A KINETIC THEORY OF CRYSTAL GROWTH FROM AQUEOUS SOLUTIONS

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ABSTRACT

The process of the crystal growth kinetics was investigated using the Fokker-Planck equation. The use of the diffusion Fick equation to relate the surface concentration and diffusion requires the use of the modified surface diffusion coefficient which is $D = D_s(1+o(\beta))$ where: D_s – is a diffusion coefficient witch the absence of adsorption and desorption, $\beta = 1/\xi \tau_D$ is a ratio of relation time characterizing the diffusion surface $(1/\beta)$ and desorption τ_D.

INTRODUCTION

The basic kinetical process in the BCF theory is a (strong) surface diffusion. Adsorbing molecules from the solution to the surface diffuse along it to the terrace. They desorp along the tarrace to the kinks, where they build themselves into the lattice. The density of the absorbing molecules is an equilibrum value, so steps are not very good absorbents. They only keep the number of the molecules necessary for the thermodynamic equilibrium. The exchange of the molecules by the adsorption and desorption is represented by the II Fick law.

$$D_s \, d^2n/dx^2 + c_\beta -n/\tau_D = 0 \qquad \text{for } x = \tfrac{1}{2} L \qquad (1)$$
where: n- is the density of the adsorbed molecules
    c_β- is a constant proportional to the solution concentration

$$c_\beta = KN = KN^0(1+\sigma) \qquad (2)$$

In the adsorption and desorption equilibrium state

$$c^0_\beta = KN^0 = n^0/\tau_D \qquad (3)$$
where: L- is the length of the terrace   N- is solution concentration
n_0 – equilibrium surface concentration

For the low supersaturations σ, N is approximately equal equilibrium N^0.

The equation (1) is an equilibrium flux, which contains the flux described by the I Fick law $j = - D_s \, dn/dx$. The Fick equation is limited to the macroskopic level. While, the Fokker- Planck one allows to describe the process of difuson on the microscopic level in more detail [1]. For the one-dimentional system the equation is the following

$$\upsilon \, \partial f/\partial x = \xi(\, kT/m \, \partial^2/\partial \upsilon^2 \, + 1 \, + \upsilon \partial /\partial \upsilon)f = \Omega f \qquad (4)$$

where: $f(x,\upsilon)$ is the density in the dimention position-rate and ξ is a cofficient related to the diffusion coefficient through the Einstein relationship $D_s = kT/\xi m$ where m is molecule mass,
Ω is an own function for the Hermite´a multinomial.

The equation (4) solution, in a general, is

$$f = \sum a_s(x) \, H_s \, (\upsilon) \, \exp(-\upsilon^2/2kT)/(2\Pi kT)^{1/2} \qquad (5)$$

where: a_s – is a constant related with the temporary f, $H_s \, (\upsilon)$ are Hermite´a multinomials.
The equations (5) system of temporary values f for the simplified arrangements gives a solution of the adsorped and desorped flux quantites

$$j_+ = n^0(kT/2\Pi)^{1/2} \, [1 + \delta(2\beta\Pi)^{1/2}(1 + 1/2\beta) \, \mathrm{tagh}1/2L\alpha^{1/2} \, -\beta\sigma + o(\beta^{5/2})] \quad (6)$$

$$j_- = n^0(kT/2\Pi)^{1/2} \, [\beta\sigma + (2\Pi\beta)^{1/2} \, \mathrm{tngh}1/2L\alpha^{1/2}- o(\beta^{5/2})] \qquad (7)$$

If a step is a perfect adsorbent then $j_- = 0$. If σ and β are small j_- is small as well. The flux difference $\Delta j = j_+ - j_-$ describes the growth kinetics for the positive σ value

$$\Delta j = n^0(kT/2\Pi)^{1/2} \, + n^0\sqrt{kT} \, (3/2\sigma -1) \, \beta^{1/2}\mathrm{tngh}1/2L\alpha^{1/2} \qquad (8)$$

The experimental werification of the solution was carried out using the kinetical data obtained from the in situ measurements.

