# STABILITY OF A CRYSTAL SURFACE IN FRACTIONAL CRYSTALLIZATION ON A BAND

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*The problem on the morphological and thermal stability of a crystal surface in fractional crystallization on a band has been investigated theoretically. A model to describe the dynamics of the development of a striped perturbation of the crystal surface is suggested. It is used as a basis for analyzing the influence of the main factors on the stability, and a stability criterion has been derived. It has been established theoretically that the thermal instability must appear at small Reynolds numbers (Re < 10). Numerical experiments have shown that an increase in the length of the band, its inclination angle, as well as a decrease in the rate of melt feed and in the band motion velocity increase the thermal instability.*

*Keywords: fractional crystallization, band crystallizer, constitutional supercooling.*

**Introduction.** Crystallization on mobile cooled surfaces can be used for fine purification of organic and inorganic substances. Precisely for this purpose German scientists [1–3] have suggested to use a countercurrent scheme of purification on a cooled band (Fig. 1). A melt is supplied to the upper (outer) side of an inclined band and then it runs down the band to a lower tank, from which it is fed again into the circulation loop. In zones 1, 2, and 3 the inner surface of the band is cooled by water at three different temperatures. Due to the cooling of the band, in zone No. 3 on its outer surface a thin layer of a crystal is formed that moves upward together with the band surface and becomes thicker with decrease in the cooling temperatures in the direction from zone No. 3 to zone No. 1. On the upper drum a scraper is installed that removes the crystal. The process of crystal formation is steady-state and continuous, and the purity of the crystal may exceed many times that of the melt itself.

A model of one-dimensional heat and mass transfer in the process of crystallization on a band was suggested by the present author in [4]. The model was used to optimize heat and mass transfer in crystallization on a band and a forward-flow scheme of fractional crystallization was suggested [5, 6]. The experiment carried out by us has shown that the degree of purification in the forward-flow scheme is many times higher than in the counter-current one. In [7], a more precise two-dimensional model of heat and mass transfer is suggested, and the problem of the limits for the use of a one-dimensional approximation was investigated.

Many organic and inorganic substances can be purified at a low melt feed velocity. Such slow regimes are technologically optimal; however, at too small Reynolds numbers, crystal surface instability appears. This phenomenon is extremely undesirable, since it leads to a sharp decrease in the crystal purity at the exit. The present article is devoted to a theoretical study of the loss of stability by the surface of the crystal formed on a band. The study is based on the following model of heat and mass transfer.

**One-Dimensional Model of Heat and Mass Transfer.** *Equation of the crystal surface.* Heat transfer and the temperature profiles are shown schematically in Fig. 2. In [4], on the assumption of crystal surface stability for a stationary profile of a crystal, the following equation is obtained:

$$\rho H u_{\mathrm{b}} \frac{d\delta_{\mathrm{cr}}}{dx} = \mathrm{Nu}\, \lambda\, \frac{T(x,\delta) - T_{\mathrm{m}}}{\delta} - Q_{\mathrm{cr}}(\delta_{\mathrm{cr}}), \tag{1}$$
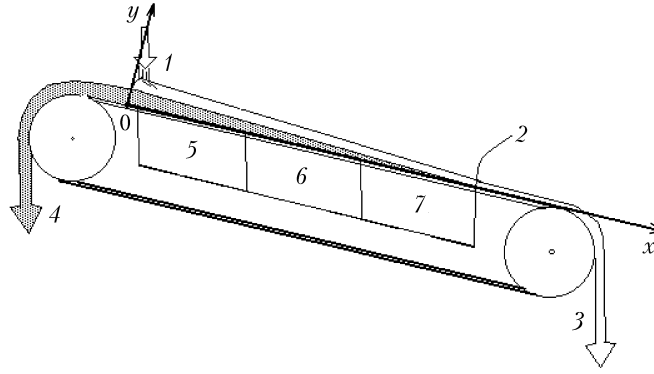
where heat sink toward the band is introduced:

