

New Insights in the Substep Mechanism of Twinned AgBr Crystals

D. Bollen^a, G. Bögels^b, T.M. Pot^b, H. Meekes^b and P. Bennema^b

^aAgfa-Gevaert N. V., Septestraat 27, B-2640, Mortsel, Belgium

^bRIM laboratory for Solid State Chemistry, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands

Abstract

In a recent study we have explained the growth mechanism of tabular AgBr crystals grown in DMSO. In this study we will complete the proposed mechanism with new experimental data and new insights.

The different growth stages of single twinned crystals are observed. These crystals are not able of expressing preferential lateral growth as only crystals with at least two parallel twin planes do. With etch techniques the location of twin planes is made visible for tabular crystals with multi parallel twin planes. These twin planes are essential for the substep mechanism. This mechanism describes the preferential lateral growth of the tabular crystal. It explains the increase of growth rate of a {111} side face that is linked with a twin plane to a fast growing {100} face. The importance of the substep mechanism for the preferential lateral growth will be examined. The growth rate of the substep mechanism will be compared with that of other kinds of defects during the precipitation and physical ripening stage.

I. Introduction

There is a lot of interest in the growth mechanism of tabular silver halide crystals. Most of the studies were performed on micro size tabular crystals grown with the industrial precipitation method in water^[1-5]. In a recent paper we examined the growth mechanism of millimeter size tabular AgBr crystals grown in DMSO^[6]. We observed that the side-face structure of the tabular crystals is built up by flat {111} and {100} faces. Three different morphologies were found and classified into groups. From these morphologies the number of twin planes could be deduced. The preferential lateral growth of the tabular crystals was explained by the substep mechanism developed by Ming et al.^[7-9]. This mechanism explained the increase of growth rate of a {111} side face that is linked with a twin plane to a fast growing {100} face. This {100} face can provide, owing to the twin plane, substeps on the {111} face. It was found that for tabular crystals a minimum of two parallel twin planes was required. In this study we will give a short overview of the

proposed growth mechanism^[6] together with new experimental data and insights which complete the model further.

Single twinned crystals will be examined at different stages of the growth process. Single twinned crystals are formed at the same conditions as tabular crystals. However, single twinned crystals cannot express preferential lateral growth and thus, will be dissolved during the physical ripening stage, after the precipitation.

The location of parallel twin planes in tabular crystals was made visible by chemical etching. The theoretical part focusses on the importance of the substep mechanism during the different stages of growth. From this, we will be able to estimate the importance of the substep mechanism as compared to other kinds of defects that can also act as step sources like screw dislocations and stacking faults.

2. Experimental

A solution of 1.0 M AgBr and KBr dissolved in DMSO was prepared. To this solution a mixture of DMSO and water (2/1) was added dropwise while stirring until a precipitate was formed. The stirring was thereafter stopped and the mixture was kept in the dark. After two weeks some crystals were separated from the mother liquid and the other crystals were grown for a month.

After two weeks {111} tabular crystals, single twinned crystals and cubo-octahedral crystals were observed. These crystals were examined using Scanning Electron Microscopy (SEM).

After one month, the large majority of the crystals was {111} tabular with aspect ratios around 6. These crystals were thus, left to grow to sizes of 1 to 10 mm in a physical ripening process. The crystals were carefully separated from the mother liquid. Their side-face structure was determined with an optical goniometer and a SEM. The large top and bottom faces ((111) and (-1-1-1)) of the tabular crystal were taken as reference faces. The angles of the side faces were measured with respect to the chosen reference faces. The results were included in a stereographic projection and indexed to (hkl) faces. While tabular crystals have twin planes parallel to a {111} face, they contain side face

orientations that are not present in single crystals. For those 'twin faces', a prime was added in the indexation ($\{hkl\}'$).

The side-face structure is still too small to be observed directly on the goniometer. The next step was to examine with a SEM, the side-face profile to find the correct order of side faces.

Some of the prepared crystals were first etched before they were examined with a SEM. These crystals were etched for one minute in pure DMSO and carefully dried.

3. Results

We examined the side-face structure of 42 tabular crystals. All crystal sides were built up by flat $\{100\}$ and $\{111\}$ faces forming a ridge structure (see figure 1). There were three kinds of morphology observed and classified into groups. Group 1 crystals have the morphology of a flat cubo-octahedron (figure 1a and 2). Group 3 crystals have the morphology of a single twinned crystal. On the long crystal side two adjacent $\{111\}$ faces are present whereas the short side (if visible) contains two $\{100\}$ faces (figure 1c and 3). Later we will discuss that single twinned crystals cannot have preferential lateral growth and therefore, the group 3 crystals must contain at least three parallel twin planes. Group 2 crystals have the same morphology as group 1 crystals; only an additional twin plane that is formed during