EXPERIMENTAL

The growth of the ammonium oxalate crystal was observed under a microscope "Jenavert" with the attached camera CCD [2]. To prepare the solution the demineralized water was used ($2\mu S$) as well as pure for the analysis $(NH_4 \,)_2 C_2 O_4 \, xH_2O$ (produced by POCH). The solution with $\sigma = 0 \div 0,1$ flowed over the crystal surface (010).
The supersaturation of the solution was established using the curve of the ammonium oxalate solubility [3]. The temperature (in limits of $25^\circ C$)

was settled by a computer program "Easy Temp" in a termostat "Julabo" with the exactness 0,05°C. The shifting steps on the crystal surface were recorded by a PC computer.

RESULTS AND DISCUSSION

The characteristic elements of the micromorphology of the ammonium oxalate surface (010) changing during the growth are presented in Fig.1

Fig. 1. The changing surface (010) of the ammonium oxalate crystal
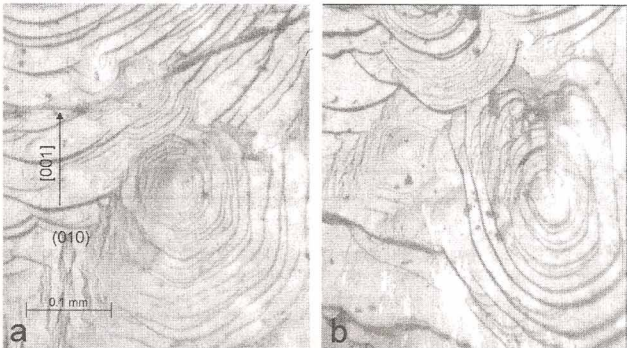
From the recorded micromorphologies during changes it was possible to calculate the velocity of the steps movement (u) and the slope of the hillock growth (p) (Fig.2) [2].
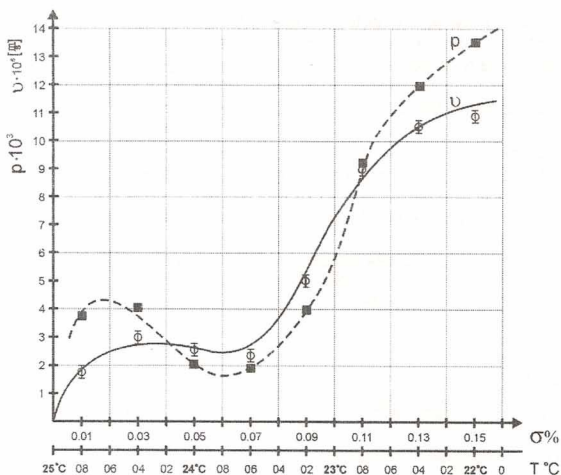
Fig.2. Dependences of the slope of the hillock growth (p) and the velocity of the step movement (υ) on the supersaturation (σ)

Using these data we calculated the experimental flux Δj of the adsorbed particles versus the supersaturation (σ) Fig.3 presents the comparison of the experimental flux and the theoretical one calculated according to the equation (8).
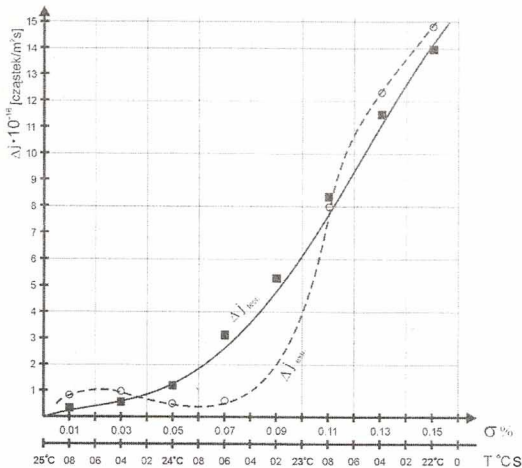
Fig.3. The comparison of Δj fluxes experimental and theoretical ones

The obtained results prove that in the supersaturation range $\sigma = 0,03 \div 0,05$ the velocity of the steps movement gets lower distinctly which disagreas with the theoretical establishments. The reference theoretical considerations concerning the influence of the impurities of the foreign ions show that they can slow down the steps movement [4]. In this case the impurities activate in this range of supersaturations.

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