

**EFFECT OF THE VELOCITY MODE OF A MODULATIONALLY ROTATING
AMPOULE ON THE THERMAL STRUCTURE OF A MELT
IN GROWING SINGLE CRYSTALS BY THE STOCKBARGER METHOD**

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The effect of the velocity mode of the ACRT on the thermal structure of a melt and the flow rates in it in growing single crystals by the Stockbarger method in ampoules of diameter 100 mm at values of the Taylor number $Ta > 10^8$ is studied. Optimum conditions for mixing of the melt for trapezoidal modes of modulated rotation are found.

Introduction. At present, the accelerated crucible rotation technique (ACRT) [1, 2] is successfully used for growing single crystals of a broad class of compounds by various (Bridgman–Stockbarger, Czochralski, zonal melting, solution–melt, etc.) methods. The principle of accelerated rotation of a growing ampoule consists of the periodic change of the velocity of its rotation according to a certain law. As is shown in [3–6], in growing single crystals by the Bridgman–Stockbarger method, the accelerated rotation of a container with a melt causes periodic temperature oscillations in the melt and the crystallization front and a change in the growth rate of the crystals during each ACRT cycle. These oscillations can stimulate, as is shown for Te-doped InSb crystals [6], the appearance of impurity banding in the crystals. Therefore, the determination of the time dependence of periodic temperature oscillations and their amplitude on the ACRT parameters is one of the basic conditions for optimization of single-crystal growth.

Various laws of change in the velocity of rotation of a container during crystallization have been used by researchers and various designs of velocity-of-rotation regulators (see, e.g., [7]) have been proposed. During the growth of single crystals, both reverse rotation of the container and rotation without changing the direction of motion were used. It was shown that reversion of the direction of rotation is not obligatory to attain a uniform impurity distribution in crystals [8]. For single-crystal growth, various modes of variation in the velocity of rotation were used: sawtooth (with linear [1–3, 8, 9] and nonlinear [10] variations of the velocity of rotation), trapezoidal [1–5, 8], and sinusoidal [8] modes. It was shown that in growing high-quality single crystals, the trapezoidal mode and the sawtooth mode with a linear change of the velocity of rotation are optimum. In both cases, high-quality single crystals were obtained. Although it was found that the constant maximum and minimum velocities (trapezoidal mode) are not necessary for high uniformity of the compound and monocrystallization, it was shown in [3–5] that the presence of velocity “ledges” at constant parameters leads to an increase in the amplitude of temperature oscillations and the rates of axial flows in the melt (i.e., to the amplification of forced convection). In addition, it was shown in [8] that in the sinusoidal mode with a large period of rotation, high-quality single crystals with a uniform distribution of impurities are not grown.

The effect of the velocity modes of rotation of an ampoule on the amplitude of temperature oscillations in model experiments and in the formation of real crystals (with the use of an ampoule of diameter 40 mm)

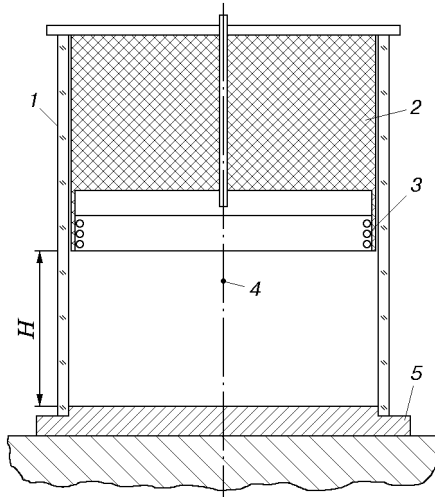


Fig. 1. Layout of the setup: 1) quartz ampoule; 2) cylindrical fluoroplastic diaphragm; 3) heater; 4) central thermocouple; 5) thermostatic base.

was studied most completely by Masalov et al. in [3]. It was shown that keeping of the ampoule at constant maximum and minimum velocities of rotation (in the ACRT cycle) increases the amplitude of temperature oscillations. In their opinion, the trapezoidal mode of variation of the velocity of rotation is a more promising mode compared to the sawtooth mode and modes with only the minimum or maximum velocities of rotation. However, the temperature field which varies periodically along the height of the entire column of a melt was not investigated in [3], and measurements were performed only at the crystallization front. The ACRT modes with different values and relations of the acceleration and deceleration times of the velocity of rotation of the ampoule were not considered as well. The effect of the velocity modes on the flow rates in a melt and the time of stabilization of the temperature field after the beginning of rotation of a growing container at constant velocity (the time of inertia), which determines the optimum time intervals at the maximum and minimum velocities of rotation, were not estimated.

