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MODELING OF HEAT TRANSFER IN A MELT IN GROWING SINGLE CRYSTALS BY THE STOCKBARGER METHOD USING THE ACCELERATED CRUCIBLE ROTATION TECHNIQUE (ACRT)

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In model experiments, the layer of melt bounded by the crystallization front and the heater for heating the diaphragm in a growing furnace is shown to determine crystal growth by the Stockbarger method under conditions of induced convection and also to control the crystallization process. The free volume of the melt exerts no effect on its hydrodynamic and thermal structures. Optimum values of the exposure time are estimated for constant maximum and minimum velocities of modulated rotation of the growing ampoule.

In studying the effect of the temperature field in a growing furnace on the optical quality of crystals grown by the Stockbarger method, Godovikov et al. [1] noted that the determining factors are the position of the crystallization front in the growing furnace and the perturbation of the thermal field in close proximity of this front. It is clear that studying the effect of one parameter is possible only if the other controlled parameters that determine the crystallization conditions are constant. As in the classical Stockbarger method (see Fig. 1), we formed a temperature field in a growing furnace by three heaters: an upper heater, a lower heater, and a middle heater (a heater for heating the diaphragm).

We studied three positions of the crystallization front relative to the annular heater for the diaphragm and its effect on the optical quality of proustite single crystals (Ag_3AsS_3, a nonlinear-optics material with T_{melt} = 485°C). Single crystals of high optical quality were grown only if the crystallization front was positioned below the diaphragm, although Stepanov and Vasil'eva [2] noted that it is impossible to obtain high-quality single crystals under similar conditions. Meanwhile the most positive effect in creating large single crystals for optoelectronics by the Stockbarger method is attained with the use of forced stirring of the melt by the method of modulated rotation of the growing container [3]. Stirring is caused by the presence of intense flows in the melt. These flows are directed radially from the cylinder's generatrix to the axis of rotation if the velocity of rotation of the ampoule slows down and from the axis to the cylinder's generatrix upon acceleration [4] (Fig. 2a and b).

In experiments on physical modeling of the hydrodynamics and heat and mass transfer in the melt in growing single crystals by the ACRT, we considered the case where the thickness of the melt layer was equal to or slightly exceeded the distance from the crystallization front to the annular heater for heating the diaphragm [5]. Since in the process of growing real crystals by the Stockbarger method (especially at its initial stage), a melt layer positioned above the level of the middle heater always exists, it is important to know its effect on the general hydrodynamic and thermal structure of the melt. Under real conditions, this layer has a constant temperature along the axis of the growing furnace already at a small distance above the diaphragm.

In the present paper, we model the thermal structure in a melt layer whose thickness exceeds considerably the distance from the lower level of the middle heater to the crystallization front. Model experiments were performed, the thermal structure of the liquid (96% C_2H_5OH was used as the model working

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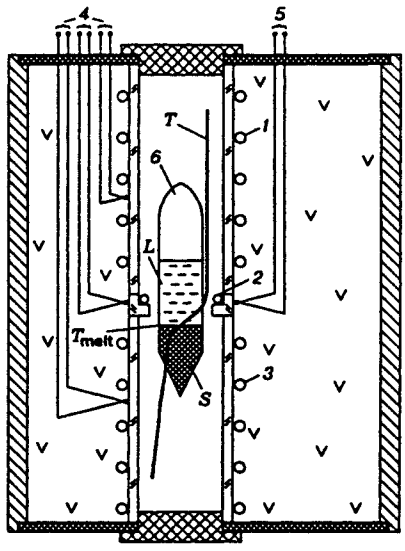

Fig. 1. Schematical view of a growing furnace and the temperature distribution in this furnace: 1) upper heater; 2) annular heater for heating the diaphragm; 3) lower heater; 4) regulating thermocouples; 5) control thermocouple; 6) growing ampoule.

