

KINETICS OF THE CRYSTAL GROWTH FROM THE SOLUTION

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INTRODUCTION

The crystal growth may occur only in the metastable region, whose width is limited from one by the curve of solubility and from the other side by such a value of supersaturation where three-dimensional nucleuses are intensely created, and outside this region the monocrystals cannot be obtained. The width of the metastable region, determined by the value of supersaturation, is a measurable parameter. It depends on the following factors stirring, temperature, the presence of impurities, however it is a characteristic value for a given substance. To determine the role of dislocations in very low supersaturations, measurements of perpendicular rate of growth (R) on supersaturation and the slope of the hillock of growth (p) on supersaturation for the monohydrate ammonium oxalate have been carried out. Therefore, these measurements have been done using CCD camera, fixed to "Jenavert" microscope interconnected with a computer PC.

The observed patterns were recorded by a thermostatic vessel. During the investigation the supersaturation has been changed by the change of the solution temperature. The analysis of the rate of the mobility steps (v) and the rate (R) and the slope of the hillock of growth (p) proves that the surface diffusion in the interstep spaces does not affect the rate of growth in the applied supersaturation. The acting of dislocations, which provide the growth steps and are responsible for the growth fluctuations need solving of two relations in the measurements: the rate perpendicular to the surface (R) on the supersaturation, described by an equation

$$\sigma = (C - C_0) / C_0 \quad (1)$$

where C and C_0 are actual and equilibrium solution concentration slope of the growth hillock (p) on supersaturation.

The classical equations BCF (Burton, Cabrera, Frank) for the rate of step shifting (v) and the growth rate (R) state that the power of step source (dislocations) depends on the supersaturation value applied to measure kinetical data. According to BCF theory, in the range of low supersaturations the dependence of the slope of the hillock (spiral) and the rate (v) are linear dependences on supersaturation and the rate (R) is parabolic. However, these dependences are sometimes violated [1,2]. The present work is devoted to study of the effect of solution supersaturation on growth rates of ammonium oxalate crystals.

EXPERIMENTAL PROCEDURE

The experimental procedure for the growth of ammonium oxalate monohydrate has been reported in our previous paper [3]. They were grown on seeds from solutions of known supersaturations, at a temperature of 30° C and at different impurity concentration in 0,5 l round-bottomed flasks containing supersaturated solutions surrounded by a water jacket. The solutions were prepared from double distilled water and analytically pure ammonium oxalate (with 0,005% SO₄, 0,001% Cl, 0,001% Pb and 0,00055% Fe impurities). Small self-nucleated crystals with dimensions between 4 and 5 mm along the [001] direction growth at temperature of about 30° C from solutions by solvent evaporation were used as seeds.

The solutions supersaturation σ was calculated from the relation: $\sigma = (C - C_0) / C_0$, where C_0 is the equilibrium solubility and C is the actual solubility at the growth temperature 30° C. The supersaturations used for the growth were between 1% and 8%. The equilibrium concentration C_0 was determined on the basis of the data from the paper [4]. The growth solution was being pumped parallelly to the growing face. The linear velocity of the solution as related to the face was ~ 1 cm/s (in the laminar range flow). The temperature growth conditions were provided by a thermostat MV-4 computationally programmed (program Easy Temp) with the approximacy 0.02° C. The growth of face (110), (100) and (010) was observed (Fig.1).