Since knowledge of these parameters is necessary to choose optimum technological conditions for the velocity mode of the ACRT, especially in large-diameter ampoules, in this work, the effect of various velocity modes on the thermal structure of the melt and the flow rates in it in ampoules whose minor diameter is 100 mm was simulated at the following values of the Taylor number:

$$\text{Ta} = (\omega_{\max}^2 - \omega_0^2)r^4/\nu^2 > 10^8.$$

Here ω_{\max} and $\omega_0 = (\omega_{\max} + \omega_{\min})/2$ are the maximum and average angular velocities of rotation of the ampoule, respectively, r is the internal radius of the ampoule, and ν is the kinematic viscosity. As a model liquid, 96% ethanol was used (Prandtl number $9.7 < \text{Pr} < 10.8$).

Experimental Technique. The thermal structure in the ampoule was studied on a setup which makes it possible to change the sawtooth law of variation of the angular velocity of the ampoule with time to a trapezoidal one for any relation of the intensities of increase and decrease in the angular velocity and time intervals for constant minimum and maximum angular velocities.

In model experiments, a cylindrical optical-quartz ampoule (Fig. 1) and with a minor diameter of 100 mm was placed coaxially with the vertical axis of rotation. To obtain the temperature field in the model liquid, a cylindrical fluoroplastic diaphragm with a heater of height 10 mm (its resistance was 22 Ω) produced in the form of a bifilar coil from a wire of diameter 0.2 mm was placed in the ampoule. The upper coil of the heater was 10 mm below the level of the free surface of the liquid. The heat exchanger of this design did not introduce additional hydrodynamic perturbations as the velocity of rotation of the ampoule was changed. The temperature of the liquid was measured by a central Nichrome–Constantan thermocouple (wire diameter 50 μm) built in the diaphragm and located in the orifice of the fluoroplastic cylinder. The cold junction of the

thermocouple was located on the thermostatic copper base of the quartz ampoule located on a rotating table. The flat base of the ampoule was cooled (controlled thermostatically) by water supplied by means of sliding water lines from a UT-4 thermostat to the rotating table and then to the ampoule bottom through a system of channels cut inside it. The temperature was reckoned from the temperature of the cooled surface simulating the flat crystallization front ($y = 0$). In experiments, the difference between the temperatures of the liquid and the cooled bottom of the quartz ampoule was measured: $\Delta T = T_l - T_b$. The error of temperature measurement in the experiments was $\pm 0.05^\circ\text{C}$. The heater power was 10.2 W, and the temperature of the substrate was 24.5°C .

In modeling the thermal structure of the melt in growing crystals by the Stockbarger method, the annular heater in the model ampoule (like the annular heater of the diaphragm in the growing furnace) creates a temperature drop between the heater and the thermostatic base of the ampoule. The function of the base simulating a flat crystallization front is similar to the function of the lower heater of a growing furnace.

The thermocouple coordinates were measured by a V-630 catetometer. The constant component of the e.m.f. of the thermocouple was compensated for and was measured by a small-sized potentiometer calibrated by an R3003 comparator with an error of $0.5 \mu\text{V}$. The noncompensated component of the e.m.f. (with the comparator switched off) was amplified by a dc amplifier with a smoothly controlled amplification factor. To weaken the noise, after the dc amplifier, the signal was passed through a low-frequency filter with a cut-off frequency of 1.5 Hz. The dc amplifier had low noise and a “zero” drift of $1 \mu\text{V/h}$. The measuring complex is described in detail in [4]. The instantaneous values of the thermocouple e.m.f. were measured synchronously in the same time scale with recording of the variation in the number of revolutions of the ampoule rotating about the vertical axes by means of an N-3030-3 three-channel automatic potentiometer. The record of the number of revolutions was transmitted at an automatic recorder from a ТЭ30-5P electronic tachometer.