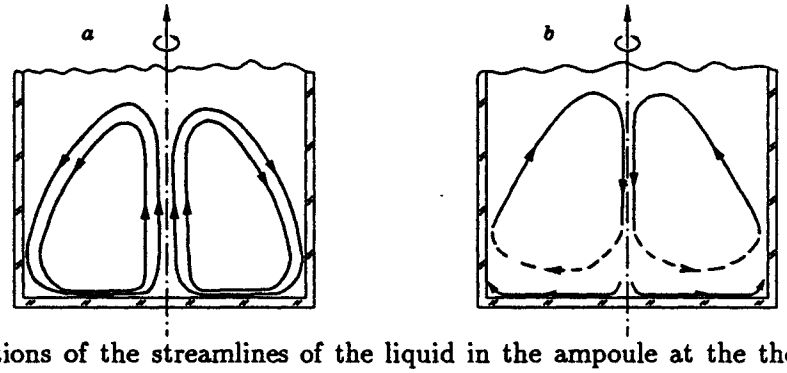

Fig. 2. Directions of the streamlines of the liquid in the ampoule at the thermostatically controlled substrate for slowed (a) and accelerated (b) rotation of the ampoule.

liquid) was studied for an immobile and a modulated-rotating ampoule, with a vertical axis of rotation. To measure the temperature field in the volume of the melt, we used a special fluoroplastic insert. A spiral heater 4 (Fig. 3) made of Constantan wire of diameter 0.15 mm (the resistance $R = 70\ \Omega$) was wound on this insert. The insert was placed in a cylindrical optical-quartz ampoule 1 of diameter 44.5 mm. There was a free volume of ethanol A over the heater that is comparable in height to the working volume of ethanol H_1. The height of the ethanol column was varied by raising or dropping a fluoroplastic shutter 3. Central straight 5 and L-shaped 6 Nichrome–Constantan ($\varnothing = 0.05$ mm) differential thermocouples were mounted in an orifice in this shutter. The free surface of the melt was 5 mm lower than the horizontal surface of the shutter 7. The cold junctions of the thermocouples were placed on the thermostatically controlled copper base of a quartz ampoule 2 positioned on a rotating table. Reckoning was done from the temperature of the cooled surface that models the growing face of the crystal. The measured temperature T_{rel} is equal to the difference in the values of the temperature in the liquid volume and the temperature of the cooled bottom of the quartz ampoule ($T_{rel} = T_{melt} - T_{bot}$). The power of the heater is 3 W, and the temperature of the substrate is 24.5°C.

The coordinates of the positions of the thermocouples were measured by a B-630 cathetometer that is placed on a coordinate table. This device makes it possible to measure the displacement in a horizontal direction with an accuracy of 0.01 mm. Instantaneous values of the electromotive force (e.m.f.) of the thermocouples were measured synchronously by the measuring facility described in [5]. Unlike what was

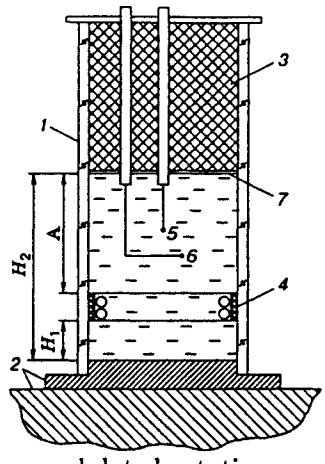

Fig. 3. Design of the modulated-rotating ampoule: 1) cylindrical ampoule; 2) thermostatically controlled copper substrate; 3) cylindrical fluoroplastic shutter; 4) heat exchanger; 5) central thermocouple; 6) L-shaped thermocouple; 7) surface of the liquid layer; H_1 is the height of the working volume of the liquid, H_2 is the height of the entire column of liquid, and A is the height of the free volume of liquid.

