



L.T. Strutynska

**SIMULATION OF Bi_2Te_3
THERMOELECTRIC MATERIAL
GROWTH PROCESS BY VERTICAL ZONE
MELTING METHOD**

L.T. Strutynska, V.V. Zhikharevich
(Institute of Thermoelectricity, 1, Nauky Str,
Chernivtsi, 58029, Ukraine)



V.V. Zhikharevich

-
- This article furnishes the results of computer simulation of thermoelectric material growth process by vertical zone melting method with the use of asynchronous cellular automata theory. Based on the constructed models of thermophysical processes in liquid and solid phases, the optimal kinetic, thermal and quantitative growth conditions are determined for the multi-component thermoelectric materials based on Bi_2Te_3 .

Introduction

Intensive development of techniques for single crystal growth from the melt has heightened interest in the simulation of physical effects underlying growth processes. The critical technological goal is manufacture of homogeneous single crystals with a perfect structure and assigned electrophysical properties. Hence the relevance of simulation processes enabling optimization of the choice of technological parameters with a considerable reduction of material expenses.

The Bi_2Te_3 - Bi_2Se_3 and Bi_2Te_3 - Sb_2Te_3 semiconductor solid solutions are widely used for creation of thermoelectric power converters working in the temperature region of 250 – 600 K. In the manufacture of thermoelectric materials (TEM) based on Bi_2Te_3 by vertical zone melting method, the stability of single crystal growth and material homogeneity are greatly affected by the radial and axial temperature gradients, as well as by crystallization front curvature which is the main technological characteristic. In so doing, great importance is assumed by the mathematical and laboratory simulation results which enable to trace detailed patterns of physical processes occurring over a wide range of given technological parameters and to get sufficiently precise quantitative outcome. This makes it possible to use computer simulation for the search of optimal technological processes and engineering solutions.

Traditionally used mechanism of differential equations is not always efficient and calls for big expenses of time and capacities. In recent decades, increasing acceptance has been gained by simulation with the use of cellular automata (CA).

The CA theory is based on the simulation of complex systems consisting of simple subsystems, collective functioning of which results in a complex behaviour of the entire system. The CA models reduce macroscopic effects to precisely specified microscopic processes. Such an approach takes into account the real physics of the process enabling one to assign complex boundary conditions, consider complex phase transitions with intermediate compounds and propose various hypotheses as to formation of phases and distribution of concentration and temperature fields which are impossible in the case with differential equations [1]. At the same time, the use of CA allows studying complex behaviour without the use of a cumbersome mathematical description.

The use of CA models for computer simulation of spatial dynamics in chemistry and physics is appealing for the following reasons [2]:

- CA simulates discrete changes occurring in discrete space and time which allows reflecting

- directly in the model the motion and transformations of real parts or agents;
- no restrictions are imposed on CA transition functions: they can be nonlinear, discontinuous and probabilistic permitting simulation of such processes as phase transitions and chemical transformations, as well as taking into account conditions whereby changes of some or other state are permissible;
 - CA permit simulation of nonsynchronized processes (asynchronous CA) corresponding to natural course of events in all real phenomena that are not synchronized artificially;
 - CA simulate objects which in works [3, 4] are called complex systems, since they have very simple mathematical representations, but simulate complex space-time processes.

Our objective in this work is to develop physical and computer models of the growth process of single crystals of thermoelectric material based on Bi_2Te_3 by vertical zone melting method with the use of asynchronous CA theory and to determine the optimal kinetic, thermal and quantitative conditions of TEM growth.

1. Description of CA algorithms

Simulation program of thermoelectric material growth by vertical zone melting method is based on CA algorithms of heat transfer, diffusion and phase transition simulation. The adequacy of using CA for simulation of such processes is substantiated in works [5 – 7]. Transition from physical representation of some effect to its CA model and back is done by comparing physical characteristics with the average number of particles falling on certain number of cells [6].

The program employs a method of continuous asynchronous CA. The main dissimilarity of this method from the other methods of CA-simulation lies in the specific organization of local interaction rules. Calculating the state of two interacting CA at each next time moment in case of continuous CA reminds the process of numerical solution of differential equations by explicit methods. In this connection, some explicit schemes of finite-difference representation of differential equations are sometimes called continuous CA.

