The influence of Prandtl numbers of melts and crucible materials on the features of crystal growth by the Bridgman method

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Abstract. The processes of crystallization of silicon and heptadecane in flat-bottomed cylindrical crucibles in conjugate convective heat transfer regime were studied numerically by the finite element method. Crystallization of silicon was investigated in a graphite crucible. Crystallization of heptadecane was investigated in a Plexiglas crucible. The possibility of existence of two convective vortices over a solidification front during the crystallization of silicon and heptadecane has been discovered. Crystallization of heptadecane was studied at two rates of lowering the crucible into the cold zone. Lowering of the crucible was simulated by moving the breakpoint in the temperature distribution on the outer side of the crucible walls. The breakpoint was the boundary of transition from the wall area heated to the initial temperature to the area with a given temperature gradient. Adaptive grids on triangles tracking the position of the crystallization front at each time step were used. The software package of developed by the authors was used.

1. Introduction

Single crystals and ingots of various materials, which are the starting materials for the creation of products of microelectronics, optoelectronics, nonlinear optics, etc., are obtained by Bridgman method [1-4]. The method is used for crystallization of solar-quality silicon (multi-silicon) in flat-bottomed crucibles of cylindrical and rectangular shape [5-7]. In this method, the melt located in the crucible and overheated relative to the crystallization temperature of the starting material from the hot upper zone of the furnace is lowered at a predetermined rate to the lower cold zone. After the generation of the crystal on the cooled bottom, the crystallization front (CF) spreads from the bottom up. All variants of the Bridgman method are characterized by regimes of conjugate convective heat transfer in the crucible-melt-crystal system. The development of technologies for growing high-quality single crystals requires an understanding of the features of conjugate convective heat transfer in different combinations of thermal conductivity of melts, crystals and crucible materials. This work aims at studying this influence. Numerical studies of the effect of conjugate convective heat transfer on the crystallization rate and on the CF forms were carried out for silicon-graphite and heptadecane-Plexiglas systems. For the silicon-graphite system, the research is a development of works [5-7]. Heptadecane-Plexiglas system is considered as an object of complex physical and numerical modeling. The results of numerical studies will be used in the construction of a physical model and planning of experimental studies of hydrodynamics and heat transfer during crystallization of heptadecane. Despite a large number of technological and numerical studies of crystallization processes in the classical
Bridgman method, due to the nonlinearity of the interaction of various mechanisms of flow generation, there are no answers to many questions. Technological practice shows that in all methods of directional crystallization, the growth of crystals with a flat CF provides the most uniform radial-azimuthal distribution of electrophysical properties in the plane normal to the direction of growth [8]. In the Bridgman method, due to the occurrence of radial temperature gradients caused by the difference in the thermal conductivity of the melt and the crucible walls, convective flows inevitably appear in the melt [5-7]. Selecting the regime of convective heat exchange, it is possible to correct the shape of CF and organize the entrainment of impurities rejected from CF [3-7]. Direct studies of high-temperature technological processes are expensive and time-consuming. It is almost impossible to measure the characteristics of unsteady temperature fields in the crucible-melt-crystal composite region of the growth vessel. Therefore, it is advisable to numerically investigate the conjugate processes of heat exchange occurring in the system. To verify the adequacy of the numerical model, it is desirable to compare the results with experimental data. The experiments will be carried out using heptadecan in crystallization modes on the physical model of Bridgman method by analogy with [9].

2. Model

The problems are solved in the axisymmetric formulation in the composite computational domain, the scheme of which is shown in figure 1. Only the right side of the axisymmetric computational domain is shown here. At the initial time \( t = 0 \) the crucible is filled with melt \( \Omega_1 \), that is overheated relative to the crystallization temperature. On the outer side of the walls of the crucible \( S_7 \), a temperature profile is set. It consists of an upper section with a constant temperature and a lower section with a linear temperature distribution. Lowering the crucible from the hot zone to the cold zone is simulated by the rate of movement of the temperature breakpoint at the outer boundary of the crucible \( S_7 \). The constant temperature at the top of the crucible has the initial temperature of the overheated melt. The crystallization process begins in the bottom part of the melt when the inner surface of the bottom is cooled to the crystallization temperature. The processes of cooling of the outer surface and crystal growth continue until the area of solidified substance \( \Omega_2 \) occupies the entire inner space of the crucible. The upper free boundary of the melt is given to be flat and non-deformable. The total volume of the crystallized substance and the melt is assumed to be constant [5].