In all the experiments, the maximum and minimum velocities of rotation of the ampoule remained constant and constituted 60 and 20 rpm, respectively. The velocity of rotation was changed by a regulator allowing one to specify the law of its control in a broad interval of time parameters. Four velocity modes with different values of the acceleration time τ_a and the deceleration time τ_d were used in the experiments: for the symmetric-sawtooth mode with a linear change of the velocity of rotation, $\tau_a = \tau_d = 7 \text{ sec}$ (Fig. 2a), for the symmetric-sawtooth mode with a linear change of the velocity of rotation, $\tau_a = \tau_d = 20 \text{ sec}$ (Fig. 3a), for the asymmetric-trapezoidal mode, $\tau_a = 7 \text{ sec}$, $\tau_d = 20 \text{ sec}$, and $\tau_{\max} = \tau_{\min} = 10 \text{ sec}$ (Fig. 4a), and for the symmetric-trapezoidal mode, $\tau_a = \tau_d = 20 \text{ sec}$ and $\tau_{\max} = \tau_{\min} = 10 \text{ sec}$ (Fig. 5a). The asymmetric-trapezoidal mode of rotation was selected only for $\tau_a < \tau_d$, since upon abrupt deceleration of the container with a liquid in it, a roller structure of Taylor rings appears and stratification occurs [11–13].

Results and Discussion. The intensity of mixing of a melt is determined by the value of the Taylor number, which is $1.8 \cdot 10^8$ in these experiments. Periodic flows occur upon modulated rotation of the ampoule in the neighborhood of its thermostatic flat bottom [4]: as the number of revolutions decreases, a vortex flow directed along the radius to the center and upward along the ampoule’s rotation axis occurs as the number of revolutions increases, a flow near the surface of the crystallization front along the radius to the cylinder generatrix and a descending flow along the ampoule’s axis are observed. The nature of these flows is as follows. As the number of revolutions decreases, the liquid core in the ampoule has a larger angular velocity than the substrate. As a result, the flows similar to those near the immobile disk upon rotation of the liquid with constant angular velocity occur: the decelerated liquid particles have a smaller centrifugal force because of deceleration and move along the radius to the ampoule’s axis.

With increase in the number of revolutions, the angular velocity of the substrate becomes greater than that of the liquid in the core. In this case, a flow near the growing face of the crystal, which is similar to the flow upon rotation of a disk in a quiescent liquid is observed: the liquid involved in rotation is ejected outside in a thin boundary layer at the surface owing to centrifugal forces and causes a descending flow along the axis of the ampoule.

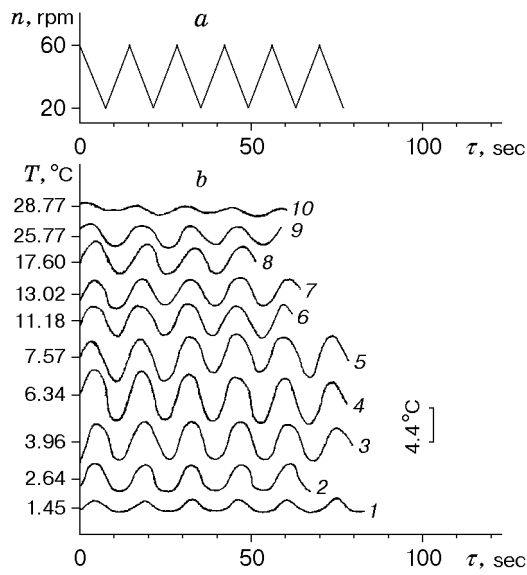


Fig. 2

Fig. 2. The law of modulated rotation of the ampoule ($n_{\max} = 60$ rpm and $n_{\min} = 20$ rpm) (a) and the dependence of the instantaneous temperature values along the ampoule's axis (b) for the symmetric-sawtooth mode with a linear change of the velocity of rotation of the ampoule ($\tau_a = \tau_d = 7$ sec and $H = 37.1$ mm): curves 1–10 refer to $y = 1.12, 2.63, 4.18, 5.43, 8.21, 11.45, 15.48, 21.68, 29.92,$ and 34.47 mm, respectively.