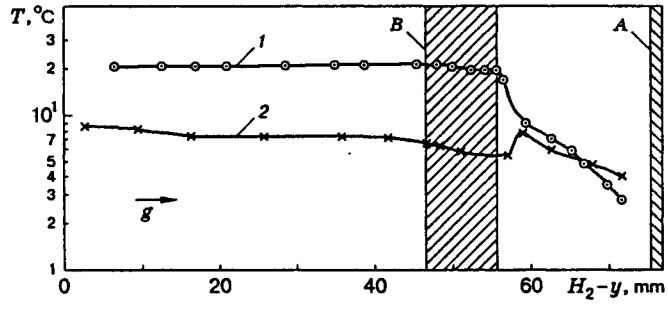

Fig. 4. Temperature distribution over the thickness of the liquid layer (H_1 = 19.02 mm and H_2 = 75.18 mm): curve 1 refers to the temperature for y = const (without rotation) and curve 2 refers to the time-averaged temperature in the cross section y = const (upon modulated rotation); A is the thermostatically controlled substrate and B is the heater (g is the acceleration of gravity).

done in [5], the change in the number of revolutions of the ampoule about the vertical axis was recorded from a TÉSA-type electronic tachometer by an H-3030-3 three-channel self-recording potentiometer.

In modeling crystal growth by the Stockbarger method, the annular heater in the model ampoule, just like the annular heater 2 for heating the diaphragm in the growing furnace (see Fig. 1), creates a temperature difference between the thermostatically controlled substrate of the ampoule (the crystallization front) and the heater and simultaneously ensures a constant temperature of the free volume of ethanol, just like the upper heater of the growing furnace 1 (see Fig. 1); the function of the thermostatically controlled substrate of the ampoule, which models a planar crystallization front, is similar to the function of the lower heater 3 in the growing furnace (see Fig. 1).

The temperature values along the axis of the immobile ampoule were measured first (curve 1 in Fig. 4). It was found that the temperature is constant above the heater, i.e., in the entire free volume of the liquid. Meanwhile, in the working volume, i.e., below the heater, the temperature changed according to an exponential law, similarly to the temperature distribution obtained in experiments with ampoules of smaller

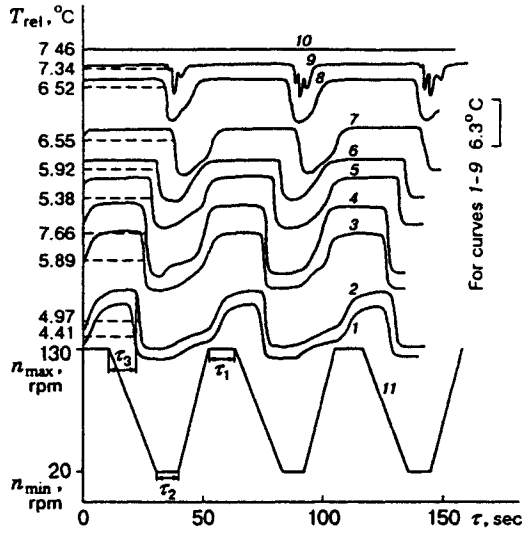

Fig. 5. Time dependences of the instantaneous temperature values measured along the ampoule's axis (H_1 = 19.02 mm and H_2 = 75.18 mm, y = 0 on the thermostatically controlled substrate; the coordinates of the heater are 19.02 < y < 27.87 mm): curves 1–10 refer to y = 3.67, 7.23, 12.71, 16.2, 18.27, 24.22, 27.06, 29.06, 33.46, and 39.16 mm; curve 11 refers to the law of modulated rotation of the ampoule, where n_{max} = 130 rpm (maximum velocity of rotation), n_{min} = 20 rpm, τ_1 and τ_1 are the times of exposure of the ampoule at the maximum and minimum velocities of rotation, respectively, and τ_3 is the time lag of the temperature variation relative to the corresponding variation of the velocity of rotation.

diameter and without a free liquid volume [5]. The temperature distribution obtained is identical to that used in growing single crystals from a melt by the Stockbarger method. The regularity of the variation of the mean temperature along the height of the flow core in the entire liquid volume in a modulated-rotating ampoule is shown by curve 2 in Fig. 4.

We performed studies according to the law of trapezoid-shaped modulated rotation (curve 11 in Fig. 5). The acceleration time was equal to the deceleration time and constituted 20 sec. For constant minimum and maximum velocities, the exposure time was the same (τ_1 = τ_2 = 10 sec). The time of inertial delay τ_3 of the temperature variation relative to the variation of the velocity of rotation of the growing container increased with distance from the rotating thermostatically controlled base, i.e., as y increases. Similarly to the case of an immobile ampoule, a constant temperature was observed along the height of the free liquid volume above the heater, with subsequent variation (curve 2 in Fig. 4) according to an exponential law in the working volume of the liquid. In the liquid volume bounded by the cylindrical heater along the circumference. a local drop in the mean temperature by 2.2°C was observed because of vortex flows in the vicinity of the annular heater.

