

DISTRIBUTION OF TEMPERATURE IN SEMI-TRANSPARENT SINGLE CRYSTALS DURING THE PROCESS OF THE CZOCHRALSKI PULLING. I. THERMAL EMISSION OF SEMI-TRANSPARENT MEDIA

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Temperature distribution in a single crystal during the process of the Czochralski pulling is determined by the product of the Bessel function of the first kind and zero order (in the radial direction) and a hyperbolic function \sinh or \cosh (in the axial direction). Semi-transparent single crystals emit thermal energy from the entire volume. The value of heat lost in such a way is evaluated by a mending boundary condition at the crystals side surface. The authors have taken into account the radiation of a point at the crystal directed to the interior of the crystal, which passes through the solid and out the other side.

1. Statement of the problem

The determination of temperature distribution in a crystal during the process of pulling means, theoretically, calculating the thermal field of a limited cylinder subjected to some given boundary conditions and some simplifying assumptions. The general formula at the beginning is the so called equation of heat conduction, which for a cylindrical set of coordinates is:

$$\kappa \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) + \left(\frac{\partial \kappa}{\partial r} \frac{\partial T}{\partial r} + \frac{\partial \kappa}{\partial z} \frac{\partial T}{\partial z} \right) = \rho c \frac{\partial T}{\partial t} \quad (1)$$

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This form can be solved, however, only for a very few specific cases, mainly because of lack of information concerning the temperature dependence of the conductivity coefficients, and because of boundary conditions, that may be sometimes very complex. For most cases, the authors used some simplifying assumptions, e.g. considering the medium isotropic or the generally accepted assumption that the thermal conductivity coefficient is constant, $\kappa(T) = \text{const}$. In equation (1) we used following notation: T — temperature, κ — coefficient of thermal conductivity, ρ — density, c — specific thermal capacity, r — radial coordinate, z — axial coordinate.

The above problem for a boundary in the shape of a semi-infinite cylinder ($h \gg R$) and disc ($h \ll R$), where R is radius of a cylinder, and h its height, has been already solved [1-5]. The problem of temperature distribution in a finite isotropic cylinder has been studied prior to World War II by Nancarrow [6, 7] (this was the subject of his doctoral dissertation). The results of Nancarrow were used by Billing [8] and others.

When a crystal grows, heat transfer occurs in different directions Fig. 1. According to Brice [9] we distinguish the following thermal fluxes: 1 — flow of energy from the heat source heater to the crucible; 2 — loss of energy from the external walls of the crucible

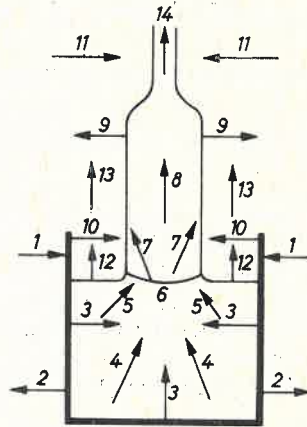


Fig. 1. Heat transport in the process of pulling of single crystals by the Czochralski technique explanation in the text

to the insulating material by means of conduction or radiation; 3 — heating up of a ingot which receives heat from the crucible; 4 — heat transfer in the melt by convection and conduction; 5 — heat transfer through the liquid — solid interface; 6 — liberation of latent heat of solidification at the melt — crystal interface; 7 — draining of energy from the phase boundary; 8 — thermal conductivity of the crystal; 9 — radiation of energy by the side surface; 10 — radiational heating up of walls of the crucible; 11 — thermal flux emitted by the afterheater; 12 — emission from the surface of the liquid phase; 13 — convection through the protective atmosphere; 14 — heat offtake through the seed handle.

In these calculations for the reason of simplicity only half of the processes mentioned is taken into account, namely the fluxes 5-9 and 11, 14. The remaining processes will be included as experimental amendments.