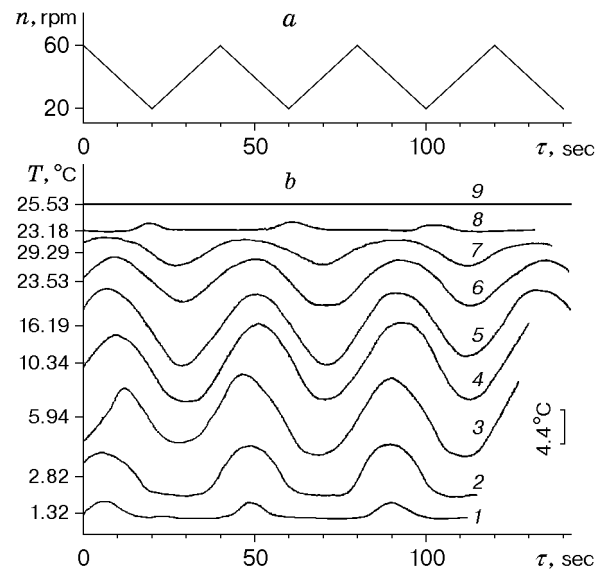


Fig. 3

Fig. 3. The law of modulated rotation of the ampoule ($n_{\max} = 60$ rpm and $n_{\min} = 20$ rpm) (a) and the dependence of the instantaneous temperature values along the ampoule's axis (b) for the symmetric-sawtooth mode with a linear change of the velocity of rotation of the ampoule ($\tau_a = \tau_d = 20$ sec and $H = 37.1$ mm): curves 1–9 refer to $y = 1.24, 5.66, 11.43, 15.76, 21.61, 29.49, 34.44, 38.78,$ and 49.43 mm, respectively.

With variation of τ_a and τ_d without changing ω_{\max} and ω_{\min} , the general flow pattern in the melt remains the same. Only the period of change of the flow direction and the dimension of the ascending vortex change.

Figures 2–5 show the time dependences of temperature (over the height of the liquid layer) for different laws of variation in the velocity of rotation of a vertical ampoule for a constant thickness of the liquid layer ($H = 37.1$ mm). The heater power was constant in all the experiments. In addition, these figures show the laws of change in the velocity of rotation of the cylindrical ampoule and the values of the maximum and minimum angular velocities. One can see that the character of the curves is similar to the law of change in the velocity of rotation. The amplitude of temperature oscillations caused by modulated rotation decreases with distance from the annular heater upward (see Figs. 3 and 4). In accordance with the data obtained earlier for ampoules of diameter 44.5 mm upon modulated rotation according to the symmetric-trapezoidal law [5], the temperature oscillations disappear at a height corresponding to the coordinate where the mean temperature reaches a stationary value. For the symmetric-sawtooth mode ($\tau_a = \tau_d = 20$ sec), a complete degeneration of temperature oscillations was observed at the height 12.4 mm from the upper cut of the annular heater. For the asymmetric-trapezoidal mode ($\tau_a = 7$ sec and $\tau_d = 20$ sec), the temperature oscillations degenerated only at a height of 19.76 mm from the heater. Therefore, for this mode, the height of propagation of the ascending flow increases.

Figure 6 shows the change in the amplitude of temperature oscillations ($\delta T = T_{\max} - T_{\min}$) over the height of the liquid layer for different modes of variation of the velocity of rotation. One can see that the maximum temperature oscillations are observed in the symmetric-trapezoidal mode (curve 4), and the minimum ones are observed for the symmetric-sawtooth mode with a period of 14 sec (curve 1). With increase