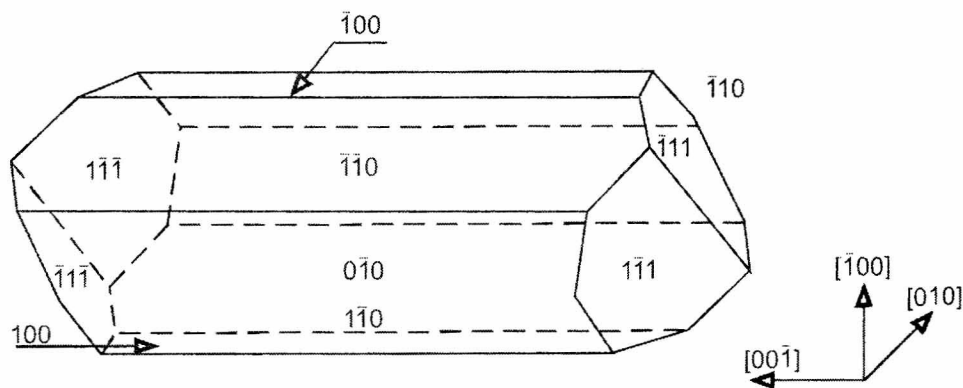


Figure 1. Schematic diagram of the typical growth morphology of ammonium oxalate crystals.

Changes of the growing surface (the slope of the growth hillock) were recorded using a camera CCD on the computer.

3. EXPERIMENTAL RESULTS

Fig.2 illustrated of the dependence of the experimental growth rate $V(\sigma)$ and $R(\sigma)$ of the (110), (100) and (010) face of ammonium oxalate monohydrate crystals.

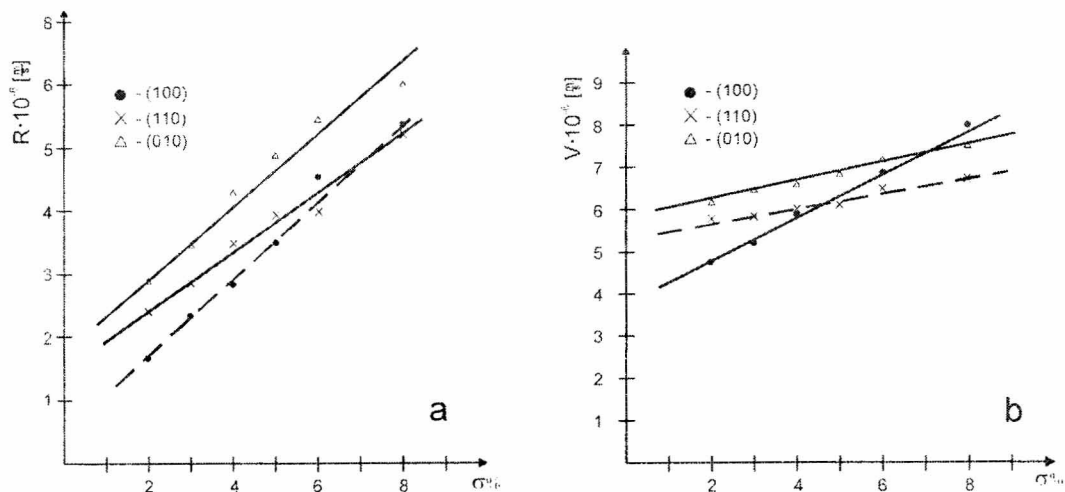


Figure 2. The influence of the supersaturation on the normal rate R and the linear velocity V .

Dependences for these walls are similar. The wall (100) shows the largest changes of speed of growth. Setting on hillocks in space 20 minutes changes on Fig.3 where showed for example..