Let us consider a method of continuous asynchronous CA which is used in this program. CA structure on a two-dimensional field of cells is shown in Fig. 1 [8]. CA is a combination of some characteristics assuming in the general case continuous real values.

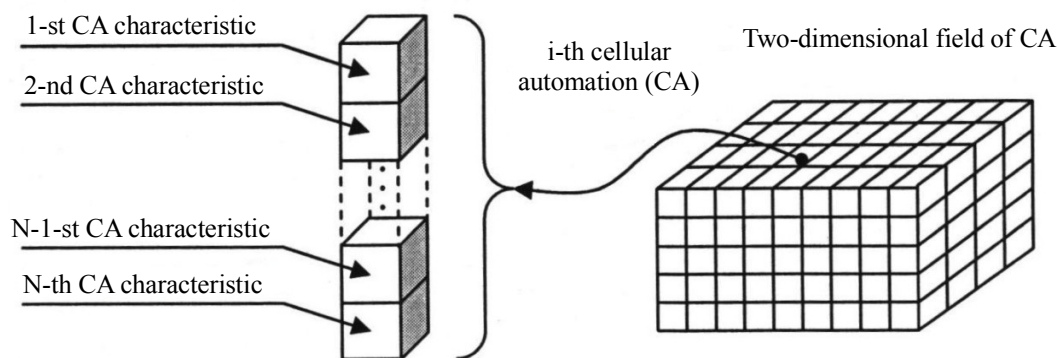


Fig. 1. CA structure on a two-dimensional field.

If we denote through c_j^i the value of j -th characteristic of i -th CA, the specific characteristic j can have certain physical meaning, for instance, concentration of some substance, field intensity, etc. In this connection, it is obvious that the total number of characteristics N is directly related to the complexity of simulated systems, i.e. N is the number of microobject parameters that should be taken

into account in the process of system simulation.

Simulation process in our case takes place according to algorithm which lies in a continuous iteration of the following three steps:

1. On a cellular field, coordinates of certain i -th cell c^i are determined at random. All the cells on the field are equally probable in terms of their selection.

2. Coordinates of cell c^k adjacent to cell c^i are determined at random. In our case we employ a 4-cell neighbourhood scheme.

3. Two selected adjacent cells interact, i.e. the values of cell characteristics at some time moment t (initial data) and interaction rules (conversion function) are used to calculate cell characteristics at the next time moment $t + 1$ (result). Such a scheme is close to real physical systems, where local microinteractions are mainly asynchronous, disordered and independent.

Interaction rules are represented as a system of the following iteration functions

$$\begin{cases} c_j^i = F_j^i(c_1^i, c_2^i, \dots, c_N^i, c_1^k, c_2^k, \dots, c_N^k) \\ c_j^k = F_j^k(c_1^i, c_2^i, \dots, c_N^i, c_1^k, c_2^k, \dots, c_N^k) \end{cases}, j=1, 2, \dots, N. \quad (1)$$

An explicit form of functions F in formula (1) depends on the nature of specific simulated system. In the general case one should strive to write down interaction functions F as a superposition of elementary interaction acts having a specific physical meaning, for instance, increase or reduction of some characteristic, gradient or diffusion travel, etc. In so doing, the intensity of different elementary interaction acts can be different, which can be taken into account by introducing certain parameters, namely “activity coefficients”.

2. Implementation features of TEM growth model by vertical zone melting

A physical model of installation for TEM growth by vertical zone melting method with ingot fragment including single-crystal material, molten zone and polycrystal is represented in Fig. 2.