2. Simplifying assumptions

Let us assume as a result of some idealization the following simplifying assumptions:

(a) the crystal considered is in the form of a cylinder characterized by a constant diameter throughout its length. We neglect the influence of a cone created during widening of the crystal. The calculations are performed using cylindrical coordinates, as shown in Fig. 2;

(b) the case is orthotropic, i.e. the properties of the material in the direction parallel to the axis of a boule differ from the properties in the direction perpendicular to the axis of a boule, and the physical properties in direction perpendicular to the axis of the boule show

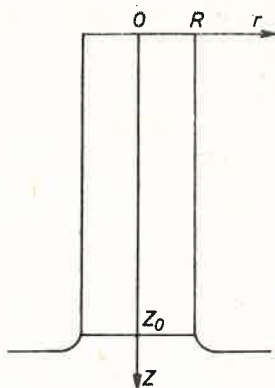


Fig. 2. Set of coordinates used for calculation of temperature distribution in a crystal

isotropy (cross isotropy or orthotropy). The results of computation may be thus applied both to isotropic media (silicon, germanium, perovskite, noble spinel, yttrium-aluminum garnet) pulling in the direction of any given axis of the elementary cell, and to single-axis crystals grown parallel to the anisotropic direction (leukosapphire, lithium niobate, lithium tantalate, sheelite, rutile oriented in the direction of axis "c");

(c) the melt-solid interface is flat. In practice, however, we generally encounter the isotherm of solidification is convex in the direction of the liquid phase. This convexity can be reduced by minimalizing heat transfer through a side surface of a crystal, e.g. by application of radiation shields or scorching the crystal. For large diameter samples the front of crystallization will be flat over a considerable area;

(d) the temperature distribution in a crystal is quasi-stationary. This assumption is in fact a substantial one and thus it should be discussed in detail, as follows.

3. Static and dynamic fluxes of heat

During the growth process both ends of the crystal are held at constant temperatures: the lower end submerged in melt — at temperature T_i , equal to the melting point of the material; the higher one, placed in a holder — at the temperature T_0 , where T_0 is the

temperature of environment of the crystal. The mean heat flux in a crystal resulting from this temperature difference is:

$$Q_s = \frac{\kappa}{l} (T_t - T_0). \quad (2)$$

Here notation is as follows: Q_s — static heat flux; l — crystal length.

This occurs even when a crystal does not grow, e.g. after seeding and before starting the pulling mechanism. Q_s depends on the crystal length and decreases with the increase in length. Let us call it a static flux.

When the pulling mechanism is started the crystal increases in size; the solid phase ought to conduct the heat of solidification liberated in the process. It is "dynamic" heat flux, Q_d .

Dynamic flux of energy is added to the former one static flux. It depends on the rate of growth of crystal mass only and is:

$$Q_d = \pi R^2 v Q L, \quad (3)$$

where v — rate crystal growth, L — latent heat of solidification.

All in all, the heat carried away by the crystal from the front of crystallization is equal to the sum of static flux Q_s and Q_d :

$$Q = Q_s + Q_d, \quad (4)$$

Q is the total heat flux.

The time variation of this flux reads:

$$\Delta Q = \frac{\partial Q}{\partial l} \frac{\partial l}{\partial t} \Delta t = - \frac{\kappa v}{l^2} (T_t - T_0). \quad (5)$$

Since oxide crystals are pulling relatively slowly, ΔQ forms a small part of Q only; e.g. for LiNbO_3 grown at the rate of 6 mm/h ($1.7 \cdot 10^{-4}$ cm/sec) the ratio $\Delta Q/Q$ equals 0.17% for $l = 1$ cm; 0.04% for $l = 2$ cm; 0.02% for $l = 3$ cm; and 0.01% for $l = 4$ cm. The heat flux thus varies significantly only within a small range. So one can assume that the crystal grows under quasi-stationary conditions.

4. Solution of the equation of heat conduction

The starting point is the equation of heat conduction which in cylindrical coordinates can be written as follows:

$$\kappa_r \left[\frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{r} \frac{\partial^2 T}{\partial \varphi^2} \right] + \kappa_z \frac{\partial^2 T}{\partial z^2} = \rho c \frac{\partial T}{\partial t}, \quad (6)$$

where κ_r — coefficient of thermal conductivity in radial direction, κ_k — coefficient of thermal conductivity in axial direction.