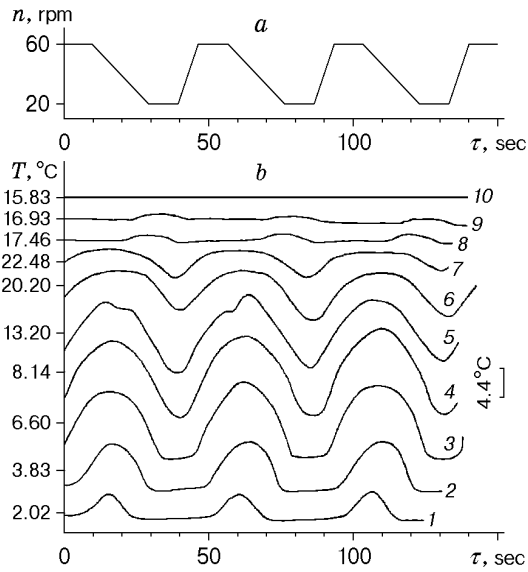


Fig. 4

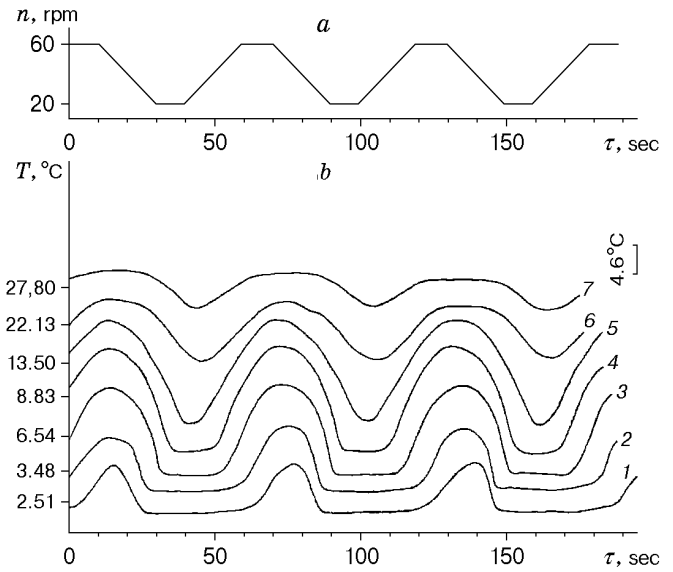


Fig. 5

Fig. 4. The law of modulated rotation of the ampoule ($n_{\max} = 60$ rpm and $n_{\min} = 20$ rpm) (a) and the time dependence of the instantaneous temperature values along the ampoule's axis (b) for the asymmetric-trapezoidal mode of rotation with a linear change of the velocity of rotation of the ampoule ($\tau_a = 7$ sec, $\tau_d = 20$ sec, $\tau_{\max} = \tau_{\min} = 10$ sec, and $H = 37.1$ mm): curves 10 refer to $y = 1.26, 6.04, 11.76, 15.13, 21.65, 29.46, 34.49, 38.81, 49.50,$ and 56.86 mm, respectively.

Fig. 5. The law of modulated rotation of the ampoule ($n_{\max} = 60$ rpm and $n_{\min} = 20$ rpm) (a) and the time dependence of the instantaneous temperature values along the ampoule's axis (b) for the symmetric-trapezoidal mode of rotation with a linear change of the velocity of rotation of the ampoule ($\tau_a = \tau_d = 20$ sec, $\tau_{\max} = \tau_{\min} = 10$ sec, and $H = 37.1$ mm): curves 1–7 refer to $y = 1.52, 5.31, 11.74, 14.90, 20.84, 30.04,$ and 34.44 mm, respectively.

in the period of the symmetric-sawtooth mode to 40 sec, the amplitude of temperature oscillations increases abruptly (curve 2). For the asymmetric-trapezoidal mode (curve 3), the oscillation amplitude is greater than for symmetric-sawtooth modes but smaller than for the symmetric-trapezoidal mode. (The points in Figs. 6–8 correspond to experimental data.)

As is shown in [4, 5], the distance from the crystallization front on which the maximum amplitude of temperature oscillations is observed correlates with the height of the axial vortex. The maximum amplitude of temperature oscillations for the symmetric-sawtooth mode with a period of 14 sec ($\tau_a = \tau_d = 7$ sec) is observed for smaller distances from the crystallization front compared to other modes, since, for the given small times of deceleration of the ampoule, the ascending axial vortex has no time to be formed completely. It is clear that this velocity mode does not ensure sufficient mixing of the melt. It follows from Fig. 6 that the symmetric-trapezoidal mode of change in the velocity of rotation is optimum from the viewpoint of mixing of the melt.