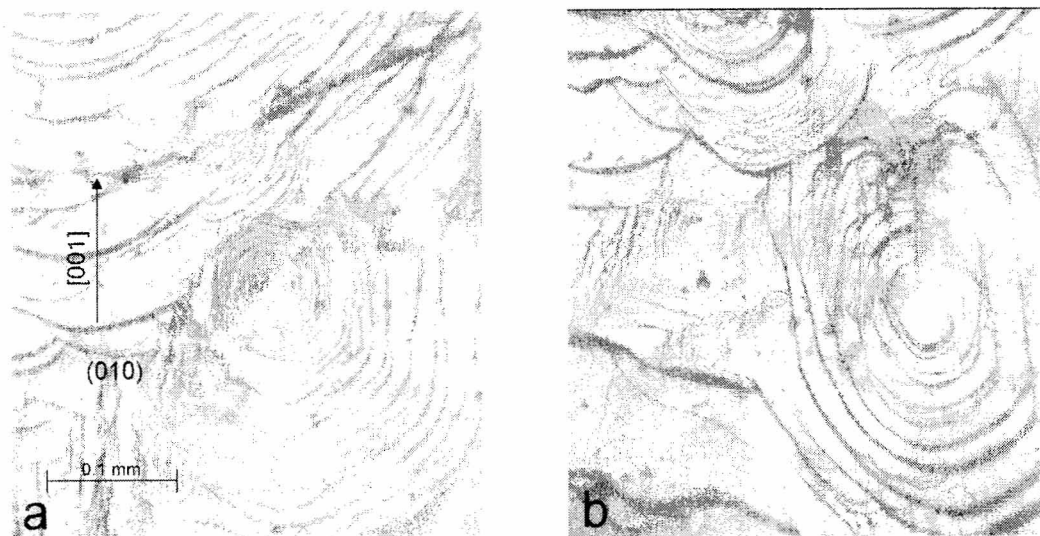


Figure 3. The change of the steps density in time.

The data on the ground the R and v were conted the inclination the hillocks of growth p (Fig.4).

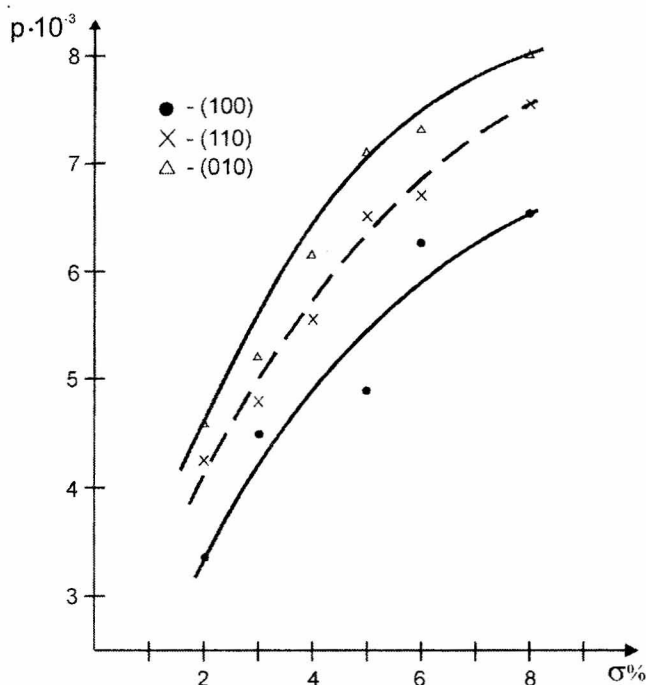


Figure 4. The dependence of the hillock slope on σ for the pure solution.

Growth kinetics depend on growth environments in two ways: through changes in the transport processes in the bulk medium, and through diffusion of the species, present in the medium, over the growing surface and their ultimate integration into the crystal surface. The transport processes in the bulk medium are also determined by the nature of the species present in it. Thus the problem of kinetics and morphology of crystals is intimately connected with the structure of entities present in the growth medium. The overall morphology of a crystal consists of faces growing at the lowest rates. A change in the growth mechanism of a face can occur with a change in the supersaturation used for growth. This may result in a change in the relative growth rates of different faces appearing in the morphology, of the growing crystal may undergo change with a change in the supersaturation used. Screw dislocations account for growth at low supersaturations too low for growth by two-dimensional nucleation. When a complicated dislocation source is active during growth, trace amounts of uncontrolled impurities may lead to the nonlinearity $v(\sigma)$ plots. Presence of relatively high concentrations of an impurity in the growth medium gives highly pronounced deviations $p(\sigma)$ dependence (Fig.4).

The step coalescence for from the point of emergence of a dislocation source and the corresponding increase in their height and smaller rates of their displacement are responsible for the deviations of $p(\sigma)$ curves from the classical liner dependence. From the above discussion it follows that the purity of crystallizing substance is a critical requirement in deducing the growth mechanism of a crystal.

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