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NUMERICAL SIMULATION OF TEMPERATURE FIELD IN THE VERTICAL BRIDGMAN METHOD CRYSTAL GROWTH

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Abstract

The mathematical model for heat transfer during the Bridgeman crystal growth, using the finite element method and the obtained result are presented. Some modifications to the method were introduced in order to incorporate the data obtained experimentally. Solving the model enabled comparison of the experimental and numerical data and to obtain sufficient accuracy. The model was used to calculate the temperature gradient in the sample and the calculated gradient was in accordance with the observed crystal growth regime.
Key words: mathematical model, temperature field, finite element method

Introduction

Research in crystal growth includes a wide spectrum of activities including experimental conditions for preparation of specified material, mathematical modeling of processes and analysis of data obtained from experimental and numerical modeling in order to explain the phenomenon that occurs during the process. Mathematical modeling is gaining the importance in design of new materials, especially with a trend of production of new materials having predetermined properties. Production of crystals having predetermined properties could be achieved by tuning the conditions of their growth to a very sophisticated level and mathematical model plays the key role in this approach. Mathematical models are the basis in establishing the control of properties of obtained crystals.

The binary alloy will solidify giving the cell growth when the growth rate (R), enables the temperature gradient in the melt (G_L) and initial concentration of soluble component (C_0) are in a controlled frame. Theory of stable cell growth was studied for a long time and by several authors [1-18].

The first systematic study was done by Chalmers and co. [1,2]. The morphology of the phase boundary at the contact solid/liquid was studied in plumb based alloys. It

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was observed that the flat phase boundary becomes unstable when the growth rate actives the critical value given by:

$$R_{PC} = \frac{G_L D_L k_0}{m(1-k_0)C_0} \tag{1}$$

where D_L is the coefficient of diffusion in liquid phase, k_0 equilibrium coefficient of distribution and m is the slope of liquidus at the corresponding phase diagram. This criterion of constitutional super cooling, also called C.S. criteria was established by Tiller, Chalmers and coworkers [2].

The purpose of this paper is the determination of the temperature gradient in the melt in the moment of solidification. In the quantitative criteria of instability of boundary surface (eq. 2) the temperature gradient in the melt in contact with boundary surface is present - G_L. The hypothesis that the temperature gradient in the melt was equal to that in the furnace was accepted as the hypothesis for this calculation. In order to verify the validity of this hypothesis a series of measurement of melt temperatures and furnace temperatures were done and according to the established mathematical model the temperature gradient in the melt was determined [18-23].

Solidification occurs when there is some sub-cooling in the material. For C_0=2,2% and from the phase diagram of Al-Cu the equilibrium solidification temperature was obtained T_0. According to the work of Burden and Hunt [14], it was observed that the temperature of the boundary surface for the system Al-2%Cu is in the domain 653-655°C. From the measured temperatures of the sample those values were established at the distance of z≈200 mm from the furnace middle line. For the given distance the temperature gradient in the furnace according to measured temperatures is 14.5°C/cm. This value was used for calculation of subcooling in front of the boundary surface according to the equation (2) and in accordance with the work of Burden and Hunt [14]:

$$\Delta T = \frac{G_L D_L}{R} + 2^{\frac{3}{2}} \cdot \left[-\frac{m(1-k_0)C_0 K}{D_L} \right]^{\frac{1}{2}} \cdot R^{\frac{1}{2}} \tag{2}$$

Data used in the calculation are given in Table 2. The value of m was calculated from the equilibrium diagram of Al-Cu, while the values of D_L [16], k_0 [17] and K [15] were accepted from literature data.

Table 1. data used for calculation of temperature difference

G_L, °C/cm	D_L, cm^2/s	1, m/s	m, °C/%	k_0	C_0, %	K, °C cm
14,5	2,2× 10^{-5}	1,45× 10^{-6}	-3,4	0,153	2,20	1,04× 10^{-7}
14,5	2,2× 10^{-5}	8,71× 10^{-5}	-3,4	0,153	2,20	1,04× 10^{-7}

According to the equation (2) for maximal and minimal values of growth rate the data of supercooling of 0.6°C and 0.077°C were obtained. According to obtained values of supercooling and their low values it was concluded that this is heterogeneous nucleation and that according to equilibrium area of solidification (653-655°C) the temperature of solidification was determined to be 653°C. It could be stated that the

equilibrium solidification temperature was 655°C, and the supposed under cooling of 2°C.