The maximum values of the axial velocity of the ascending and descending flows were estimated under the assumption that the temperature variation caused by heat conduction is much smaller than that caused by convection (the technique is described in [4]). Figure 7 shows curves of the velocities of the descending and ascending flows for different modes of change of the velocity of rotation of the growing container. The smallest values of the velocities of the ascending and descending flows and the smallest amplitudes of temperature oscillations are observed for symmetric-sawtooth modes (curves 1 and 2). The largest maximum velocities of the ascending and descending flows are realized in the symmetric-trapezoidal mode (curves 4). Somewhat smaller values of the maximum velocity of the ascending and descending flows are observed for the asymmetric-trapezoidal mode (curves 3). Therefore, studying the values of the flow rates in the model liquid (Fig. 7) has

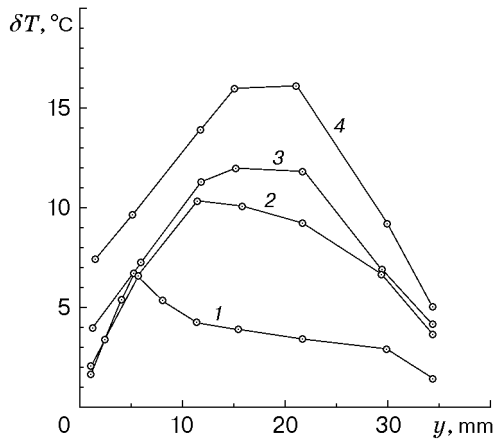


Fig. 6

Fig. 6. Variation in the amplitude of temperature oscillations over the height of the layer of a model liquid for different modes of modulation of the velocity of rotation of the ampoule ($H = 37.1$ mm): 1) symmetric-sawtooth mode for $\tau_a = \tau_d = 7$ sec; 2) symmetric-sawtooth mode for $\tau_a = \tau_d = 20$ sec; 3) asymmetric-trapezoidal mode for $\tau_a = 7$ sec, $\tau_d = 20$ sec, and $\tau_{\max} = \tau_{\min} = 10$ sec; 4) symmetric-trapezoidal mode for $\tau_a = \tau_d = 20$ sec and $\tau_{\max} = \tau_{\min} = 10$ sec.

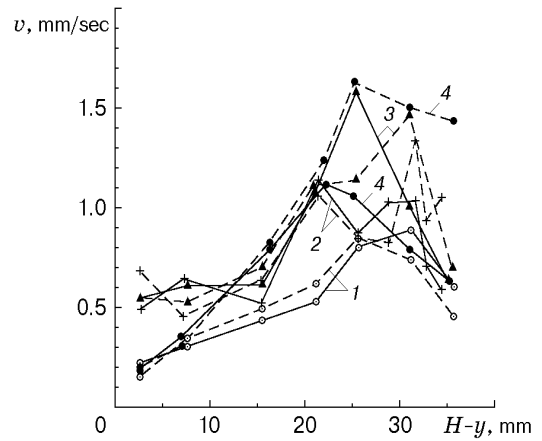


Fig. 7

Fig. 7. Distribution of the maximum velocities of the descending (solid curves) and ascending (dashed curves) flows over the height of the layer on the ampoule's axis ($H = 37.1$ mm) for different velocity modes of modulated rotation of the ampoule: 1) symmetric-sawtooth mode for $\tau_a = \tau_d = 20$ sec; 2) symmetric-tooth mode for $\tau_a = \tau_d = 7$ sec; 3) asymmetric-trapezoidal mode for $\tau_a = 7$ sec, $\tau_d = 20$ sec, and $\tau_{\max} = \tau_{\min} = 10$ sec; 4) symmetric-trapezoidal for $\tau_a = \tau_d = 10$ sec and $\tau_{\max} = \tau_{\min} = 10$ sec.

shown that the symmetric-trapezoidal mode with a linear change of the velocity of rotation (see Fig. 5a) is also an optimum mode for mixing of a melt.

We used successfully a symmetric-trapezoidal mode of rotation similar to the model mode with the same time parameters in growing Ag_3AsS_3 [4] and PbBr_2 [14] single crystals of high optical quality from a melt by the Stockbarger method.