Different actual values of temperatures along the ampoule's axis in a modulated-rotating container were obtained along the entire height of the liquid (below, inside, and above the annular heater) depending on the vertical coordinate y of the point of temperature measurement (y = 0 on the cooled flat bottom of the ampoule). The total height of the liquid column was H_2 = 75.18 mm, the thickness of the working layer of the liquid from the lower end of the heater to the thermostatically controlled bottom of the ampoule was H_1 = 19.02 mm, the height of the heating unit was 8.85 mm, and the height of the free liquid volume above the heater was A = 48.71 mm. Figure 5 shows that the periodic changes in the actual values of the temperatures that are caused by the modulated rotation, which are similar to the changes in the velocity of rotation of the

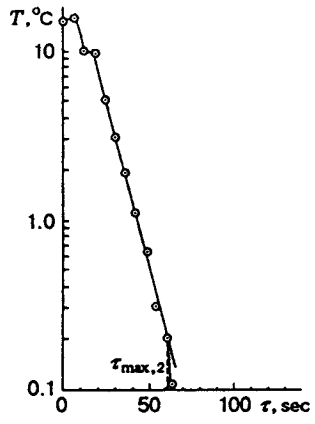

Fig. 6

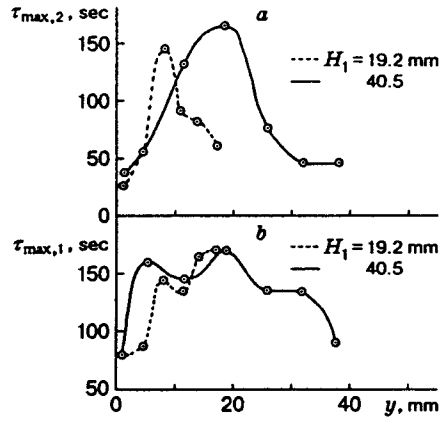

Fig. 7

Fig. 6. Temperature T versus time τ for a stabilized velocity of rotation of the container ($n_{\min}$ = 20 rpm = const, H_1 = 19.2 mm, and y = 16.95 mm).

Fig. 7. Stabilization time of the temperature $\tau_{\max,2}$ versus the vertical coordinate y for $n_{\min}$ = 20 rpm = const (a) and $\tau_{\max,1}$ for $n_{\max}$ = 130 rpm = const (b).

ampoule, decrease in amplitude with distance from the annular heater upward. They disappear completely at a height of 11.2 mm above the upper level of the heater, which corresponds to the coordinate y where the mean temperature reaches a stationary value (curve 2 in Fig. 4). This is the level of the influence of the vortex flow at the thermostatically controlled base of the ampoule that is formed during its modulated rotation. The maximum amplitude of temperature oscillations was recorded at a height of 2.28 mm below the heater and was 9.29°C. At the thermostatically controlled bottom of the ampoule, which models the plane front of crystallization, the amplitude of temperature oscillations equaled 7.24°C.

To determine the optimum time parameters of the modulation law of the velocity of rotation for fixed values of the maximum ($n_{\max}$ = 130 rpm) and minimum ($n_{\min}$ = 20 rpm) velocities, we performed experiments on the time lag of the system and the damping times of the vortex flows in the melt after constant minimum and maximum velocities were reached. The experimental results enable one to choose the optimum time of existence of "stepwise sections" where the velocity of rotation is constant. To do this, a regime of modulated rotation in which periodic variations in temperature had constant amplitude values was established first. The velocity of rotation was stabilized after it attained a minimum value ($n_{\min}$ = const), and the temperature variation in time was recorded simultaneously. The period $\tau_{\max,2}$ during which the temperature reached a constant value was found from diagrams of the dependence of the temperature on the time at a point of deviation from the exponential dependence (Fig. 6) [5]. The time $\tau_{\max,1}$ during which the velocity of rotation was stabilized at its maximum value was found similarly. The temperature was measured along the vertical axis of the ampoule (r = 0). Experiments were performed at thicknesses of the working liquid layer of H_1 = 40.5 and 19.2 mm.