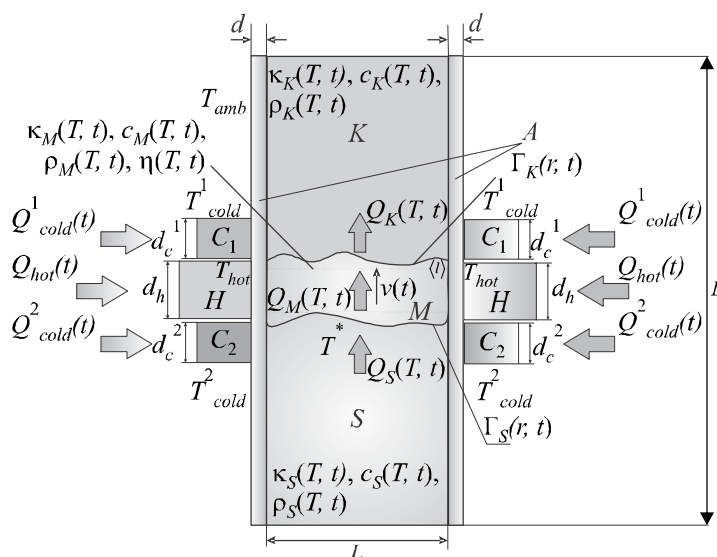


Fig. 2. Physical model of installation for growth of single-crystal thermoelectric material by vertical zone melting method: S – material in solid phase (single crystal); M – melt zone (liquid phase); K – material in solid phase (polycrystal); Γ_K, Γ_S – crystallization front and melt front boundary, respectively; C_1, C_2 – coolers; H – heater; A – quartz ampoule.

For the construction of a computer model the geometrical dimensions of a quartz ampoule (L – ingot thickness; d – quartz container wall thickness) where material is grown, the temperature dependences of parameters (thermal conductivity $\kappa(T, t)$, heat capacity $c(T, t)$, density $\rho(T, t)$, viscosity $\eta(T, t)$) of single-crystal, polycrystalline material and the melt in the form of polynomials, as well as melting temperature and heat of phase transition were assigned. The model allows varying in a wide range the geometrical and temperature parameters of growth installation, material characteristics in poly-, single-crystal state and in the melt (thermal conductivity, heat capacity, density, melting heat), as well as material growth rate (molten zone travel velocity).

Diffusion process is described by the Laplace equation which in the unsteady condition for a two-dimensional case is of the form [8]

$$D \cdot \left(\frac{\partial^2 C(x, y, t)}{\partial x^2} + \frac{\partial^2 C(x, y, t)}{\partial y^2} \right) = C(x, y, t), \quad (2)$$

where $C(x, y, t)$ is substance concentration at point with coordinates x, y at time moment t ; D is diffusion coefficient.

Thermal conductivity process is described by second-order differential equation [9, c. 139]

$$\alpha \cdot \left(\frac{\partial^2 T(x, y, t)}{\partial x^2} + \frac{\partial^2 T(x, y, t)}{\partial y^2} \right) = \frac{\partial T(x, y, t)}{\partial t}, \alpha = \frac{\kappa}{c\rho}, \quad (3)$$

where T is temperature at point with coordinates x, y at time moment t , α is thermal diffusivity; κ is thermal conductivity, c is heat capacity; ρ is density.

Computer model takes into account cylinder-symmetrical material geometry which causes introduction of a proper multiplier $1 + 3.14|x - x_c|$ for the representation of heat capacity and melting heat with a two-dimensional system mapping. The model does not consider the entire ingot, but its fragment which is due to increased rate and precision of simulating the most important portion, i.e. crystallization front. The other ingot parts are unimportant for crystallization process, so wasting on them considerable computational resources is inexpedient.

As long as interaction of two CA in our case results in leveling temperature between them, then, knowing the size of cells and having calculated the thermal diffusivity, one can determine time unit for the calculation of heaters rate, i.e. the number of CA interactions occurring with a heater travel by one cell. This process can be described by a flow-diagram (Fig. 3).

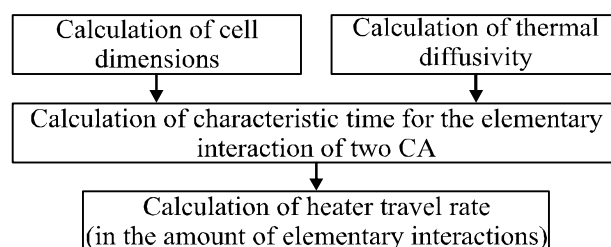


Fig. 3. Time parameters calculation sequence.