Fig. 1. Schematic diagram of a band for continuous fractional crystallization:
1) feeding; 2) beginning of crystallization; 3) melt; 4) crystal; 5) cooling zone
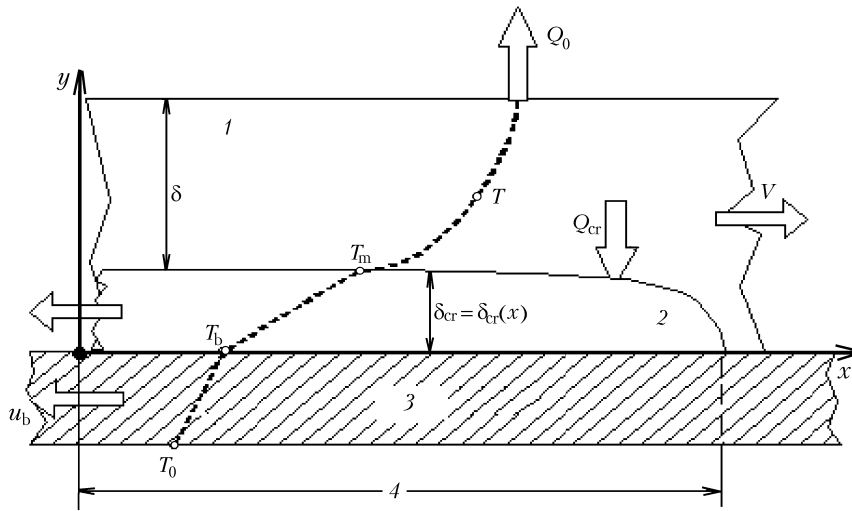No. 1; 6) zone No. 2; 7) zone No. 3.



Fig. 2. Schematic of heat transfer in crystallization on a band: 1) melt film; 2)
crystal; 3) band; 4) cooling zone No. 3.

$$Q_{cr}(\delta_{cr}) = \frac{T_m - T_0(x)}{\delta_{cr}/\lambda_{cr} + \delta_b/\lambda_b} , \qquad (2)$$

with the Nusselt number characterizing the coefficient of heat exchange between the melt and the crystal surface $\alpha = Nu\lambda/\delta$.

**Thickness of a melt film.** Equation (1) involves the melt film thickness $\delta$. Introducing the characteristic thickness of the film

$$\Delta = \left( \frac{3v^2}{g \sin \beta} \right)^{1/3} , \qquad (3)$$

we will write the well-known relations for the film thickness [8–10] in the form

$$\delta = 0.302 Re^{8/15} \Delta \quad \text{for } Re \geq 400 \quad \text{(turbulent regime)} , \qquad (4)$$

$$\delta = Re^{1/3} \Delta \quad \text{for } Re < 400 \quad \text{(laminar regime)} .$$

The inverted relations

$$\text{Re} = \text{Re}\,(\delta) = 0.302^{-15/8}\left(\frac{3v^2}{g\sin\beta}\right)^{-5/8}\delta^{15/8}, \quad \text{Re} \geq 400\,;$$

(5)

$$\text{Re} = \text{Re}\,(\delta) = \left(\frac{3v^2}{g\sin\beta}\right)^{-1}\delta^3, \quad \text{Re} < 400$$

demonstrate a strong dependence of the Reynolds number on the film thickness.

***Heat transfer coefficient of the film.*** Equation (1) contains the Nusselt number $\text{Nu} = \text{Nu}(\delta) = \text{Nu}(\text{Re}(\delta))$. It is entirely defined by the Reynolds and Prandtl numbers with the aid of the relations [8–10]

$$\text{Nu} = 1.88, \quad \text{Re} < \text{Re}^* = 615\text{Pr}^{-0.646}\,;$$

$$\text{Nu} = 0.0614\text{Re}^{8/15}\text{Pr}^{0.344}, \quad \text{Re}^* \leq \text{Re} < 400\,;$$

(6)

$$\text{Nu} = 0.00112\text{Re}^{6/5}\text{Pr}^{0.344}, \quad 400 \leq \text{Re} < 800\,;$$

$$\text{Nu} = 0.0066\text{Re}^{14/15}\text{Pr}^{0.344}, \quad 800 \leq \text{Re}\,.$$

These relations were obtained experimentally for a smooth wall of constant temperature. In crystallization on a band the surface of the crystal serves as such a wall. We note that for the crystal surface to be smooth it is necessary that dendrite growth of the crystal be absent [10–12].