Since the problem is quasistationary, the time derivative vanishes. We separate the variables twice in a homogeneous equation, assuming that

$$T(r, \varphi, z) = P(r)\Phi(\varphi)Z(z). \quad (7)$$

We obtain the following set of equations

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dP}{dr} \right) + \frac{1}{\kappa_r} \left(\beta^2 - \frac{v^2}{r^2} \right) P = 0, \quad (8)$$

$$\frac{d^2\Phi}{d\varphi^2} + \frac{v^2}{\kappa_r} \Phi = 0, \quad (9)$$

$$\frac{d^2Z}{dz^2} - \frac{\beta^2}{\kappa_z} Z = 0. \quad (10)$$

The solution of the second equation is

$$\Phi = Ae^{iv\varphi} + Be^{-iv\varphi}. \quad (11)$$

Due to the axial symmetry of the problem

$$\Phi = 1 \quad \text{and} \quad A = B = \frac{1}{2}; \quad v = 0. \quad (12)$$

The solutions of the (8) and (10) are

$$P(r) = \sum_{n=1}^{\infty} A_n J_0(\beta_n r / \sqrt{\kappa_r}), \quad (13)$$

$$Z(z) = T(0, z) - T_0 = C \exp\left(\frac{\beta_z z}{\sqrt{\kappa_z}}\right) + D \exp\left(-\frac{\beta_z z}{\sqrt{\kappa_z}}\right). \quad (14)$$

So the temperature distribution is

$$T(r, z) = T_0 + (T_t - T_0) \sum_{n=1}^{\infty} A_n J_0(\beta_n r / \sqrt{\kappa_r}) \left[C_n \exp\left(\frac{\beta_n z}{\sqrt{\kappa_z}}\right) + D_n \exp\left(-\frac{\beta_n z}{\sqrt{\kappa_z}}\right) \right]. \quad (15)$$

The solution should be assumed to be the form of a series of the Bessel functions, since a single Bessel function does not fulfill the boundary condition $T(r, z) = T_t$. The boundary conditions for $T(0, 0)$ and $T(0, z_0)$ yield

$$T(0, 0) = T_0, \quad T(0, z_0) = T_t, \quad (16)$$

i.e.

$$C_n = -D_n = \frac{T_t - T_0}{2 \operatorname{sh}(\beta_n z_0 / \sqrt{\kappa_z})}. \quad (17)$$

5. Determination of the constants β_n and A_n

The further procedure involves determination of constants β_n and A_n . The procedure used here differs from that of other authors. Two approaches are possible:

- (a) an analytic solution of the problem, which requires the transformation of boundary condition at the cylinder side surface to linear form;
- (b) solution by numerical methods.

In the first case, the constant β_n is determined from the boundary condition for the side surface of a crystal

$$-\kappa_r \left(\frac{\partial T}{\partial r} \right)_R = \frac{\delta}{2} (\varepsilon_1 T_R^4 - \varepsilon_2 T_0^4), \quad (18)$$

where σ — Stefan-Boltzmann constant, ε_1 — emissivity of a crystal, ε_2 — emissivity of environment radiation shields or afterheater, T_R — temperature of side surface of crystal. The right hand side of this formula may be written as follows:

$$\frac{\sigma H}{2} T_{av}^3 (T_R - T_0), \quad (19)$$

where

$$T_{av} = \frac{1}{2} (T_i + T_0), \quad (20)$$

and H — average emissivity of crystal.

The formulae (15), (17), and (18) yield

$$\sum_{n=1}^{\infty} A_n \frac{\text{sh}(\beta_n z / \sqrt{\kappa_z})}{\text{sh}(\beta_n z_0 / \sqrt{\kappa_z})} \left\{ -\sqrt{\kappa_r} \beta_n J_1(\beta_n R / \sqrt{\kappa_r}) + \frac{\sigma H}{2} T_{av}^3 J_0(\beta_n R / \sqrt{\kappa_r}) \right\} = 0, \quad (21)$$

from where

$$\sqrt{\kappa_r} \beta_n J_1(\beta_n R / \sqrt{\kappa_r}) = \frac{\sigma H}{2} T_{av}^3 J_0(\beta_n R / \sqrt{\kappa_r}). \quad (22)$$

Here A_n and β_n are constants. Making the simplifying substitutions

$$\beta_n R / \sqrt{\kappa_r} = \kappa, \quad \frac{\sigma H}{2} R T_{av}^3 = a, \quad (23)$$

we can rewrite (22) in the form

$$x J_1(x) = a J_0(x), \quad (24)$$

The functions $x J_1(x)$ and $a J_0(x)$ in terms of x are presented in Fig. 3. From the point of intersections of the curves we read x , and from (23) — the corresponding values of β_n . This method has been presented by Nancarrow [7].