The two-dimensional field of CA has three layers: 1) cell temperature; 2) internal energy (taken into account in simulation of phase transitions); 3) state of matter index (single crystal, polycrystal or melt) is taken into account in the selection of polynomials for the determination of thermal conductivity, heat capacity and density.

The laws of interaction of cells have been assigned:

$$C_{ij}^{(n+1)} \rightarrow C_{ij}^{(n)} + \frac{D}{m} (\langle C_{kl}^{(n)} \rangle - C_{ij}^{(n)}) \quad (4)$$

$$T_{ij}^{(n+1)} \rightarrow T_{ij}^{(n)} + \frac{\alpha}{p} (\langle T_{kl}^{(n)} \rangle - T_{ij}^{(n)}), \quad (5)$$

where m and p are parameters characterized by space and time discretization; the values in angle brackets are the average values for cells of the immediate environment (k, l).

Also assigned are the laws of interaction between cells at phase transition. The phase transition of (i, j)-th cell from a liquid to solid state is attended with a rise in its temperature by the value dT and a decrease in substance concentration in liquid cells of the immediate environment, that is

$$T_{ij}^{(n+1)} \rightarrow T_{ij}^{(n)} + dT \quad (6)$$

$$C_{kl}^{(n+1)} \rightarrow C_{kl}^{(n)} - q \cdot \Delta_{kl}^{(n)}, \quad (7)$$

where q is a coefficient defining the kinetic constant of crystal growth rate; $\Delta_{kl}^{(n)}$ is supersaturation in (k, l)-th cell.

To increase the calculating speed, computing is divided into two stages: “rough” approximation for CA-field of size 30×60 and “precise” approximation for a field of tenfold size, i.e. 300×600 . It is obvious that calculating time is the less, the less is field size, but computing accuracy is reduced accordingly. Thus, it is from the analysis of a “precise” model that the results of calculating temperature fields and crystallization front are derived.

On reaching the steady-state mode of a “precise” model, the program displays temperature dependences along the length and across the width of the ingot and selection of respective cross section is assigned in percentage. It is possible to display plots showing the shape of crystallization front and polycrystal lower boundary, as well as the employed temperature dependences of thermoelectric material parameters.

An example of program interface is shown in Fig. 4.

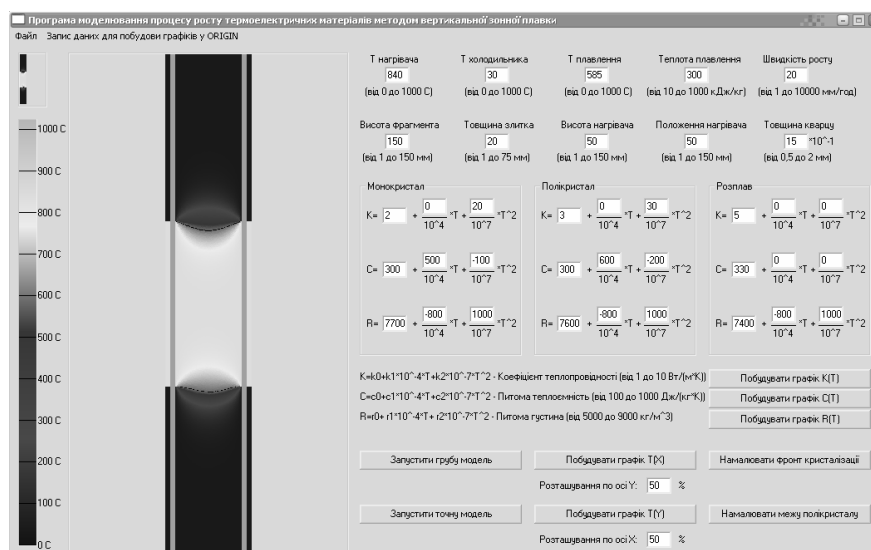


Fig. 4. Interface of TEM growth simulation program.

3. Computer simulation results

Asynchronous CA method was used to construct models of Bi_2Te_3 material growth process by vertical zone melting method. Heater temperature varied within 780 – 840°C, ingot diameter from 24 to 10 mm, heater width from 15 to 50 mm, growth rate from 1 to 50 mm/hour.