***Temperature of a melt along the flow.*** The equation for the section-average temperature of the film is given in [4, 7]:

$$\delta R\rho V\frac{dT}{dx} = -\alpha\left\{T\,(x) - T_{\text{m}}\right\} - Q_0\,.$$

(7)

At the point of melt feed $x = 0$ the temperature is known:

$$T\,(0) = T_{\text{in}}\,.$$

(8)

On the assumption that the heat losses by evaporation and convection are constant along the $x$ axis, as well as that the heat transfer coefficient is also constant, the solution of problem (7), (8) can be written in the form

$$T\,(x) - T_{\text{m}} + T_{\text{ev-c}} = \left\{T_{\text{in}} - T_{\text{m}} + T_{\text{ev-c}}\right\}\exp\left\{-x/L\right\},$$

(9)

where we introduce the characteristic dimension

$$L = \delta\,\text{Pr}\,\text{Re}\,(\delta)/\text{Nu}\,(\delta)$$

(10)

and the temperature

$$T_{\text{ev-c}}\,(\delta) = Q_0\delta/(\lambda\,\text{Nu}\,(\delta))\,.$$

Heat losses by evaporation and convection from the free surface of a melt ($Q_0$) are determined from relation (9) by substitution of the experimental value of temperature at the point $x = l$.

**Instability of the Crystal Surface on a Band.** In fractional crystallization, two forms of crystal surface stability are particularly important: morphological (the microscopic level, where the dimension of perturbation is of the order of fractions of a millimeter) and thermal (the macroscopic level with the dimension of perturbation of the order

of several centimeters). It is known [11] that the stability of the first kind is disturbed at the so-called constitutional supercooling. The loss of the second kind of stability was observed by the present author in experiments on a pilot plant during crystallization at small melt flow rates (Re < 10). We will consider in detail the above-noted instabilities.

*Constitutional supercooling and morphological instability of the crystal surface.* It is known that for efficient purification of a crystal the crystal surface must be smooth [10–13]. Otherwise the crystal surface grows in the form of needle-like minute crystals (dendrite growth) between which an appreciable percent of heavily dirty melt is entrained, and this sharply decreases the purity of the product. A detailed study of the phenomenon of melt entrainment is made in [12]. The smoothness of the surface is connected with the morphological stability. The latter is present if the temperature gradient in the melt at the crystal-melt interface exceeds the value calculated from the phase state diagram by the impurity concentration gradient [10, 11, 14, 15]:

$$\frac{T(x) - T_m}{\delta_{h.tr}} \geq \frac{c_0 \tan \gamma}{\delta_d} \frac{Pe}{k_0/(1 - k_0) + \exp(-Pe)} , \tag{11}$$

where $\tan \gamma$ is the tangent of the inclination angle to the liquidus curve on the phase state diagram at the concentration of the main mass of the melt $c_0$; $Pe = Pe(x) = \delta_d V_{cr}(x)/D$ is the local mass transfer Peclet number and $V_{cr}(x)$ is the local rate of crystal growth. When the above-given condition is not obeyed, one speaks of constitutional supercooling. In relation (11) the thicknesses of the diffusion and heat-transfer layers are connected by the similarity relation:

$$\delta_d = \delta_{h.tr}\left(\frac{Pr}{Sc}\right)^{0.344} = \delta_{h.tr}\left(\frac{m^* D}{a}\right)^{0.344} .$$

Since for typical cases $a \cong 10^{-7}$ m$^2$/sec, $D = 10^{-10}$ m$^2$/sec, and $m^* \cong 1$, the diffusion layer thickness is ten times smaller than the thickness of the heat-transfer layer. Calculating, from Eq. (1), the profile of the crystal $\delta_{cr}(x)$ and the local rate of crystal growth $V_{cr}(x) \cong -u_b d\delta_{cr}(x)/dx$, it is possible, by using Eq. (11), to locally estimate the morphological stability of the crystal surface.

The investigations carried out by D. Hurle [11] on the technique of growing semiconductor crystals have shown that the crystal surface for very pure melts can be morphologically stable (dendriteless growth) even when condition (11) is not strongly violated.