Convective heat transfer in the melt is described by a system of equations of unsteady natural convection in the Boussinesq approximation, which are represented in dimensionless variables:

\[
\begin{align*}
\frac{\partial \omega}{\partial t} + u \frac{\partial \omega}{\partial r} + v \frac{\partial \omega}{\partial z} + \frac{\omega}{r} \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} \right) & = 1 \left( \frac{\partial^2 \omega}{\partial r^2} + \frac{1}{r} \frac{\partial \omega}{\partial r} \right) + Gr \frac{\partial T}{\partial r} \\
\frac{\partial^2 \psi}{\partial r^2} + \frac{\partial^2 \psi}{\partial z^2} + 1 \frac{\partial \psi}{r \partial r} - \frac{\partial^2}{\partial z^2} + \omega & = 0 \\
\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial r} + v \frac{\partial T}{\partial z} & = \frac{1}{Pr} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right)
\end{align*}
\]

where \( Pr = \frac{\lambda_i}{\nu_i \rho_i (T_c) c_i} \) is the Prandtl number, \( Gr = \frac{g \beta_i (T) H^3 \Delta T}{\nu_i^2} \) is the Grashof number, \( \beta \) is the coefficient of volumetric thermal expansion, \( g \) is the acceleration of gravity; \( \lambda_i, c_i, \nu_i \) are the thermal
conductivity, heat capacity and kinematic viscosity of the melt, and $T_0$ is the temperature at which the fixed values of the thermal properties are taken. The stream function and the velocity vorticity are related to the velocity components by the following relations:

$$u = -\frac{\partial \psi}{\partial z}, \quad v = \frac{1}{r} \frac{\partial (r \cdot \psi)}{\partial r}, \quad \omega = \frac{\partial u}{\partial z} - \frac{\partial v}{\partial r}.$$ 

The height of the liquid layer $H$ is chosen as the scale of the geometric dimensions. For speed and time scales, $\psi / H$ and $H^2 / \nu_f$, respectively, are selected. The scale of the temperature $\Delta T$ is a characteristic temperature difference.

The problem is solved under the following boundary conditions:

1. At the interface between crucible–melt and crucible–crystal media, the conditions of ideal thermal contact are fulfilled, i.e. temperature and heat flow are inseparable:

$$\lambda_i \frac{\partial T}{\partial n} \bigg|_{S_{\text{SS}}} = \lambda_i \frac{\partial T}{\partial n} \bigg|_{S_{\text{SS}}}, \quad \lambda_i \frac{\partial T}{\partial n} \bigg|_{S_{\text{SS}}} = \lambda_i \frac{\partial T}{\partial n} \bigg|_{S_{\text{SS}}}, \quad \lambda_i \frac{\partial T}{\partial n} \bigg|_{S_{\text{SS}}} = \lambda_i \frac{\partial T}{\partial n} \bigg|_{S_{\text{SS}}} \quad (i = 1, 2, 9).$$

2. At the melt-crystal interface, the Stefan condition applies:

$$\lambda_2 \frac{\partial T}{\partial n} \bigg|_{S_{\text{SS}}} = \lambda_3 \frac{\partial T}{\partial n} \bigg|_{S_{\text{SS}}} + \rho L V_{fc}.$$ 

where $V_{fc}$ is the velocity of the point lying on the interface in the direction of the normal to the crystallization front, $L$ is the latent heat of the phase transition.

3. Non-flowing conditions are given at the non-deformable boundaries of the melt region and at the crystal-melt boundary: $\psi \bigg|_{b_i} = 0 \quad (i = 1, 2, 3); \quad \psi \bigg|_{b_i} = 0$.

