

CONTACT NUCLEATION: IN SITU AND EX SITU OBSERVATIONS OF SURFACE DAMAGING

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To investigate the damaging done to a crystal surface (potassium dihydrogen phosphate, KDP and potassium hydrogen phthalate, KAP) due to a crystal–rod contact, both ex situ and in situ experiments were performed and the impact sites studied either using an interference contrast microscope or a scanning electron microscope. An ex situ contact (performed in air) causes subsurface cracks and the breakage of small fragments (KDP) or the removal of thin plates (KAP) from the surface. In the former case the fragments have thicknesses roughly corresponding to the height of macrosteps present on the surface. Contacts during growth on KAP produced secondary nuclei; the crystal size distribution of these nuclei displays a log-normal behaviour.

1. Introduction

In industrial crystallization, secondary nucleation is the most important source of the production of new crystals. It is known that collisions of crystals with moving parts of the crystallizer (such as stirrer and pump impellers) as well as crystal–wall and crystal–crystal interactions enhance secondary nucleation [1].

To investigate secondary nucleation, in situ microscopy is a valuable technique, since crystal and contact site can be observed before, during and after the contact. The first to apply this technique were Garside and Larson [2]. Before them, Clontz and McCabe [3] performed pioneering experiments on contact nucleation, but they could not detect any damage of the mother crystal after a rod had fallen on it and nuclei were produced. However, the in situ technique used in ref. [2] clearly revealed damaging of the crystal due to contacting.

One step beyond the experiments of Garside and Larson [2], is the use of advanced microscopic techniques such as interference contrast. Contrary to ref. [2], where no features on the crystal surface

such as steps or growth spirals could be observed, Wissing et al. [4] were able to follow these kinds of growth phenomena during growth and contacting by observing from beneath the growth cell, through the crystal, the upper (100) surface of potassium dihydrogen phosphate (KDP). The most important result of their work was that a crystal–rod contact leads to damage of the surface and thereby to a great number of secondary nuclei at and above a critical impact energy E_c . The value of E_c strongly depends on the density of macrosteps on the contacted crystal face: a part of the surface with many macrosteps is more easily damaged than a part with shallow steps. These results could explain a number of features of secondary nucleation: the dependence of the nucleation rate on supersaturation and impurity concentration, its negative temperature coefficient, the proportionality of the nucleation rate and the radius of the contacting tip.

Derks et al. [5] performed similar experiments to Wissing on the (010) face of potassium hydrogen phthalate, using a more sophisticated design of the contacting device. KAP turned out to behave quite differently from KDP: no critical im-

pact energy was found and the 20–100 secondary nuclei that appeared whether or not a contact had been performed, were due to initial breeding. Hence, no statements could be made on the contact nucleation rate, only that it had to be smaller than the initial breeding rate or that it was even zero. However, Derks et al. found that a crystal–rod contact can have other consequences than surface damaging as well, namely the formation of new growth spirals. Experiments on KDP(100) performed later, showed the same feature. Furthermore, subsurface cracks were reported [5], implying that the impact energy of the rod is large enough to cause damage to a crystal.

Here we present results on contact experiments performed ex situ (in air) both on KDP(100) and KAP(010) and during growth on KAP(010). Besides optical microscopy (interference contrast), we also used a scanning electron microscope (SEM) to examine the impact sites.

2. Experimental details

The contacting device we used is described elsewhere [5]. The design is such that the contacting rod, made of glass with a round tip having a radius of curvature of 0.5 mm, hits the crystal only once; after the contact the rod is moved upwards again.

The ex situ contacts were performed in air, using both KAP and KDP crystals which were prepared in the same way as in the in situ experiments (see ref. [4] for KDP and ref. [5] for KAP).

Both the KDP and KAP solutions were saturated at 30.0 °C while growth was performed 28.0 °C. The crystal–rod contact was performed 10 min after the removal of the crystal from the solution. The crystals are observed from beneath, through the crystal in reflected light, using an interference contrast microscope (Olympus BHM) with a resolution of ~ 10 nm vertical and ~ 4 μm lateral (if a $5\times$ objective with numerical aperture of 0.13 is used). Due to the reversed arrangement of microscope and sample, one is restricted to the use of an objective having a relatively low numerical aperture (NA) [6]. In our specific case, this means that only objectives with $\text{NA} < 0.25$ can be

used, which limits the lateral resolution. Thus, with optical microscopy it is hardly possible to gain more information of the damage done to the crystal surface due to contacting. However, if the samples are coated with an electrically conductive layer (e.g. gold), they can be studied with a scanning electron microscope (SEM) as well. The advantages of a SEM with respect to optical microscopy are obvious: it makes oblique views and higher magnifications of the impact site possible. The lateral resolution of the SEM used (type JEOL JSM-T300) was ~ 5 nm. SEM micrographs of the impact sites were made.

3. Results

We treat the results on KDP(100) and KAP(010) separately.