To determine the optimum time intervals at constant maximum and minimum velocities of rotation of the symmetric-trapezoidal mode of modulation of the velocity of rotation for $n_{\max} = 60$ rpm and $n_{\min} = 20$ rpm and the layer height $H = 37.1$ mm, the time lag of the system and the time of damping of rotational flows in the melt after reaching constant maximum and minimum velocities of rotation were studied. The results of these studies allow one to choose the optimum time of existence of these "ledges," where the velocity of rotation is constant. For this purpose, a symmetric-trapezoidal mode of modulated rotation in which the temperature was varied periodically with a constant amplitude was primarily reached. After reaching a constant value, the velocity of rotation was stabilized ($n_{\min} = \text{const}$ or $n_{\max} = \text{const}$) and the temperature variation with time was recorded simultaneously. The time for which the temperature reached a constant value was found from the time dependence of the temperature at the point where a deviation from the exponential dependence [5] was observed. The time $\tau_{\max 1}$ of stabilization of the velocity of rotation at its maximum value and the time $\tau_{\max 2}$ of stabilization of the velocity of rotation at its minimum value were determined. The dependences $\tau_{\max 1}(y)$ and $\tau_{\max 2}(y)$ are depicted in Fig. 8. The optimum values of the durations of rotation of the ampoule with a constant (maximum and minimum) velocity should be smaller than the characteristic time lags of the system: $\tau_1 < \tau_{\max 1}$ and $\tau_2 < \tau_{\max 2}$.

Conclusions. It has been found on the basis of studies dealing with the intensity of convective flows (the maximum flow rates) and the maximum amplitudes of temperature oscillations (caused by modulated rotation) in growing single crystals by the Stockbarger method with the use of ACRT that the symmetric-trapezoidal mode of rotation of a growing ampoule is optimum.

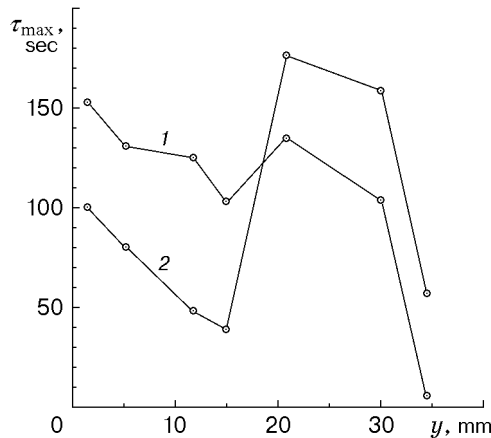


Fig. 8. Times of temperature stabilization: curves 1 and 2 refer to $\tau_{\max 1}$ ($n_{\max} = 60$ rpm) and $\tau_{\max 2}$ ($n_{\min} = 20$ rpm), respectively.

The small times of acceleration and deceleration of the velocity of rotation of the ampoule (as in the absence of a time interval at constant maximum and minimum velocities of rotation) in the symmetric-sawtooth mode hinder the formation of an intense eddy flow, since these times are much smaller than the time of stabilization of the temperature field after reaching a constant velocity of rotation.

For constant maximum and minimum velocities of rotation of the growing ampoule and the heater power, changing only the parameters of the law of modulation of the velocity of rotation, one can realize various temperature conditions in a melt or keep them constant during crystallization.

The optimum values of the time intervals at constant n_{\max} and n_{\min} lie in the intervals $\tau_{\text{lag}} < \tau < \tau_{\max 1}$ and $\tau_{\text{lag}} < \tau < \tau_{\max 2}$, respectively (τ_{lag} is the time lag [5]).

The periodic temperature oscillations in the melt caused by modulated rotation of the ampoule according to the symmetric-sawtooth and asymmetric-trapezoidal laws disappear in the free volume of the melt above the annular heater-diaphragm, similarly to that shown in [5] for the symmetric-trapezoidal law. In the symmetric-trapezoidal mode of change of the velocity of rotation of the ampoule, the vortex flow at the crystallization front exerts an effect at a larger distance in the free volume of a melt than in the symmetric-sawtooth mode.

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