Then the constants A_n are determined. We utilize the properties of the Lommel integrals [10]. There are two kinds of these integrals that are suitably modified in some specific cases. If α and β are two different roots of the equation

$$\alpha J_n(\alpha R) + a J_n(\alpha R) = 0,$$

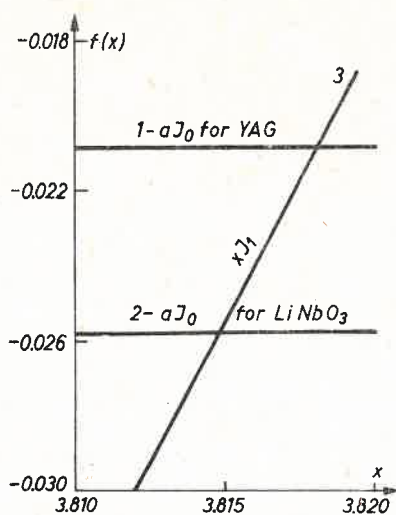


Fig. 3. Plots of functions $xJ_1(x)$ and $aJ_0(x)$ in the vicinity of zero points of the equation $xJ_1(x) = aJ_0(x)$

the Lommel integral of type

$$L_2 = \int_0^R [J_n(\alpha r)]^2 r dr,$$

will read after integration

$$\frac{1}{2\alpha^2} \{R^2 a^2 + (R^2 \alpha^2 - n^2) [J_n(\alpha R)]^2\}. \quad (25)$$

For $z = z_0$ we obtain from* (17)

$$\sum_{n=1}^{\infty} A_n J_0(\beta_n r / \sqrt{\kappa_r}) = 1.$$

By multiplication of both sides of the above formula by $r \cdot J_0(\beta_m r / \sqrt{\kappa_r})$ and by integration in the interval from 0 to R we obtain:

$$\sum_{n=1}^{\infty} A_n \int_0^R J_0(\beta_n r / \sqrt{\kappa_r}) J_0(\beta_m r / \sqrt{\kappa_r}) dr = \int_0^R r J_0(\beta_m r / \sqrt{\kappa_r}) dr.$$

The right hand side of the above formula equals

$$\frac{\sqrt{\kappa_r}}{\beta_m} R J_1(\beta_m R / \sqrt{\kappa_r}). \quad (26)$$

The left hand side is determined from Lommel's integral due to necessity of meeting the boundary condition (18). Thus for n differing from m the left hand side vanishes and for $n = m$ one obtains

$$A_m \frac{R^2}{2} \left(\frac{\kappa_r a^2}{\beta_m^2} + 1 \right) [J_0(\beta_m R / \sqrt{\kappa_r})]^2. \quad (27)$$

From (26) and (27) we have

$$A_n = \frac{2\beta_n}{R \sqrt{\kappa_r}} \frac{1}{a^2 + \beta_n^2 / \kappa_r} \frac{J_1(\beta_n R / \sqrt{\kappa_r})}{[J_0(\beta_n R / \sqrt{\kappa_r})]}. \quad (28)$$

6. Thermal emission of semi-transparent media

Semi-transparent materials emit thermal energy from the entire volume. Due to small coefficients of absorption of oxides and their high melting points a part of this emission goes outside and is lost from the crystal. The problem of thermal radiation of semi-transparent media have been studied by Pigalskaja [11], O'Hara with coworkers [12] and Troitsky [13].

This phenomenon is usually accounted in the form of amendment at the right hand side of boundary condition (18). Two approaches to the solution of this problem are possible:

(a) determination of the total energy radiated by the point D at the crystal surface. This energy originates from the thermal radiation of internal volume elements;

(b) determination of the energy emitted by the point D at the crystal surface to its interior and through to the environment.