3.1. KDP(100)

A crystal–rod contact often caused the formation of cracks. Because (after coating the sample with gold) SEM observations rarely revealed surface cracks, the cracks must have been formed beneath the surface. In fig. 1 an example of an impact site is shown. We observed that a contact causes small fragments to break off from the surface. These fragments are more or less cubic

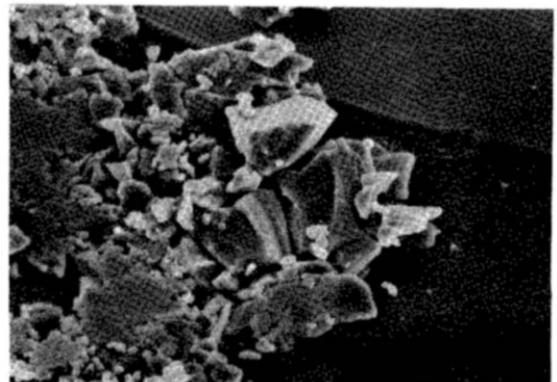


Fig. 1. Damage after crystal–rod contact on KDP(100) performed ex situ (in air): breakage of small fragments from the surface. Note the correspondence between the height of the macrostep and the thickness of the smaller fragments. The thin black bar denotes 10 μm .

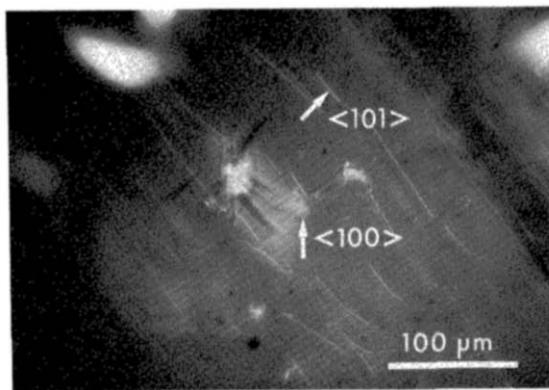


Fig. 2. Optical microtopography of impact site on KAP(010). Surrounding the actual impact site, subsurface cracks along $\langle 101 \rangle$ and $\langle 100 \rangle$ are visible.



Fig. 3. SEM photograph of impact site on KAP(010). The contact caused partial removal of thin plates from the surface, probably due to (010) being a cleavage plane. The thin black bar denotes 10 μm .

particles, ranging in size from ~ 1 to 20 μm , and are concentrated at the impact site. This is contrary to the in situ experiments [4] where the secondary nuclei become suspended in the solution.

In fig. 1 also a macrostep is visible. The height of this macrostep ($\sim 2.5 \mu\text{m}$) roughly corresponds to the thickness of the smaller fragments, which means that apparently parts of the surface with thickness of a macrostep are removed as a result of the contact.

3.2. KAP(010)

Similar ex situ experiments on KAP(010) showed that also in this case subsurface cracks are formed as a result of the contact. The cracks are formed in crystallographic directions along $\langle 101 \rangle$ and $\langle 100 \rangle$ and in a plane parallel to the surface, i.e. (010). An example of these subsurface cracks is depicted in fig. 2 (optical microscope). Using a SEM, surface cracks were sometimes observed as well. In contrast with KDP(100), no small fragments were found at the impact site. The damage to the crystal surface was more like the removal of thin plates, which is probably due to the fact that (010) is a cleavage plane (see fig. 3). Surface cracks often occurred along macrosteps, as can be seen from fig.4.

Contact experiments on KAP during growth did not give rise to secondary nuclei suspended in

the solution, besides those due to initial breeding, according to Derks et al. [5]. However, if the crystal is removed from its supersaturated solution and studied with the SEM, clearly faceted secondary nuclei can be observed (see fig. 5), which are concentrated at the impact site, and randomly distributed both in size and crystallographic orientation (with respect to the underlying mother crystal) over the impact site [7]. With the help of SEM photographs of the impact site, several crystal size distributions (CSDs) could be obtained by counting and measuring the nuclei. All the CSDs display a log-normal behaviour – a typical example is depicted in fig. 6. This means that if the

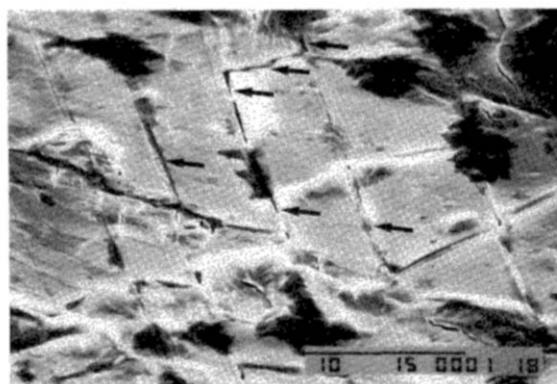


Fig. 4. Besides subsurface cracks, surface cracks were also observed on KAP; these cracks are aligned to macrosteps (arrows) or leave one macrostep, cross the terrace between two macrosteps and continue along the next.