Temperature dependence over the cross section of ingot $T(x)$ (Fig. 5, 6) is an important characteristic for the estimation of radial homogeneity of material in the course of growth by vertical zone melting method. As can be seen from Fig. 5 and 6, with a decrease of ingot diameter from 24 to 20 mm, the radial gradient is reduced more than a factor of 3. In so doing, according to analysis of the entire series of constructed models, the radial temperature gradient is almost unaffected by the rate of zone travel (the rate of crystal growth).

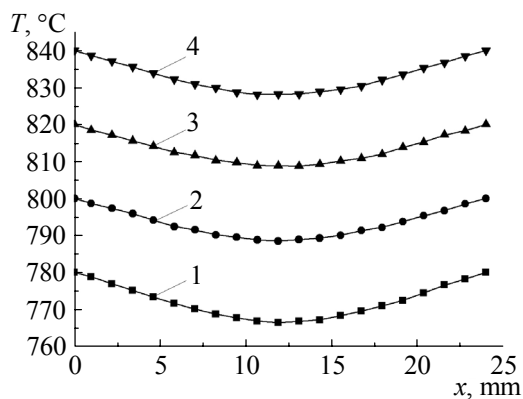


Fig. 5. Dependences of temperature over the cross section of ingot $T(x)$ for conditions $d = 24$ mm; $v = 20$ mm/h at temperature: 1 – 780°C; 2 – 800°C; 3 – 820°C; 4 – 840°C.

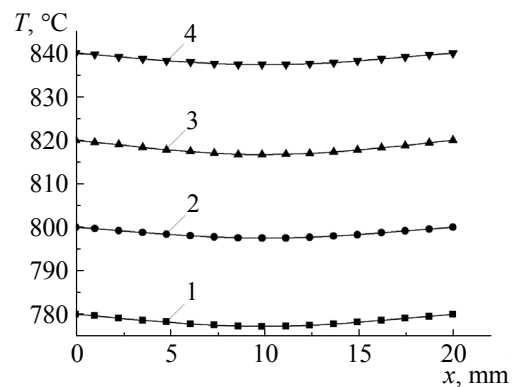


Fig. 6. Dependences of temperature over the cross section of ingot $T(x)$ for conditions $d = 20$ mm; $v = 15$ mm/h at temperature: 1 – 780°C; 2 – 800°C; 3 – 820°C; 4 – 840°C.

At the same time, growth rate affects considerably the axial gradient of temperatures calculated according to temperature dependences along the ingot (Fig. 7, 8).

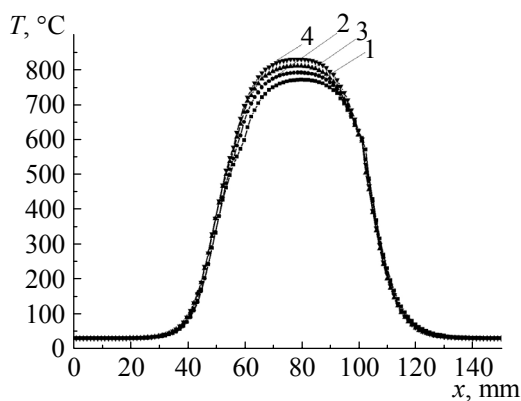


Fig. 7. Dependences of temperature along the ingot $T(y)$ for conditions: $d = 24$ mm; $v = 20$ mm/h at temperature: 1 – 780 °C; 2 – 800 °C; 3 – 820 °C; 4 – 840 °C.

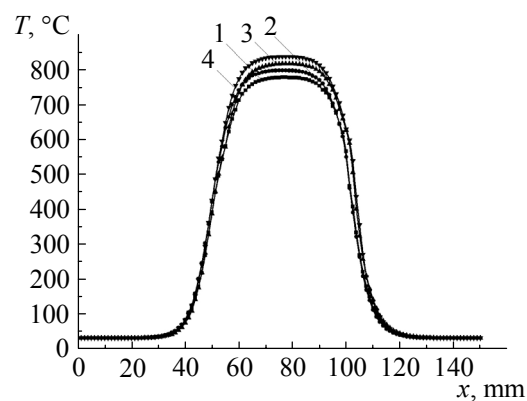


Fig. 8. Dependences of temperature along the ingot $T(y)$ for conditions: $d = 20$ mm; $v = 15$ mm/h at temperature: 1 – 780 °C; 2 – 800 °C; 3 – 820 °C; 4 – 840 °C.

