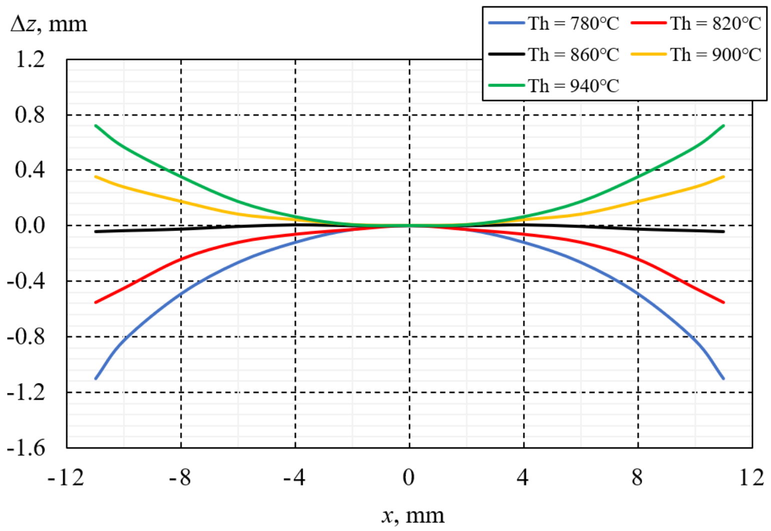

Fig 7 Crystallization front for quartz glass container at different heater temperatures

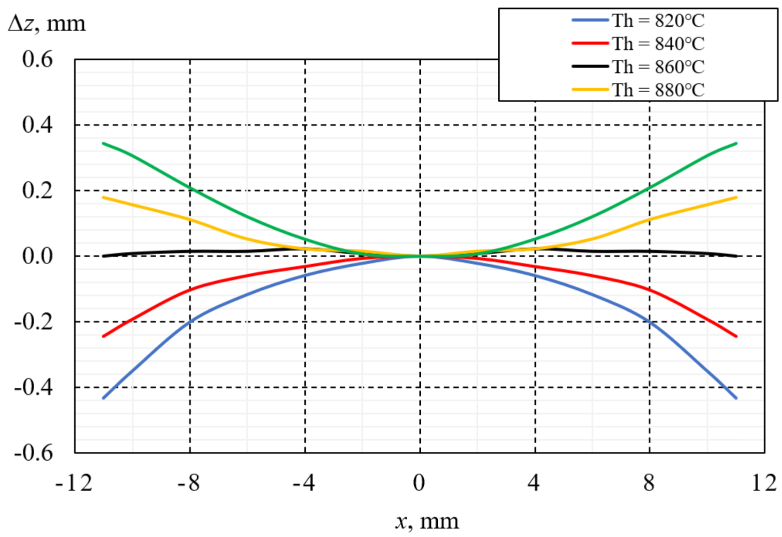

Fig.8. Crystallization front for ceramic container at different heater temperatures

As is known [26], increasing the temperature gradient at the crystallization front has a positive effect on its shape and stability, and therefore on the quality of single crystal growth. Fig. 9 shows the values of this quantity calculated in the model when using different container materials, provided that the front is flat.

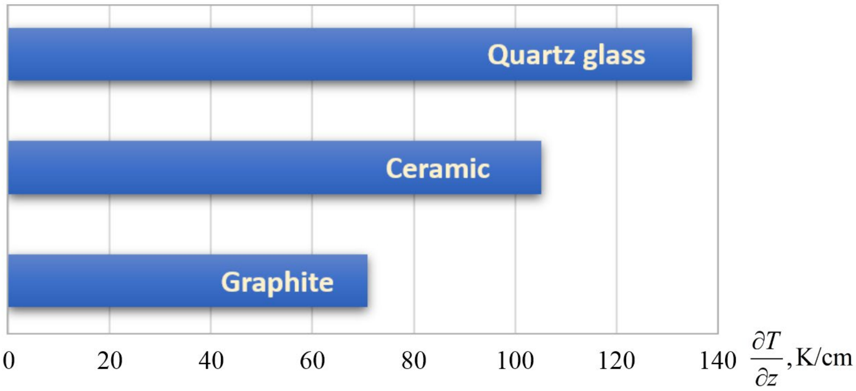

Fig.9. Temperature gradient at the crystallization front for different container materials

As can be seen from Fig. 9, the container material significantly affects the temperature gradient at the crystallization front. The gradient increases with decreasing thermal conductivity of the container material and, in the case of quartz glass, reaches the highest value among the container materials studied in this work.

Conclusions

1. Using circular ingots of thermoelectric material to obtain thermoelement legs by cutting can lead to 30 % losses due to defective legs along the perimeter of the disks. These losses can be avoided by using square ingots.
2. By computer simulation of the zone melting process for obtaining square-section ingots, the shape of the crystallization front and the temperature gradient on it were found for cases of using different container materials. It was shown that by adjusting the heater temperature in all cases it is possible to achieve satisfactory flatness of the crystallization front and the temperature gradient on it.
3. Quartz glass as a container provides the highest temperature gradient at the crystallization front. However, given the complexity of forming a quartz container, ceramics as a container material may be the best option for technologically and inexpensively ensuring the process of growing square-section ingots.

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Комп'ютерне моделювання методу вертикального зонного плавлення для виготовлення злитків термоелектричних матеріалів на основі телуриду вісмуту з квадратним поперечним перерізом

Показано, що втрати термоелектричного матеріалу при розрізанні дисків з круглим перерізом на гілки для термоелементів є суттєвими – вага бракованих гілок може сягати 20 – 30 %, залежно від розмірів гілок та дисків. Цього можна уникнути, виготовляючи термоелектричний матеріал у вигляді злитків з квадратним перерізом. Представлено результати комп'ютерного моделювання вертикального зонного плавлення для отримання злитків термоелектричних матеріалів на основі телуриду вісмуту з квадратним перерізом. Отримано залежність форми фронту кристалізації від геометричних розмірів нагрівача і охолоджувачів, їх температур, швидкості переміщення та інших технологічних параметрів. Ці залежності було проаналізовано для різних матеріалів, використаних для виготовлення контейнера, в якому вирощується матеріал – кварцу, кераміки та графіту. Проведено багатофакторну комп'ютерну оптимізацію технологічних режимів процесу та конструкції обладнання. Бібл. 26, рис. 9.

Ключові слова: моделювання, вертикальне зонне плавлення, термоелектричний матеріал, телурид вісмуту.

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