Experimental

Crystals were prepared using the normal solidification method - vertical Bridgman. The graphite vessel with the batch was cylindrical and was positioned in the quartz ampule. The ampule was descending in the furnace using the mechanism for sample movement. The furnace temperature profile was known from previous experiments. The speed of movement was regulated using the motor with regulation of rotation speed. Solidification starts in the bottom part of the vessel, and the boundary surface is moved upwards by moving the vessel trough the furnace. Schematic representation of the apparatus and the sample position in the furnace is given in figure 1.

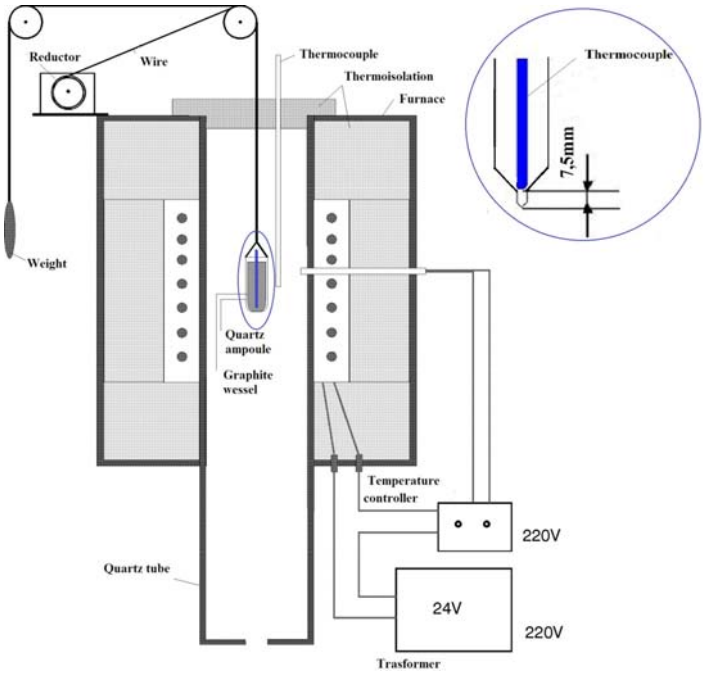

Fig. 1. Schematic representation of apparatus and sample position in the furnace and the position of the thermocouple in the specimen.

The temperature profile in the furnace was known from experimental measurements, and at the hottest spot it could attain the temperature of 1350°C. Furnace temperature was controlled using two thermocouples, one of which was placed near the heating element and was used for temperature control and other was near the vessel and monitors temperature near the sample. Temperature is regulated using a temperature controller. One thermocouple was inserted in the sample in order to measure the temperature in the sample as seen in upper right corner of Figure 1. This thermocouple was used for data acquisition of temperature in the sample during the experiment obtained data were used in the mathematical model development.

For the purpose of establishing the mathematical model and temperature field calculation in the melt, the temperature was measured in the furnace and in the sample during the growth of the crystal. The apparatus was modified for this purpose and the thermocouples were connected to the computer via a data acquisition system. The Ni-Cr-Ni thermocouples were used and temperatures in the melt and in the furnace were measured at the same time as it could be seen in upper right corner of Figure 1. The sample used in the experiment was the one previously solidified containing (C_0=2.2 % Cu) having defined shape so the position of the thermocouple could be determined precisely as presented in figure 1. This thermocouple was moved continuously trough the furnace with the speed of R= 8.71×10^{-5} m/s. The second thermocouple, that was used to measure the furnace temperature was moved every 2 min for some 10 mm down following the sample movement.