4. On the inner rigid surfaces of the crucible walls and on the crystal-melt boundary, the adhesion conditions are satisfied, so that the condition for the velocity vorticity is represented as:

$$\alpha_i = -\frac{\partial \psi}{\partial z} - \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial (r \cdot \psi)}{\partial r} \right), \quad i = 1, 2, 4, 9.$$ 

5. The temperature at the outer edges of the crucible ($S_6, S_7$) changes with time:

$$T \bigg|_{b_{s,7}} = T_1 - V_C \frac{dT}{dz} \bigg|_{b_{s,7}}, \quad \text{if} \quad T \bigg|_{b_{s,7}} < T_{\text{min}}, \quad \text{then} \quad T \bigg|_{b_{s,7}} = T_{\text{max}}, \quad \text{if} \quad T \bigg|_{b_{s,7}} > T_1, \quad \text{to} \quad T \bigg|_{b_{s,7}} = T_1,$$

where $T_1$ is the temperature in the hot zone of the furnace, $T_{\text{min}}$ is a fixed minimum cooling temperature, $V_C$ is the rate of lowering the crucible, and $\frac{dT}{dz}$ is a given temperature gradient.

6. The conditions are set on the symmetry axis: $\psi \bigg|_{r=0} = 0, \quad \omega \bigg|_{r=0} = 0, \quad \frac{\partial T}{\partial r} \bigg|_{r=0} = 0$.

7. The upper horizontal boundary of the computational domain is adiabatic: $\frac{\partial T}{\partial z} \bigg|_{b_{s,8}} = 0$.

8. At the initial time, the temperature throughout the system is constant and equal to the temperature in the hot zone of the furnace, there are no convective flows: $T \bigg|_{b_{s,0}} = T_1, \quad \psi \bigg|_{b_{s,0}} = 0, \quad \omega \bigg|_{b_{s,0}} = 0$.

In solving the problem, the latent heat of crystallization is taken into account. For this purpose, the dimensionless energy equation in the crystallization zone is modified as follows:

$$\left(1 + \frac{L}{c_i \Delta T} \right) \left\{ \frac{\partial T}{\partial t} + u \frac{\partial T}{\partial r} + v \frac{\partial T}{\partial z} \right\} \right. = \frac{\lambda_2}{\lambda_3 \nu_f} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right).$$ 

The boundaries of the crystallization zone are determined by the position of the crystallization front at the current time step and, presumably, by the new position of the front, determined in the iterative process of solving the equations.

In the walls of the crucible and in the crystal, heat transfer is carried out due to thermal conductivity. Accordingly, the dimensionless heat equation is solved in the domains $\Omega_i \ (i = 2, 3)$:
where \( c_i, \rho_i, \lambda_i \) are the heat capacity, density, and thermal conductivity of the material corresponding to a particular area.

The problems are solved by the finite element method. Linear functions on triangles are used to approximate the solution. Grid generation is based on the direct method of constructing the Delaunay triangulation at the highest angle with cellular acceleration. The grid is built for each time step, so as to track the shape of the CF at the current step and at the next step with automatic determination of the volume of the crystallized substance. In addition, the meshes are condensed to the CF (current and future) on both sides, to the solid boundaries and angular areas of the computational domain. A fragment of the grid on one of the time layers is shown in figure 2. It also demonstrates a portion of the parietal region with CF silicon at time \( t = 9160s \) at a speed of lowering of the crucible of 2.81 cm/h and the temperature gradient on the outside of the crucible wall of 35K/cm. A grid with approximately 17 thousand of nodes is used; the number of nodes could vary depending on the specific time step.