*Thermal instability of the crystal surface.* Some organic and inorganic mixtures can be purified effectively at small Reynolds numbers (Re < 10) at crystallization rates of the order of 1 cm/h. Regimes with low Reynolds numbers may turn out to be advantageous, but they often lead to the loss of stability of the crystal surface. This instability has a thermal nature and consists in the formation of rivulets from a melt that flow within the banks made from the wavy surface of the crystal. The width of such rivulets in the experiments carried out by the present author is of the order of several centimeters. The formation of rivulets is extremely undesirable, since in this case the efficiency of purification decreases sharply; therefore we will consider the problem of the loss of stability by the crystal surface and derive the criterion of thermal stability.

*Equation of the dynamics of growth of a striped perturbation.* In actual fact there are always fluctuations of the crystal thickness. The real thickness of a crystal, along with a constant component, also contains an oscillating component. The experiment shows that the most important for us are the striped perturbations of the crystal thickness along the band (Fig. 3):

$$\delta_{cr}(x, z, t) = \delta_{cr0}(x) + \varepsilon(t)\Delta(z) . \tag{12}$$

Further on we will consider these perturbations to be small, i.e., $\varepsilon(t)\Delta(z) \ll \delta_{cr0}(x)$ and local along $z$ (i.e., $\Delta(z) \neq 0$ on a small part of the band width). The constant component $\delta_{cr0} = \delta_{cr0}(x)$ satisfies the stationary equation (1). This equation can be generalized to a nonstationary case and written for perturbations of the type of Eq. (12) along each strip in the following form:

$$\rho H\left\{-\frac{\partial \delta_{cr}}{\partial t} + u_b \frac{d\delta_{cr}}{dx}\right\} = Nu \lambda \frac{T(x, \delta) - T_m}{\delta} - \frac{T_m - T_0(x)}{\delta_{cr}/\lambda_{cr} + \delta_b/\lambda_b} , \tag{13}$$
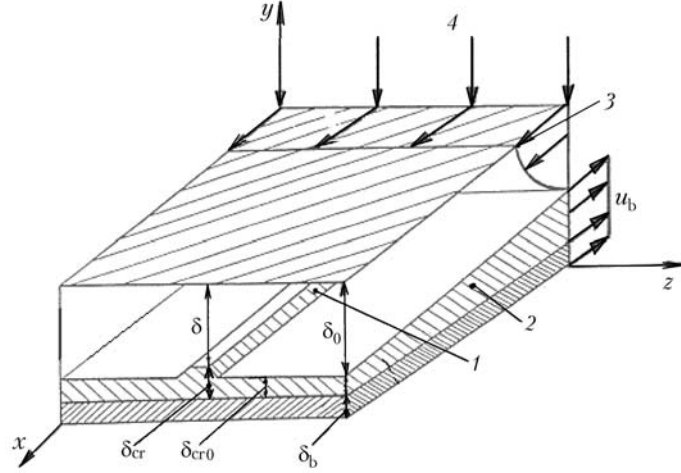
Fig. 3. Perturbations of crystal thickness over the band width: 1) crystal surface perturbation; 2) nonperturbed surface of the crystal; 3) velocity distribution in the melt film; 4) feeding.

where the melt film thickness

$$\delta = \delta_0 - \varepsilon(t)\,\Delta(z) \tag{14}$$

fluctuates opposite to the crystal thickness fluctuation. The perturbation of the crystal thickness changes the thickness of the film above it and also the local (i.e., for a strip) Reynolds number: the larger the local thickness of the crystal, the smaller the local film thickness and the Reynolds number. It is evident that relations (9), (10), and (13) can be used along each strip due to the constancy of the film thickness along the $x$ axis for perturbations of type (12). Here, it is necessary to use local (for each value of $z$) Reynolds and Nusselt numbers.