The character of the dependences of $\tau_{\max,1}$ (for $n_{\max}$ = const) and $\tau_{\max,2}$ (for $n_{\min}$ = const) on the distance to the thermostatically controlled bottom of the ampoule y is similar to those for an ampoule of diameter 29 mm [5]. For the case $n_{\min}$ = const (Fig. 7a), for various values of the height H_1 there is a peak of the maximum value $\tau_{\max,2}$ for some value of y/H_1 = const. For example, $\tau_{\max,2}$ = 145 sec for H_1 = 19.2 mm. y/H_1 = 0.41 and $\tau_{\max,2}$ = 165 sec for H_1 = 40.5 mm and y/H_1 = 0.48. The average value of $\tau_{\max,2}$ is of the same order of magnitude as that for an ampoule of diameter 29 mm: $\tau_{\max,2}$ = 80 sec for H_1 = 40.5 mm and $\tau_{\max,2}$ = 75 sec for H_1 = 19.2 sec [5]. In the case $n_{\max}$ = const (Fig. 7b), the average value of $\tau_{\max,1}$ is 130 sec. which is twice the average value of $\tau_{\max,1}$ for ampoules of diameter 29 mm. This is caused by an increase in the time lag of the system for ampoules of large diameter without a change in the modulation law of their

velocity of rotation. This should be taken into account in selecting and changing the regime of modulated rotation when going from one ampoule diameter to another provided that $Ta_1 = Ta_2$, where Ta is the Taylor number [4]:

$$Ta = (\omega_{max}^2 - \omega_0^2)r^4/\nu^2.$$

Here ω_{max} and ω_0 are the maximum and average angular velocities of rotation of the ampoule, r is the inner radius of the ampoule, and ν is the kinematic viscosity. In model experiments, the value of Ta was varied from $6.3 \cdot 10^6$ (for $r = 1.45$ cm) to $3.7 \cdot 10^7$ (for $r = 2.25$ cm). The optimum values of the duration of rotation of the ampoule with constant minimum and maximum velocities should be smaller than the characteristic time lags of the system: $\tau_1 < \tau_{max,1}$ and $\tau_2 < \tau_{max,2}$.

In concluding, we draw the following conclusions.

(1) The region of the melt that is bounded by the crystallization front and the annular heater for heating the diaphragm (the working volume of the melt) when the point corresponding to T_{melt} is below this heater is decisive in crystal growth by the Stockbarger method. This region is characterized by the presence of intense periodic flows caused by periodic changes in the temperature values that are similar to the changes of the velocity of rotation of the ampoule. As is shown in [5], a decrease in the height of the working volume of the melt increases sharply the amplitudes of the temperature oscillations in the melt at the crystallization front, thus leading to the appearance of thermoelastic stresses in the growing crystal. An increase in the height of this zone leads, as a rule, to the need to warm up the melt strongly. This circumstance also causes large temperature gradients in the melt and the growing crystal, exerting a negative effect on its structural perfection. This imposes restrictions on the height of the working volume of the melt, and hence, on the position of the melting point of the substance being examined relative to the middle heater in growth of single crystals by the Stockbarger method. The optimum height of the working volume of the melt ranges from 10 to 30 mm.

(2) The height of the free volume of the melt (above the heater for heating the diaphragm) has no effect on the hydrodynamic and thermal structure in the working volume of the melt. The periodic temperature oscillations in the melt that are caused by the modulated rotation of the ampoule completely disappear in the free volume of the melt when the mean temperature measured along the vertical axis of the ampoule reaches a stationary value.

(3) For constant maximum and minimum velocities of rotation, the optimum time values of exposure lie in the interval from the time lag τ_3 to the time of temperature stabilization ($\tau_{max,1}$ or $\tau_{max,2}$) after the constant velocity of rotation is reached.

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