Calculations are carried out at the values of thermophysical parameters typical for crystallization of silicon in graphite crucibles and heptadecane in Plexiglas crucible [10-13]: thermal conductivity coefficients, \( \lambda \): silicon melt - 67 J/(m·s·K), crystal - 22 J/(m·s·K); melt and solid heptadecane - 0.145 J/(m·s·K); graphite - 50 J/(m·s·K); plexiglass - 0.195 J/(m·s·K); density, \( \rho \): melt and silicon crystal - 2530 kg/m³; melt and solid heptadecane – 776.5 kg/m³; graphite - 1800 kg/m³; plexiglass - 1180 kg/m³; specific heat, \( C \): graphite - 2100 J/(kg·K); Plexiglass - 1270 J/(kg·K); melt and silicon crystal - 1000 J/(kg·K); melt and solid heptadecane – 1629J/(kg·K); kinematic viscosity, \( \nu \): the melt of silicon - 3.4·10⁻⁷ m²/s; melt heptadecane – 5.04·10⁻⁶ m²/s; coefficient of volume expansion, \( \beta \): silicon melt - 1.4·10⁻⁴ 1/K; heptadecane melt – 1.05·10⁻³ 1/K; heat of crystallization, \( L \): silicon melt - 1.8·10⁶ J/kg, heptadecane melt – 1.674·10⁵ J/kg; Prandtl number, Pr: silicon melt - 0.0128 and heptadecane – 43.97.

3. Results and discussion

The process of silicon ingot growth at the crucible lowering rate of 2.81 cm/h was investigated. The temperature gradient on the outside side walls of the crucible is linear in the lower part after the inflection point and equals 35 K/cm. In the upper part of the wall, temperature is constant and higher than the crystallization temperature of silicon = 1410°C by 40°C. Figure 3 shows the position and shape of crystallization fronts (isotherms correspond to 1410°C) in the silicon-graphite at two time points. For figure 3 and below only the right-hand parts of the axisymmetric system are shown. The area with the lower temperature and with the crystallized substance is painted gray. In [5-7] it was shown that in the hydrodynamic sense the system is absolutely unstable and at all stages of the process there is a melt flow of thermogravity nature. Radial temperature gradients in the melt, causing the appearance of convection, arise due to lateral heating, bottom cooling and differences in the thermal conductivity of the walls of the crucible and the melt. An updraft of the melt is formed along the heated side wall of the crucible. As a result, in the center of the crucible there is a downward flow of
heated melt, which slows down the growth rate of the crystal. Figure 3 demonstrates that convection has a noticeable effect on the shape of the crystallization front.

Figure 3. Fields of isotherms and contours of stream function (cm²/s) at time a – t = 6580s, b – t = 9160s. Values at the neighboring isolines of the stream function of the primary vortex differ by 0.05 cm²/s. Values on the isolines of a stream function of the secondary vortex are different at 0.0025 cm²/s.

As the CF moves upwards, its shape changes from convex to slightly concave. The curvature of the CF is significant at the periphery in the parietal region. This is explained by changes in local temperature gradients and heat fluxes in the wall region. Figure 3 shows that in the intermediate stages of the crystal growth, there is the formation of the secondary vortex, located between the crystallization front and the lower boundary of the upper convective vortex. In the upper vortex, the melt circulates counterclockwise. In the lower secondary vortex, the melt circulates clockwise. This effect was not detected in [5]. Refinement of the spatial flow pattern became possible as a result of the use of more accurate data on the properties of silicon and graphite [11, 12], the use of a more detailed grid and changes in the geometry of the computational domain. In this paper, the height of the melt layer is doubled in comparison with [5].

To clarify the reasons for the appearance of the secondary vortex, the calculations of crystallization of heptadecane in Plexiglas crucible are made. The thickness of the
walls and bottom of the crucible is 5mm, inner diameter is 100mm. The initial system temperature is 32°C, i.e. the melt is overheated by 10° C in relation to the crystallization temperature heptadecane.

Figure 5 shows the initial stage of the formation of convective flow during the bottom cooling before the start of crystallization at \( V_C = 2.81 \text{ cm/h} \), and \( dT/dz = 5\text{K/cm} \). There is a complete qualitative analogy with the case of the silicon-graphite system. The ratios of thermal conductivity coefficients of melts and crucible walls in silicon-graphite and heptadecane-plexiglass systems differ slightly. It is seen that the higher thermal conductivity of the crucible walls relative to the thermal conductivity of the melt leads to overheating of the bottom periphery and to the appearance of a radial temperature gradient in the melt. As a result, an upward flow of the melt is formed near the walls of the crucible.