The traces of oxide were removed from the vessel using the solution $HCl:HNO_3$=1:3 and then 50% HCl at 70˚C, the vessel with the specimen was positioned into the furnace. Solidification was done in protective atmosphere of nitrogen. The heating regime was chosen so the specimen was melted in 90 min and after that the specimen was moved downwards with a selected speed.

Mathematical model

Solidification process is determined by the heat transfer mechanism inside the specimen. The heat transfer model was established for directional solidification of the sample composed of aluminum alloy. The heat transfer inside the specimen was considered and heat exchange with the environment. Axial conduction was neglected as much less important compared to radial conduction. The general differential equation that describes the heat transfer could be written as:

$$\frac{\partial T}{\partial \tau} + (R\nabla)T = \alpha \nabla^2 T \tag{3}$$

where R is the growth rate, τ is time and α is heat conductivity. The heat flux of the boundary surface is taken to be equal to the flux vessel – air and could be expressed as:

$$Q_{r_s} = Q_{r_c} \cdot \left(\frac{r_c}{r_s} \right) \tag{4}$$

Where: Q_{rc} is the overall heat exchange of radiation and conduction through the air barrier.

$$Q_{r_c} = q_{r_c} \cdot p_{r_c} \tag{5}$$

Radiation heat flux is given by the equation:

$$p_{r_c} = \sigma \cdot \left(a_c \cdot \varepsilon_E \cdot T_E^4 - a_E \cdot \varepsilon_c \cdot T_c^4 \right) . \frac{r_E}{r_c} \tag{6}$$

Where σ is the Stefan-Boltzmann constant and, a is the absorption coefficient, e is emissivity, and indexes s, c and E are determining the specimen, the vessel and the environment respectively.

Heat exchange by conduction and convection through the air barrier is given using the equation

$$q_{r_c} = \frac{K_a \cdot f \cdot (T_E - T_c)}{r_c \cdot \ln\left(\frac{r_e}{r_c}\right)} \tag{7}$$

Where: f is the coefficient that determines the part due to convection. The parts of the exchange due to convection and conduction could be estimated with sufficient accuracy, using the value of this factor of 2.

Boundary conditions are defined from the experimental data. As the sample moves through the furnace the temperature at the surface changes. Measured temperatures inside the furnace are fitted with polynomial using regression analysis for data obtained from measured temperatures profiles. The temperature in the center of the specimen was measured during the experiment and those data were used to compare the validity of the numerical solution [24]. The speed of the specimen movement was $8{,}71 \cdot 10^{-5}$ m/s. Regression polynomials are given as:

$$T_p = 766{,}6869 - 0{,}14909 \cdot z - 002199 \cdot z^2 + 3{,}92989\ 10^{-5} \cdot z^3 + 3{,}86778\ 10^{-8} \cdot z^4 \tag{8}$$

$$T_u = 824{,}8249 - 0{,}26392 \cdot z + 0{,}0112 \cdot z^2 - 1{,}13145 \cdot 10^{-4} \cdot z^3 + 2{,}10979 \cdot 10^{-7} \cdot z^4 \tag{9}$$

Where T_p is the furnace temperature and T_u is the temperature in the specimen.

Results of numerical simulation

The calculation of the temperature inside the cylindrical specimen can be done using the two dimensional solution of the heat transfer equation 3. The problem can be solved using the finite element method. The mesh inside the specimen used for the problem solution is a triangular one. The program enables using of specific boundary conditions and the comparison of the selected point of the temperature field to the experimental data for model verification [24]. If the axial temperature change is chosen for the center of the specimen for selected time intervals than those calculated data could be compared to experimental. The determining comparison point of experimental and calculated data is the data for the point where the thermocouple was placed. Comparing those measurements there is a discrepancy of results as shown in figure 2.

This means that some modifications are needed for the presented mathematical model. As the model includes exclusively heat transfer and ignores the phase transformation it was supposed that this was the reason for data discrepancy. Phase transformation enthalpy was then introduced as a heat source into the model equation. The heat source was supposed to be present from the moment when the solidification temperature is attained. Introduction of the heat source in this chosen moment did not give improvement as supposed. The results for this simulation are given in figure 3.