Calculations showed that with a decrease in growth rate by 5 mm/h (from 20 to 15 mm/h) the axial gradient is increased on the average by 17 – 18 K/cm under all investigated temperatures. The axial gradient makes from 188 to 202 K/cm for the rate of 15 mm/h and heater temperature from 780 to 840°C.

The values of radial and axial temperature gradients define the shape of crystallization front (Fig. 9, 10). It can be convex, concave or, ideally, flat.

Formation of a flat crystallization front, hence, concentration homogeneity over the cross section of ingot, is assisted by a selection of optimal heater temperature 800 – 820°C (see Fig. 10) and cooler temperature 30°C, heater width 40 – 50 mm (with ingot diameter 20 – 25 mm, i.e. 2*d*), as well as zone travel rate from 5 to 15 mm/h, enabling to suppress the dendritic growth of thermoelectric material. These results were proved by experimental investigations.

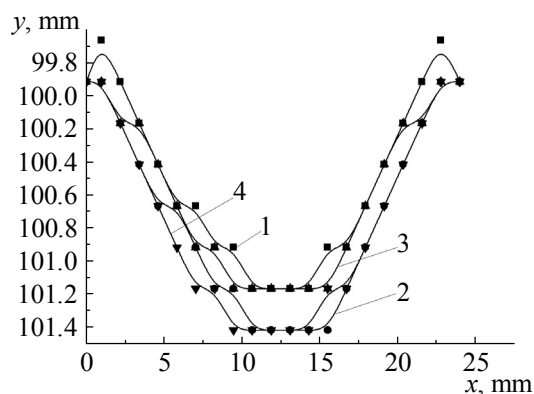


Fig. 9. Shape of crystallization front for conditions: $d = 24$ mm; $v = 20$ mm/h at temperature: 1 – 780°C; 2 – 800°C; 3 – 820°C; 4 – 840°C.

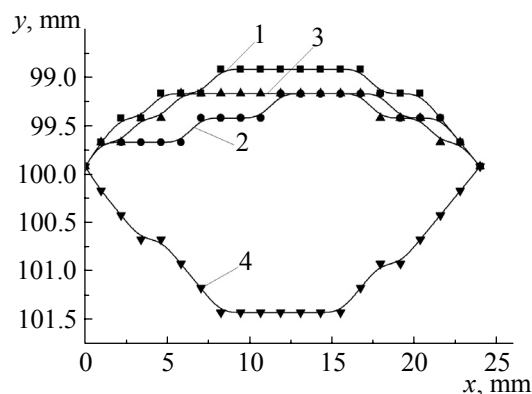


Fig. 10. Shape of crystallization front for conditions: $d = 24$ mm; $v = 15$ mm/h at temperature: 1 – 780°C; 2 – 800°C; 3 – 820°C; 4 – 840°C.

A reduction of heater width (molten zone width) leads to a considerable growth of radial gradient: it is increased by an order with the width of 30 mm and by a factor of 30 with the width of 20 mm as compared to 50 mm all other conditions being equal (Fig. 11).

Though a reduction of heater width leads to growth of axial temperature gradient (Fig. 12), which is a positive factor, at the same time there is considerable temperature decrease in the melt zone, reduction of its volume, formation of non-melted areas, which eventually results in the violation of single crystal material formation process.