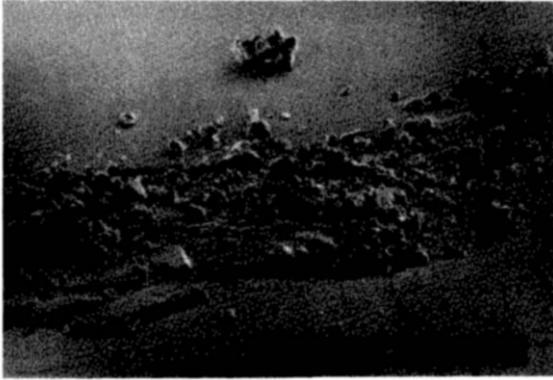


Fig. 5. SEM photograph of crystal-rod contact on KAP performed during growth. Clearly (faceted) secondary nuclei can be observed, concentrated at the impact site.

length scale is plotted logarithmically instead of linearly, the distribution becomes Gaussian. Sizes range from ~ 0.5 to $40 \mu\text{m}$. For details on the CSD of secondary nuclei we refer to ref. [7].

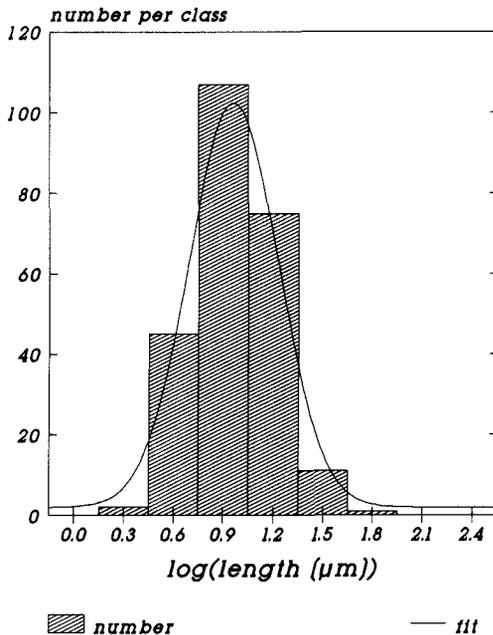


Fig. 6. Number (per class) of secondary nuclei versus the logarithm of the length. The solid line represents the fit based on a log-normal distribution.

4. Discussion

The observation of subsurface cracks in both KDP and KAP can be explained by the fact that during a contact the highest concentration of stress is at a point in the crystal at a distance from the surface approximately equal to half of the radius of projection of the contact area on the surface [8]. In our case this means that the cracks will be formed $\sim 200 \mu\text{m}$ below the surface.

In the ex situ contacts on KDP and the in situ experiments on KAP, fragments smaller than $\sim 0.5\text{--}1 \mu\text{m}$ were never observed. From fracture mechanics it is known [9] that fragments smaller than a certain size l_0 , given by $\alpha E\Gamma/Y^2$, will not be formed. This size separates brittle ($< l_0$) from ductile ($> l_0$) fragments, and is determined by three material constants, i.e. Young's modulus E , the fracture surface energy Γ and the uniaxial yield stress Y and a characteristic test constant α . Substituting $E \sim 10^8 \text{ N/m}^2$, $\Gamma \sim 1 \text{ J/m}^2$, $Y \sim 10^7 \text{ N/m}^2$ and $\alpha \sim 1$, this size is estimated at $\sim 1 \mu\text{m}$, in agreement with the minimum size observed in the experiments.

The observation that the fragment thickness roughly corresponds to macrostep heights can be explained as follows. Macrosteps are formed by bunching of, in the first instance, steps of unit lattice height. This bunching is caused by the presence of (unintentional) impurities. Thus, every new macrostep layer grows over an impurity layer. It is expected that the forces between two macrostep layers are weakened due to the built-in impurity layer and hence macrostep layers can be removed somewhat easier.

5. Conclusions

We come to the following conclusions:

- (1) As a result of a crystal-rod contact, subsurface cracks are formed. With KAP these cracks have crystallographic directions along $\langle 101 \rangle$ and $\langle 100 \rangle$ in the (010) plane, which is parallel to the surface; surface cracks often occurred along macrosteps.
- (2) Small, more or less cubic fragments in the range of $1\text{--}20 \mu\text{m}$ break off from the surface of

KDP(100), while for KAP(010) the fragments are more like partially removed plates, probably due to (010) being a cleavage plane. The thickness of the fragments produced by rod-contact on KDP(100), roughly corresponds to the height of a macrostep. This could be explained, assuming that the forces between two macrosteps are weakened due to a built-in impurity layer.

(3) Contact experiments carried out during growth on KAP(010), and a later study of the impact site with the SEM revealed that secondary nuclei are produced, but that they remain concentrated at the impact site. The size of the nuclei varied from ~ 0.5 to $40 \mu\text{m}$. Several crystal size distributions of secondary nuclei could be determined, all displayed a log-normal behaviour.

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