

PHYSICAL MODELS FOR SECONDARY NUCLEATION

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SUMMARY

We discuss the possible existence of an interface layer being a reservoir for secondary nucleation. Strong support for such a layer comes from light scattering experiments of Bilgram and coworkers which are discussed in the context of secondary nucleation.

Collision experiments are described which indicate that the attachment energy of crystal faces is an important parameter controlling contact nucleation.

1. INTRODUCTION

Despite of intense research the mechanism and origin of secondary nucleation is not clear. The evidence that the solid bulk is an important source however seems to be overwhelming. This question has been answered by experiments with crystals existing in two modifications [1] or with crystals labeled by isotops [2] or by direct in situ observation [3]. It has been suggested that tiny non smooth parts of the crystal surface are chipped off by forces originating from collisions or fluid shear [4] (we avoid the term "rough" in this context because this has nothing to do with roughening transition [5]). This seems to be an oversimplification, as we shall discuss in the second part of this paper.

In the experiments mentioned above [1,2] it became clear that not all nuclei necessarily originate from the crystal. Hence the idea of some layer above the crystal face is not ruled out. In the first part of this paper we discuss in some detail Shimizu's recent results [2] stressing the idea of an interface layer as source for secondary nuclei. Strong support for an interface layer comes from light scattering experiments which are briefly discussed and we speculate over the nature of the layer. The second part is devoted to micro attrition, the connection of fluid shear and contact forces. We describe sliding experiments on various faces of KDP and discuss the results introducing the slice energy to be important for

secondary nucleation.

2. INTERFACE LAYER

Denk and Botsaris [1] studied secondary nucleation from sodium chlorate, which exists in two modifications. The secondary nuclei were analyzed according to if they are of the same modification as the mother crystal. Above a certain supersaturation practically all nuclei had the modification of the mother crystal, but below that supersaturation only 60% had this modification.

Shimizu et al. used K-alum containing D₂O. Analysing the D₂O concentration of the secondary nuclei one gets information about their origin. The greatest content of D was found in nuclei produced by collision, while nuclei produced by fluid shear practically contained as much D as crystals grown in undeuterated solution. The authors argue that fluid shear decreases the diffusion layer, consequently the crystal grows faster and the surface contains only normal water. But the argument applies for the collision experiments too, since collisions also give rise for fluid shear. Hence we do not expect that the overgrow by undeuterated material is very much different in the experiments.

We conclude that in both experiments the fluid phase cannot be excluded as a source of nuclei: There is an indication for the existence of some pre ordered layer.

In this context we believe that very important experiments have been performed by Bilgram and his coworkers. This group investigated the light scattering from the surface of ice [6-9] growing from the melt. They find that above some critical growth velocity $R \sim 1.5 \mu\text{m/s}$ the scattering of light from the liquid-solid interface changes dramatically. The scattering power is greatly enhanced and the line width of the central line is extremely narrowed. Careful analysis showed that the active scattering volume is a thin layer of a width between 1.5 and 6 μm above the crystal.

It takes half an hour before the scattering

phenomena are fully developed. The autocorrelation spectrum can be fitted with a single exponential. One finds a correlation time $\tau = \kappa^2 D$ (κ is the length of the scattering vector) with isotropic D (with respect to the (0001) plane of the ice-crystal), and D is some 10^{-8} cm²/s, about 10^5 times smaller than the thermal diffusion constant. If the scattering were due to thermal density fluctuations (Rayleigh-scattering), the thermal compressibility were 700 times larger than that of water. The scattering is not due to surface ripples. Large outcrops can be excluded. Qualitative the same results have been found from Salol [10]: The layer is not a consequence of the rather unique properties of water. Thus one must state that there is a gel-like layer on crystals growing from the melt.

The authors argue that the scattering cannot be due to small crystals in the vicinity of the crystal surface. The main arguments are: (i) Homogeneous nucleation can be excluded. (ii) There is no reason to find nuclei alone in the vicinity of the surface. (iii) The size of the nuclei must be homogeneous. We find these arguments not convincing: (i) Secondary nucleation can not be excluded. (ii) The diffusion length varies as \sqrt{t} , while the displacement of the surface of the crystal varies as t . Hence there is a tendency to trap the nuclei at the surface. This is a pretty fast process, the time needed to trap a diffusing particle is roughly $D/R^2 = 1$ s.

If the order of D turns out to be general it is interesting to note that the time D/R^2 can be near the surface regeneration time [11,15]. (iii) The concluded homogeneity comes from the fact that the autocorrelation function of the scattered light can be fitted with a single correlation time. A distribution of sizes leads to a distribution of correlation times which is often indistinguishable from a single one.

Thus we feel that the question, if the scattering is due to nuclei or not, is open. A layer containing nuclei would explain the enormous enhancement of the scattering intensity. Anyway, whether nuclei or not, there is a strange thin layer above growing crystals, which might be well the long looked for "preordered layer" [11].