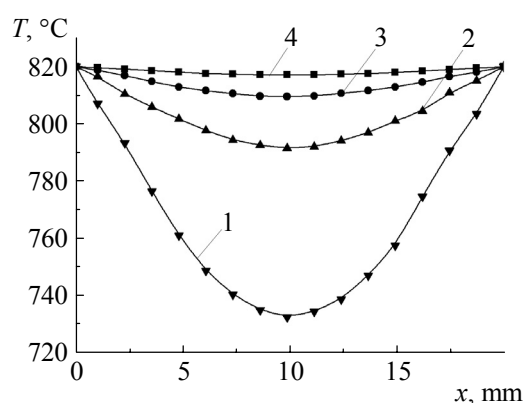


Fig. 11. Dependences of temperature over the cross section of ingot $T(x)$ for conditions: $T = 820$ °C; $d = 20$ mm; $v = 20$ mm/h at heater width: 1 – 20 mm; 2 – 30 mm; 3 – 40 mm; 4 – 50 mm.

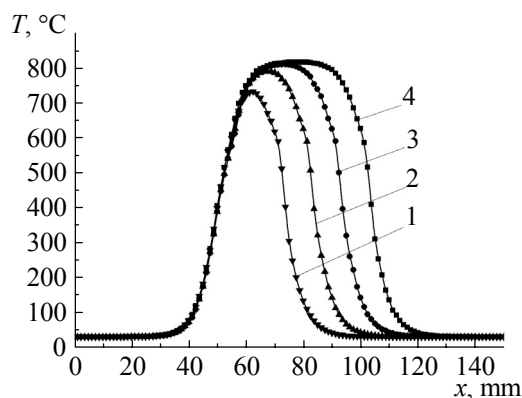


Fig. 12. Dependences of temperature along the ingot $T(y)$ for conditions: $T = 820$ °C; $d = 20$ mm; $v = 20$ mm/h at heater width: 1 – 20 mm; 2 – 30 mm; 3 – 40 mm; 4 – 50 mm.

Conclusions

Using the asynchronous CA theory, computer simulation program has been developed and the growth process by vertical zone melting method of thermoelectric material based on Bi_2Te_3 has been optimized, specifically simulation of thermophysical and diffusion processes in solid and liquid phases, phase transitions, thermal and temperature fields in crystal and melt depending on the external thermal conditions.

According to the results of computer simulation of thermophysical processes, the optimal kinetic, thermal and quantitative growth conditions have been determined for multicomponent TEM grown by vertical zone melting method. The temperature fields have been constructed; the shape of crystallization front and melt-polycrystal interface, the axial and radial gradients over a wide range of changing the geometrical and technological growth parameters have been determined. The optimal heater temperature has been determined as 800 – 820°C; crystallization front leveling is observed at low rates of molten zone travel $v = 5 - 15$ mm/h and ingot thickness $d \leq 24$ mm. Single crystals of homogeneous composition can be obtained by varying molten zone width from 40 to 50 mm. In so doing, the radial temperature gradient does not exceed 3 K/cm.

References

1. E.R. Abasheeva, Investigation and Simulation of Crystallization Processes with the Use of Cellular Automata, PhD Thesis in Engineering (University of Chemical Technology of Russia, Moscow, 2007).
2. O.L. Bandman, Method of Constructing Cellular Automata of Stable Pattern Formation Processes, *Prikladnaya Discretnaya Matematika* 4 (10), 91-99 (2010).
3. S. Wolfram, *A New Kind of Science* (Wolfram Media Inc, USA, 2002).
4. *Simulating Complex Systems by Cellular Automata* (eds. A.G. Hoekstra, J. Kroc, P.M.A. Sloot) (Springer, Berlin, 2010).
5. T. Toffoli, N. Margolus, *Cellular Automata Machines* (Mir, Moscow, 1991).
6. O.L. Bandman, Cellular Automata Models of Spatial Dynamics, *Sistemnaya Informatika*, 10, 57-113 (2005).
7. V.K. Vanag, Study of Spatially Distributed Dynamic Systems Using Probabilistic Cellular Automata, *Uspekhi Fizicheskikh Nauk* 169(5), 481-505 (1999).
8. V. Zhikharevich, S. Ostapov, Self-Organization and Evolution System Simulation by Continuous Asynchronous Cellular Automata, *Computing* 8 (3), 61-71 (2009).
9. I.T. Shvets, V.I. Tolubinsky, A.N. Aalabovsky, *Heat Engineering* (Vyscha Shkola, Kyiv, 1976).

Submitted 04.04.2012.