Figures 6, 7 show the calculations with two speeds of lowering of the crucible with the heptadecane melt in the cold area with a temperature gradient \( dT/dz = 5\text{K/s} \). Here it is seen how the lowering speed affects the field and isotherms of the form of CF of heptadecane when lowering the crucible into the cold zone. Figure 6 shows the initial stage of crystallization.

The intermediate stage of the process, when the isotherms with the crystallization temperature are at \( z = 1 \) on the outer side of the crucible wall, is shown in figure 7. It can be seen that with the increase in the rate of lowering of the crucible, the crystallization front becomes more concave in the solid. This is due to the thermal inertia of the central part of the solidified substance and the effective heat removal along the walls of the crucible in comparison with the cooling of the crystal through the bottom. At this stage, with a large length of the cooled portion of the lateral boundary of the crucible and due to cooling at the walls of the crucible, CF moves faster than in the central part. Therefore, the deflection of the crystallization front is more and more noticeable from some point in time. This can
be seen in the form of isotherms and crystallization fronts in figure 7a, b. At a certain critical height of the cold “side wall of the bowl” formed at the crucible wall cooled with increasingly efficiency, conditions are created for the formation of a downflow of the melt cooled from the side (figures 6, 7). As a result, a secondary vortex over the CF is formed. The moment of occurrence of the secondary vortex depends on the rate of lowering of the crucible, as can be seen from the comparison of figures 6, 7. The thermal inertia of the core of the melt layer and the central part of the solidified substance is visible from the comparison of the isotherm fields in figures 7a, b.

![Figure 7](image_url)

**Figure 7.** Fields of isotherms (a, b) and isolines of the stream function (b, g) at time \( t = 8985 \) s; \( V_C = 2.81 \) cm/h (a, b) and \( t = 25200 \) s; \( V_C = 1 \) cm/h (b, g).

Figure 8 shows how the intensity of the melt circulation changes in the primary and secondary vortices. This can be seen in figure 8 by the amplitudes of the flow in the main upper vortex and the return flow in the secondary vortex. The direction of circulation in the secondary vortex is opposite to that observed in the main vortex (see figure 8 bottom of the curves).

![Figure 8](image_url)

**Figure 8.** Profiles of the horizontal components of velocity in the cross-section \( r = 2.5 \) cm at \( V_C = 2.81 \) cm/h at the time moments: 1 – \( t = 1210 \) s; 2 – 3570 s; 3 – 6430 s; 4 – 8985 s; 5 – 12830 s; 6 – 14730 s.

![Figure 9](image_url)

**Figure 9.** Heptadecan volume solidification dependence on time at a speed of crucible lowering: 1 – \( V_C = 2.81 \) cm/h; 2 – 1 cm/h.
The rate of crystallization of the substance also depends on the rate of lowering the crucible into the cold zone (figure 9). The shape of the crystallization front should be influenced by the release of phase transition heat and corresponding estimates will be made from the results of calculations for different $V_C$.

4. Conclusion
A software package has been developed and the growth of silicon ingots and heptadecane in the Bridgman-Stockbarger method has been numerically simulated in the regime of natural convection at the initial overheating of melts relative to the crystallization temperature. In the case of silicon, the lowering rate of the crucible was 2.81 cm/h. The temperature gradient along the lower portion of the side wall of the crucible was linear and equal to 35 K/cm. In the considered regime, shape of CF was shown to change from convex to concave. In a real technological process a radial temperature gradient and thermogravity convection inevitably occur. Thermogravity convection significantly affects the shape of the crystallization front. Despite the significant difference in Prandtl numbers, the scenarios for the evolution of the spatial shape of the convective flow in silicon and heptadecane melts coincide qualitatively.

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