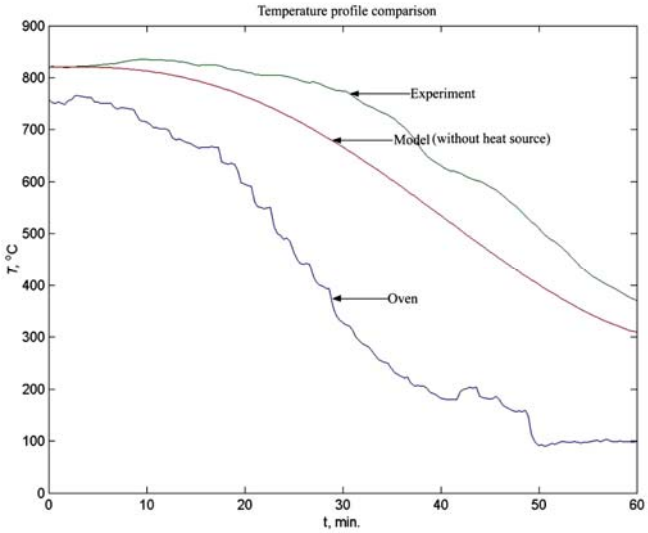

Fig. 2. Simulation results for temperature changes in the center of the specimen during solidification

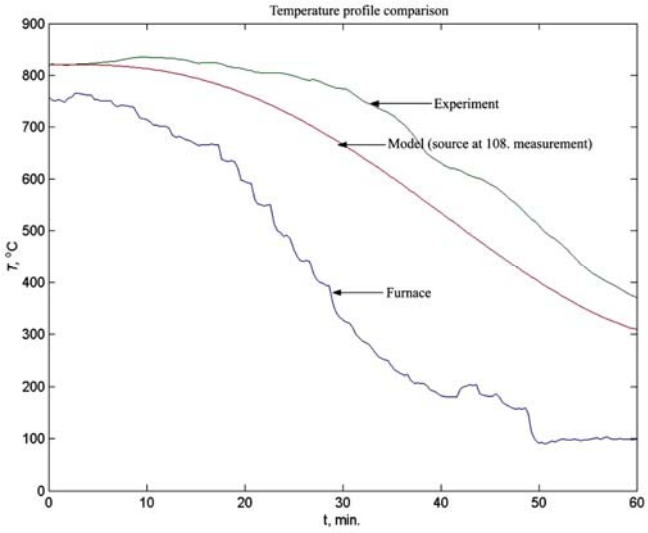

Fig. 3. Comparison of temperatures measured in the sample during the solidification process to the model with introduction of heat source in the moment that corresponds to the beginning of the solidification.

In order to achieve the marching of data the heat source was introduced earlier into account and using trial and error method it was determined that the introduction of heat source is necessary earlier. The retardation coefficient was introduced into the

model and the value of this parameter was estimated at the level of 1.07. This model modification enabled to obtain results that were in accordance with the experimental values. Figure 4 gives the changes of temperature at the measuring point of the sample obtained using the retardation coefficient. Data for measured and calculated temperatures for the specified position in the sample are in very good accordance.

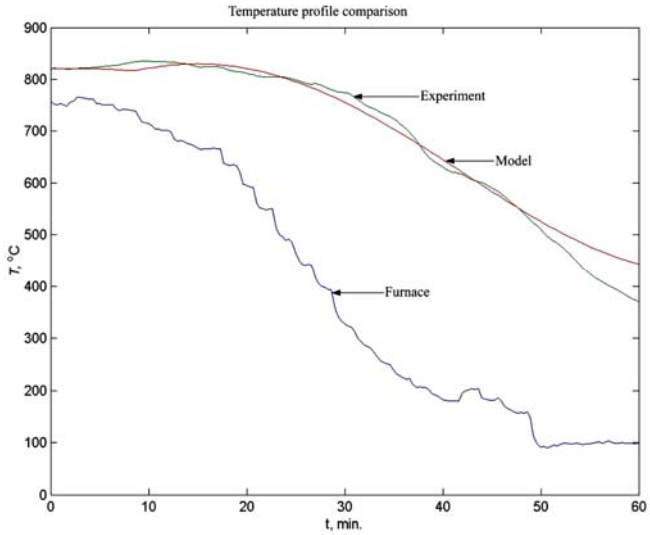

Fig. 4. Comparison of the temperature at the measuring point in the sample during solidification with introduction of heat source that appears in the calculated moment of the solidification process.

