

## INFLUENCE OF HYDRODYNAMICS ON KINETICS OF CRYSTAL GROWTH

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Intensity of mass movement in the solution depends mainly on the hydrodynamic conditions of flow around the solid state surface, from which a proper component penetrates to the flux. The hydrodynamics of the flux is represented by Navier-Stokes equation, which expresses the momentum conservation law related to the volume unit of the flowing liquid [1]. For the incompressible liquid the equation has a form

$$\rho \frac{du}{dt} = -\text{grad}p + \mu \nabla^2 u + F \quad (1)$$

where:  $u(x,y,z,t)$  – vector of velocity;  $p(x,y,z,t)$  – static pressure;  $F = \rho g$  – force of gravity;  $\rho$  – solution density;  $\mu$  – dynamic viscosity

In the theoretical consideration and particularly in preparation of the experimental data, the theory of similarity is applied, because it gives possibility to express the hydrodynamic values of one set using the relative values of the second similar set.

The similarity of the phenomenon is obtained introducing nondimensional values in place of dimensional ones. Introducing to the

above equation the relative coordinates and relative velocities  $X_i = \frac{x_i}{L}$

and  $U_i = \frac{u_i}{u_0}$ , after simple transformation, the equation equal to the

initial one is obtained. However, it already contains nondimensional values

$$\frac{\partial U_i}{\partial \left( \frac{\tau}{L} \right)} + \sum_k U_k \frac{\partial U_i}{\partial X_k} = - \frac{\partial \left( \frac{p}{\rho u_0^2} \right)}{\partial X_i} + \frac{l}{u_0 \rho L / \mu} \sum_k \frac{\partial^2 U_i}{\partial X_k^2} + \frac{g L}{u_0^2} \quad (2)$$

where:  $k$  is summing variable related to all the coordinates.

To solve the problems of the mass movement between the solid state and the solution the motion of the boundary layer is introduced as a thin

by the wall zone, in which the velocity changes from zero on the wall surface to the value with which the solution flows in the main flux. Big values of the velocity derivatives along the perpendicular to the wall surface prove the big tangential stress, caused by friction even for the solution with small values of the kinematic viscosity coefficients. In case of the solution flow on the surface crystal very important is the character of the velocity profile along it in the neighbourhood of the boundary layer next to the surface crystal. In the flux flowing with a stormy movement the solution moves in the disorder way compared to its average position. Independently on the intensity of the stormy movement, near crystal surface there is always a zone, in which the velocity of the flow is very small and the value of the Reynolds number is so small that there is laminar flow. The intensity of the crystal growth process depends on the velocity of carrying the mass between the crystal and its surrounding solution. It is usually assumed that the mass flux carried from one phase to the second is proportional to the difference of the concentration, which is usually the driving force of the process. The process of the carrying the mass consists in many proceeding stages. In other words, the flux of the carried from one to the second phase component encounters many following resistances. In the crystallization process from the solutions the crystallizing substance has to overcome first the resistance of the liquid lamina adjacent to the crystal surface next the resistance of the penetration to the crystal lattice.

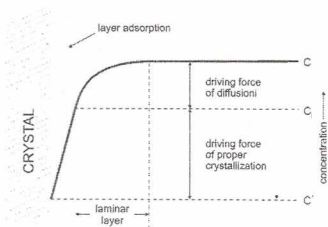


Fig. 1 Hydrodynamic layer on the crystal surface velocity of mass movement between the solution and the crystal can be described using an equation

$$\frac{dm}{dt} = k_D A (C - C_i) \quad (3)$$

where:  $m$  is the mass,  $t$  is the time,  $k_D$  – the coefficient of the mass penetration,  $A$  – is the surface of the exchange,  $C$ ,  $C_i$  is concentration of the substance in the main mass of the solution and on the surface

The coefficient of the mass penetration  $k$  and the concentration are difficult values for the experimental determination. In the theory and experiments to determine the kinetics of the growth versus the hydrodynamic conditions the theory of the phenomena similarity is applied.