3. MICROATTRITION

To disturb a layer of a few μ m thickness large fluid shear forces must act. In all experiments which concentrate on collision processes very large shear forces are also active. Consider as an example Garabedian's sliding experiments [12,13]. The $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystals of size $2 \times 4 \times 1$ mm³ slid down the

bottom of a glass tube with a velocity $v \approx 2$ cm/s. If one assumes that friction arises from a fluid layer between glass and the crystal (4×2 mm) the thickness l of the layer can be estimated to be ~ 1 μ m.

The velocity gradient active here is enormous ($2 \cdot 10^4 \text{ s}^{-1}$). To achieve this gradient an impeller of 2 cm diameter 1 cm apart from the crystal has to rotate with 3000 revolutions per second. Similar enormous magnitudes will be found in other contacting experiments, possibly exceeding that of the contacting itself. We think therefore that experiments termed "fluid shear" and that termed "collision" differ only quantitatively, in the magnitude of the acting forces, but not qualitatively.

We performed sliding experiments as done first by Garabedian and Stickland-constable [12,13] on KDP, to investigate the activity for secondary nucleation of different crystal faces. KDP is bounded by two F-faces [15,16] the prismatic (100) and the pyramidal (101) faces. On sphere experiments also the (112) face appears, which is a S-face. It is generally accepted that equilibrium forms can be obtained by calculating the relative slice energy E_{slice} of the faces, since the growth rate of the faces is proportional to the attachment energy E_{att} (the crystallization energy $E_{\text{cr}} = E_{\text{att}} + E_{\text{slice}}$).

We cut crystals out of large grown KDP crystals of the size $4 \times 10 \times 1$ mm³. Two types of orientation were used, with the large faces in (101) and (001) direction, respectively. The (001) face of KDP is a K-face.

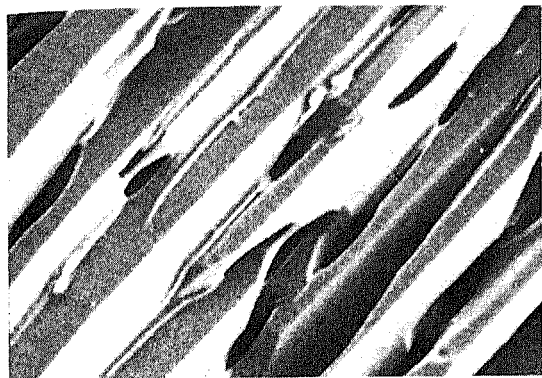
When growing, it covered itself with (112)-roots, see the figure. The properties of the (101) face have been thoroughly discussed by van Enckevort [17].

To avoid initial breeding, the crystals were introduced into the undersaturated solution at 40°C. Saturation temperature was 35°C. After about one half hour the temperature was lowered slowly within two hours to 33°C, which corresponds to 2% supersaturation. We allowed the crystal to grow about one half hour before we did the sliding experiment. Sliding times, length of the tube and θ were comparable with Garabedian's experiments. We did not lower the temperature after sliding.

The (101) face produced about 10^2 secondary nuclei while the (001) face produced never more than five, sometimes none at all. This result was unexpected in view of the structure of the (001) face. From the idea that most conveniently small hills are clipped off by the collisions [4] one should expect contrary results.

Johnson et al. [18] reported a similar result from $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystals: The slower

growing (110) face, that with the larger E_{slice} , smaller E_{att} , released 6 times more



SEM-picture of the (001)-face of KDP after 15 min. growing at 2% supersaturation. The roof-like structures are build by (112) faces. Magnification is 160x.

nuclei than the faster growing (111) face. The authors however explain this result by ex Situ observation showing that the (110) face is less smooth than the (111)-face. This is strange, since, as reported by Clontz and McCabe [11], the (111) face tends to build veils and spikes at large supersaturations while the (110) face stays smooth.

Slow growing faces are obviously more effective for contact nucleation than the fast growing ones although the fast growing ones are usually less smooth. An extreme example is given here for the (001)-face of KDP. But the fast growing faces are those faces with the larger E_{slice} and the lower E_{att} : The binding energy parallel to slow growing faces is large, normal to them is small. Usually, these planes are cleavage planes. Therefore, embryos can be easier removed from the slow -smoother-faces. The high binding energy seems to be more importance than the non smoothness of the surface.

4. CONCLUSIONS

Obviously the idea of mountains on the crystal face being chipped off by contact or fluid shear forces is too simple. We believe that experiments using large fluid shear forces (see e.g. [19]) combined with in situ observation of the surface will give more information about the process. We tend to prefer fluid shear because of the higher reproducibility [20].

Very important are light scattering experiments on growing crystals from solution to test whether Bilgram's layer is found also in this case. Note that ice in water is also active for secondary nucleation [21]. We may

also hope to gain some information about this layer by means of other techniques, e.g. fluorescence, Raman scattering, forced Rayleigh scattering etc.

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