This model improvement enables the calculation of the temperature field in the sample with an accuracy that enables the calculation temperature gradient inside the specimen. Using the improved model the temperature gradient inside the sample could be calculated at the moment of solidification. The gradient determines the growth conditions established inside the specimen and those are verified using the metallographic micrographs of the samples. The gradient in the sample at the moment of solidification is given in Figure 5.

It is possible to calculate the temperature profiles in the sample for selected time intervals as it is shown in figure 6.

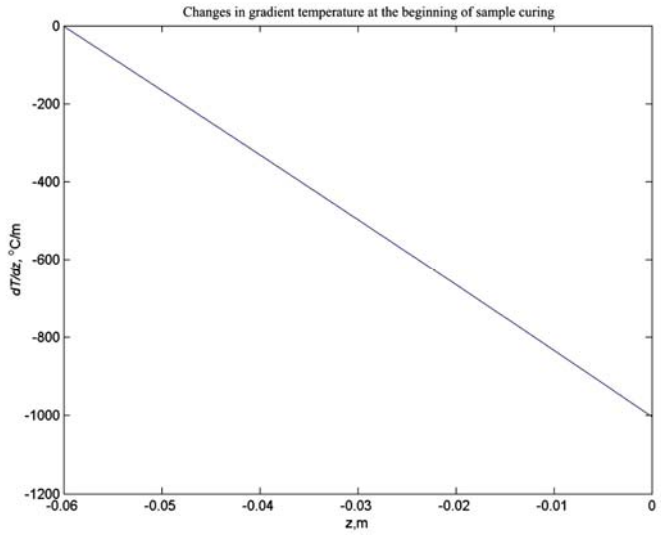

Fig. 5. Temperature gradient at the moment of the solidification start.

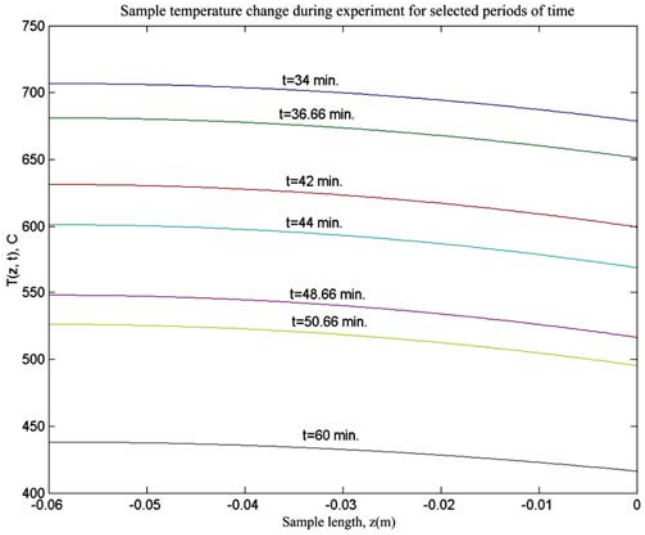

Fig. 6. Calculated sample temperature change during experiment for selected periods of time from the beginning of the experiment.

Conclusion

The mathematical model for temperature field calculation inside the sample solidifying using the vertical Bridgman method is given. The mathematical model was solved with introduction of some improvements that enabled solving equation using the

finite element method. Introduction of heat source in the sample permits simulation of the heat resulting from phase transformation. The correction that takes into account the retardation of measurement during experiments is introduced and this supported achievement of the good accordance of calculated and measured temperatures in a control point. The model is then used to calculate temperature gradient in the sample in the moment of solidification.

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