*Equations of the dynamics of infinitely small perturbations.* After substituting Eqs. (12) and (14) into Eq. (13), discarding terms of order above the first one in perturbation of $\varepsilon(t)$, and using Eq. (1), we obtain an equation that describes the dynamics of the amplitude of infinitely small perturbations:

$$\frac{d\varepsilon}{dt} = A\varepsilon\,, \tag{15}$$

where

$$A = \frac{1}{\rho H}\left\{\lambda\frac{d}{d\delta}\left[\mathrm{Nu}(\delta)\frac{T(x,\delta)-T_m}{\delta}\right]\Bigg|_{\delta=\delta_0} - \frac{T_m - T_0(x)}{(\delta_{cr0}/\lambda_{cr}+\delta_b/\lambda_b)^2}\frac{1}{\lambda_{cr}}\right\}. \tag{16}$$

The general solution of Eq. (15) has the following form:

$$\varepsilon(t) = \varepsilon_0\exp(At)\,.$$

In the case of $A < 0$, the perturbation of thickness decays in time, and the crystal surface is thermally stable. But if $A > 0$, the perturbation increases with time, and the crystal surface is thermally unstable.

*Criterion of thermal stability.* The analysis of the sign of Eq. (16) shows that the thermal instability of the crystal appears only at low Reynolds numbers (Re < 30). Since the Prandtl number is usually of the order of 100, then at Re < 30 we may always consider that Nu = 1.88 and consider the next stability criterion:

$$\lambda\frac{d}{d\delta}\left\{\frac{1.88}{\delta}(T(x,\delta)-T_m)\right\}\Bigg|_{\delta=\delta_0} - \frac{T_m - T_0(x)}{(\delta_{cr0}/\lambda_{cr}+\delta_b/\lambda_b)^2}\frac{1}{\lambda_{cr}} < 0$$
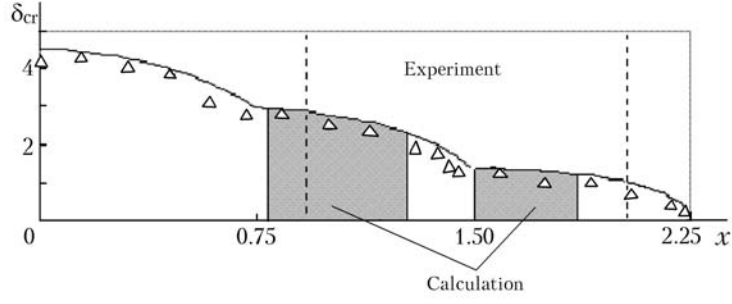
110

Fig. 4. The region of thermal instability at Re = 5.5.

or

$$\lambda \frac{1.88}{\delta} \frac{d}{d\delta} T(x, \delta) - \lambda \frac{1.88}{\delta^2} (T(x, \delta) - T_m)|_{\delta=\delta_0} - \frac{T_m - T_0(x)}{(\delta_{cr0}/\lambda_{cr} + \delta_b/\lambda_b)^2} \frac{1}{\lambda_{cr}} < 0. \tag{17}$$

Since $T_m > T_0(x)$, then the third term on the left-hand side is always negative and cannot cause instability. This term sharply decreases with increase in the crystal thickness. The second term is also negative, since in order to avoid the constitutional supercooling, the inequality $T(x, \delta) - T_m > 0$ must hold. The mechanism of the stabilization of the second term is as follows. If the crystal thickness increases accidentally at a certain point, the local thickness of the film decreases. This leads to a growth in the heat transfer coefficient $\alpha = 1.88\lambda/\delta$. The sole reason for the instability is the first term. With the aid of relation (9) it can be written in the form

$$\frac{d}{d\delta} T(x, \delta) = -\frac{Q_0}{\lambda} \frac{1}{1.88} \left\{ 1 - \exp\left(-\frac{x}{L}\right) \right\} + \left\{ T_{in} - T_m + \frac{Q_0}{\lambda} \frac{\delta}{1.88} \right\} \frac{x}{L^2} \exp\left\{ -\frac{x}{L} \right\} \frac{d}{d\delta} L, \tag{18}$$

where

$$L = \delta \frac{\Pr \operatorname{Re}(\delta)}{1.88} = \frac{\Pr}{1.88} \left( \frac{3v^2}{g \sin \beta} \right)^{-1} \delta^4. \tag{19}$$

We note that only the second term in (18) is positive and is the sole destabilizing factor. In a certain vicinity of the melt feeding point ($x/L \ll 1$) this term is as small as one likes, and the crystal surface is stable.