Every physical equation can be expressed by nondimensional modulus. In case of the mass movement in the set solid state – liquid for small relative velocities of the flow, the equation of the mass movement can be written [2,3]

$$Sh = 2 + 0.83 Re^{\frac{1}{2}} Sc^{\frac{1}{3}}$$

where:  $Sh$  – Sherwood's number;  $Re$  – Reynold's – number;  $Sc$  – Schmidt's number

These numbers are functions of the operation and physicochemical parameters

$$Sh = \frac{k_D L}{D} ; Re = \frac{u d \rho}{\eta} ; Sc = \frac{\eta}{D \rho}$$

where:  $L$  - is characteristic dimension;  $D$  - is diffusion coefficient;  $\rho$  - is density of the solution;  $\eta$  - is viscosity of the solution

Having these parameters from the equation (4)  $k_p$  can be calculated.

## EXPERIMENTAL

To determine the mass penetration coefficient  $K_p$  we used a designated thermostatic attachment for the microscope „Jenavert“ (Fig.2), [4].

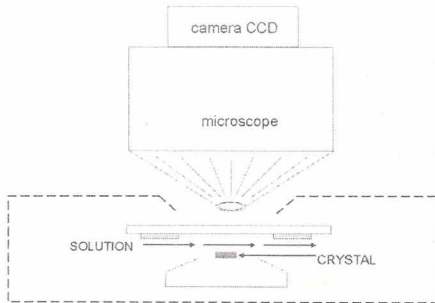


Fig.2. Scheme of the attachment

To prepare ammonium oxalate solution we used demineralized water and pure for the analysis  $(\text{NH}_4)_2 \text{C}_2\text{O}_4 \cdot x \text{H}_2\text{O}$  (produced by POCH). The solution  $\rho = 1\%$  flowed over the crystal surface with the velocity 6 – 100 mm/s. The temperature (25°C) was established by a temperature program „Easy Temp” with the exactness 0.05°C in the thermostat „Julabo”. The morphology changes of the surface for the different velocities of the flow were recorded by a PC computer.

## RESULTS

The applied velocities of the mass movement of the solution versus the growing crystal and use of the equation (4) let calculate the coefficient  $k_D$  (Fig.3)

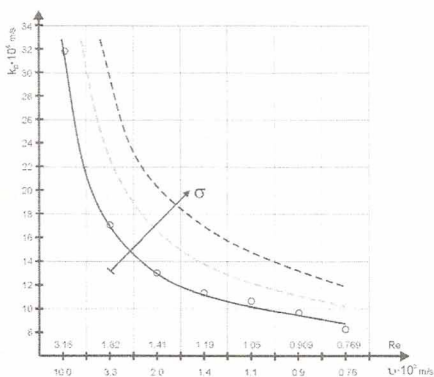


Fig.3. Dependence of the mass penetration coefficient  $k_p$  on the  $Re$  number

The experimental and theoretical kinetics of the crystal growth was calculated using the equation (3) and compared an the Fig.4

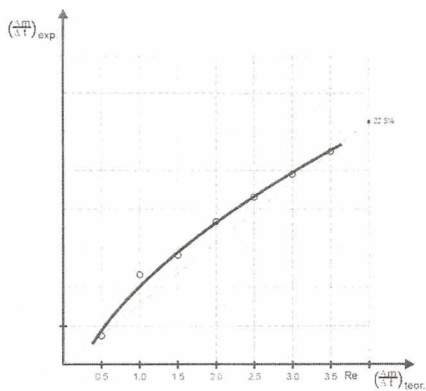


Fig.4. Comparison of the experimental and theoretical mass growth

Small deviations of the theoretical values and experimental ones of the mass movement velocities, for the small  $Re$  values, prove the equation (4) to be in a correct form for these conditions of the process.

## REFERENCE

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