The approach given in b is mathematically simpler. If a surface element $D(R, 0, z)$ emits heat in the direction of surface element $B(R, \varphi, z')$ placed also at the side surface of cylinder (and through B — to environment), the crystal absorbs energy

$$dW' = \frac{\sigma H}{2} T_{av}^3 (T_R - T_0) (1 - e^{-\mu d}) d\omega, \quad (29)$$

where μ — coefficient of light absorption, d — path of light ray travel in the crystal, W' — energy absorbed by the crystal, ω — solid angle.

The remainder, i.e.

$$dW = \frac{\sigma H}{2} T_{av}^3 (T_R - T_0) e^{-\mu d} d\omega, \quad (30)$$

will be lost. By integration of this quantity over the entire side surface of cylinder we get

$$W = \frac{\sigma H}{2} T_{av}^3 (T_R - T_0) \int \frac{e^{-\mu d}}{d^2} R d\varphi dz'. \quad (31)$$

W means here energy radiated from the crystal volume, z' — axial coordinate being the variable for integration, and φ — azimuth coordinate. Some geometrical consideration Fig. 4 yield

$$d = \sqrt{4R^2 \sin^2 \varphi/2 + (z' - z)^2} \quad (32)$$

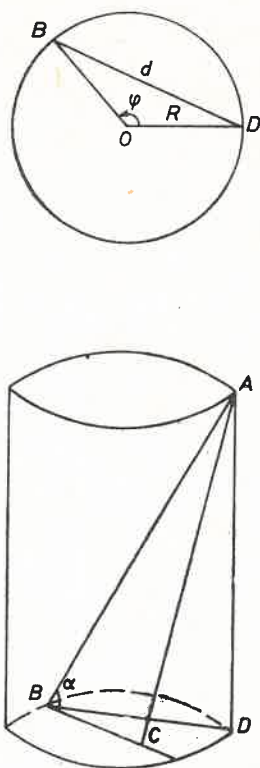


Fig. 4. Geometrical sketch for determination of volumetric emission of heat energy in the crystal

After expressing of $e^{-\mu d}$ as a series we obtain integrals

$$I_1 = \int \frac{d\varphi dz'}{d^2}, \quad (33)$$

$$I_2 = \mu \int \frac{d\varphi dz'}{d}, \quad (34)$$

$$I_3 = \frac{\mu^2}{2} \int d\varphi dz'. \quad (35)$$

Not all of these integrals can be determined analytically. In order to evaluate their numerical value one has to determine the average values of crystal absorption. In connection with this let us consider the limits of integration. We known from geometrical

optics that with the angle of incidence α being such that $\sin \alpha \geq 1/n$, a total internal reflection occurs. We have thus to take into account only the rays falling on the crystal surface at angles less than the one mentioned. The rays, for which $\sin \alpha \leq 1/n$, form at the crystal surface a curve described by the formula

$$\sin^2 \alpha = \frac{R^2 \sin^2 \varphi + (z' - z)^2}{2R^2(1 - \cos \varphi) + (z' - z)^2} = \frac{1}{h^2}. \quad (36)$$

The maximum value of h occurs for $\varphi = \pi$ and reads

$$h = |z' - z| = \frac{2R}{n^2 - 1}. \quad (37)$$

In turn for $h = 0$

$$\cos \varphi = \frac{1}{n}. \quad (38)$$

Then we determine the average solid angle

$$dW_{av} = \frac{\Delta \arccos \frac{1}{n}}{2\pi} 2Rh \frac{1}{4R^2} = \frac{\Delta \arccos \frac{1}{n}}{4\pi} \frac{h}{R}, \quad (39)$$

and the average value of d

$$d_{av} = 2R. \quad (40)$$

We obtain

$$W = \frac{\sigma H}{2} T_{av}^3 (T_R - T_0) \frac{\Delta \arccos \frac{1}{n}}{4\pi} \frac{h}{R} \exp(-2\mu R). \quad (41)$$

So the constant a from (23) equals

$$a = \frac{\sigma H}{2\kappa_r} T_{av}^3 \left[1 + \frac{\Delta \arccos \frac{1}{n}}{4\pi} \frac{h}{R} \exp(-2\mu R) \right]. \quad (42)$$

This value should be used for calculations of semi-transparent single crystals. Some detailed numerical calculations show that the thermal field is subjected to considerable changes due to volumetric radiation of energy by the solid phase [14].

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