*Rough estimation of the minimum Reynolds number for the beginning of instability.* The second term in (18) increases monotonically together with $x$ from 0 to a maximum value at the point $x = L$. It is evident that if the crystallizer length is much smaller than this dimension (i.e., $l/L \ll 1$), then within the crystallizer the second term is relatively small and cannot cause instability. Experimental and numerical calculations of criterion (17) show that the order of the Reynolds number at which the destabilizing effect of the second term can be felt at all is determined from the equality $l = L$. This condition leads to the estimate

$$\frac{L}{l} = \frac{\Pr}{1.88} \operatorname{Re} \frac{\delta}{l} = 1, \tag{20}$$

i.e., the longer the crystallizer and the thicker the melt film, the higher the Reynolds number should be prescribed to avoid the thermal instability of a crystal. The following values of the crystallizer length, film thickness, and Prandtl number are typical of crystallization on a band: $l = 1$ m, $\delta = 10^{-3}$ m, and $\Pr = 300$. The substitution of these values into Eq. (20) shows that instability can occur at Re < 6, which agrees well with the author's experimental observations. Figure 4 shows a typical calculated (curve) and experimental (points) profile of the crystal at Re = 5.5. Two regions in which the condition of stability (17) is violated are colored gray. The dashed lines show the instability re-

gion observed by the author on a pilot plant. In all of the experiments the instability appeared at low Reynolds numbers and always in zones No. 2 and No. 3, but not in zone No. 1.

**Conclusions.** The stability criteria (11) and (17), (20) together with the proposed one-dimensional model of heat- and mass transfer, allow one to numerically investigate the problem of morphological and thermal stability of a crystal surface. Numerical experiments have shown that an increase in the length of a band, in the angle of its inclination, as well as a decrease in the rate of melt feed and in the band motion velocity increase the thermal instability of the crystal surface. A more accurate investigation of stability amounts to consideration of perturbations of a general form $\delta_{cr} = \delta_{cr0} + \varepsilon(t) \exp\{\mathbf{i}(mx + nx)\}$, where $m$ and $n$ are the arbitrary spatial frequencies of perturbations along the $x$ and $z$ axes. However, such an investigation appears to be more complex and will be the aim of further investigations.

## NOTATION

$a = \lambda/(R\rho)$, thermal diffusivity; $c_0$, concentration of impurity in a melt; $D$, kinematic coefficient of diffusion; $g$, free fall acceleration; $H$, latent heat of crystallization; $k_0$, minimum coefficient of impurity distribution; $l$, total length of crystallization zones; $m^*$, ratio of molar masses of impurity and melt; $\mathrm{Nu} = \alpha\delta/\lambda$, Nusselt number; $\mathrm{Pr} = \nu\rho R/\lambda$, Prandtl number; $Q_0$, density of the power of heat losses on the free surface of the melt; $Q_{cr}(x)$, heat sink at the crystal–band interface; $\mathrm{Re} = V\delta/\nu$, Reynolds number; $R$, specific heat; $\mathrm{Sc} = \nu m^*/D$, Schmidt number; $T_m$, melting temperature of a crystal; $T$, average temperature of melt film in section; $T_0(x)$, band temperature on the side of cooling; $t$, time; $u_b$, band velocity; $V$, thickness-averaged velocity of melt film; $V_{cr}(x)$, local rate of crystal growth; $x$, $y$, $z$, coordinates along the film flow, across the film, and orthogonal to them; $\alpha$, coefficient of heat exchange between a crystal and the melt; $\beta$, angle of band inclination; $\delta_b$, $\delta$, $\delta_{cr}(x)$, thickness of a band, melt, and of a crystal; $\delta_0$, $\delta_{cr0}$, nonperturbed thicknesses of melt film and crystal; $\delta_{h.tr}$, $\delta_d$, thicknesses of heat transfer and diffusion layers; $\Delta$, characteristic thickness of melt film; $\lambda$, thermal conductivity; $\nu$, kinematic viscosity; $\rho$, density. Subscripts: b, band; cr, crystal; d, diffusion; m, melting; ev-c, evaporation-condensation; h.tr, heat transfer; in, inlet.

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