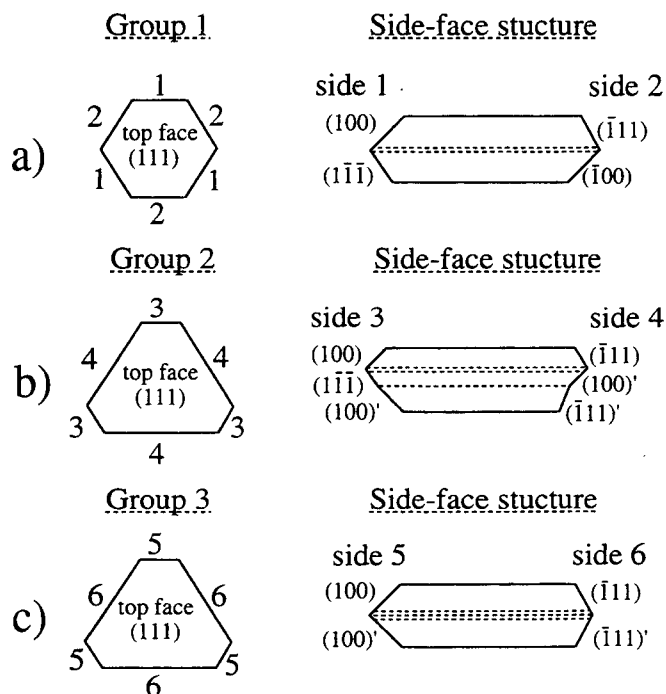


Figure 1. Side-face structure of: (a) group 1 tabular crystals; (b) group 2 tabular crystals; and (c) group 3 tabular crystals. The dashed lines in the tabular crystals indicate the position and the number of twin planes, discussed in the following. The primes refer to twin faces that do not appear on single crystals.

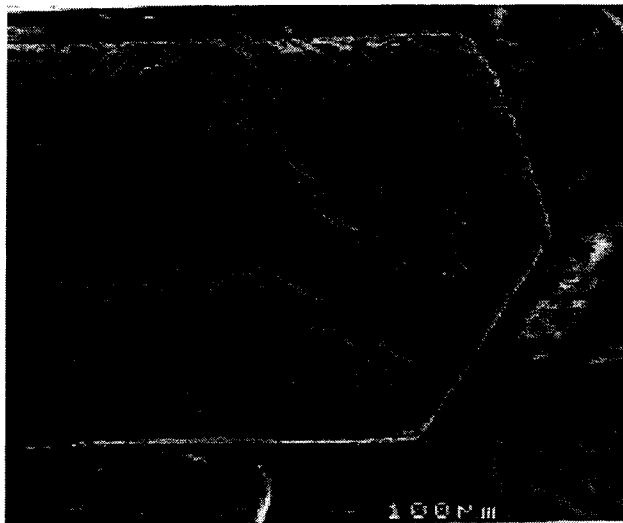


Figure 2. Side-face structure of a tabular crystal of group 1. The $\{111\}$ top face is oriented horizontally. The side-face geometry is the same as in figure 1a side 2. The bar represents 100 μm .

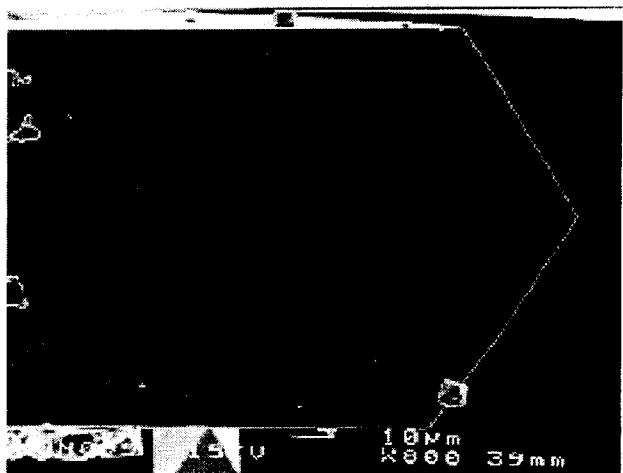


Figure 3. Side-face structure of a tabular crystal of group 3. The $\{111\}$ top face is oriented horizontally. The side-face structure is the same as in figure 1c side 5. The bar represents 10 μm .

the growth is introduced in this crystal (figure 1b).

With the twinned cubo-octahedron model we have deduced the number of twin planes for each crystal group^[6]. We found that there were two types of twin planes, nucleation twin planes formed during the nucleation and therefore, close together and accidental twin planes formed during the growth. Group 1 and 2 crystals contain two nucleation twin planes and group 3 contains three nucleation twin planes. Group 2 crystals have as only group one additional accidental twin plane. The total number of twin planes is thus, for group 1 two and for group 2 and 3 three.

The preferential lateral growth of the tabular crystals was explained by the substep mechanism developed by Ming et al.^[7-9]. In the beginning of the growth we observed cubo-

octahedral crystals with relatively little $\{100\}$ faces. Therefore, we assume that the growth rate of the $\{100\}$ faces is larger than the growth rate of the $\{111\}$ faces. If on a fast growing $\{100\}$ face a critical two dimensional nucleus appears, soon a new growth layer will be formed on the surface. If this growth layer reaches the area of the twin plane, a substep is formed, of height 1 and 2/3 of the interplanar distance $d_{\{111\}}$. This substep on the $\{111\}$ face is a preferential place for adatoms to incorporate. Thus, relatively fast steps are formed on the $\{111\}$ side faces resulting in an increase of the growth rate of all side faces. In our model we assumed that the faces between the twin planes were $\{100\}$ and $\{111\}$ faces. The faces adjacent to the tabular crystals were directly observed (see figure 3 and 4). For all tabular crystal groups the possible side-face structures were examined. For a side-face structure to have preferential lateral growth at least one $\{100\}$ face must be present on the crystal side. The other $\{111\}$ faces must be linked with a twin plane to a $\{100\}$ face. A $\{111\}$ side face linked with a twin plane to a $\{111\}$ face where the substep mechanism is active can also have preferential lateral growth.

3.1 Single twinned crystals

In figure 4 the morphology of a single twinned crystal is presented. On three crystal sides two $\{111\}$ faces can be seen in a ridge structure. On the other crystal sides two $\{100\}$ faces in a ridge structure are present. These crystals were separated from the solution after two weeks. The fast growing $\{100\}$ faces will grow out of the crystal habit

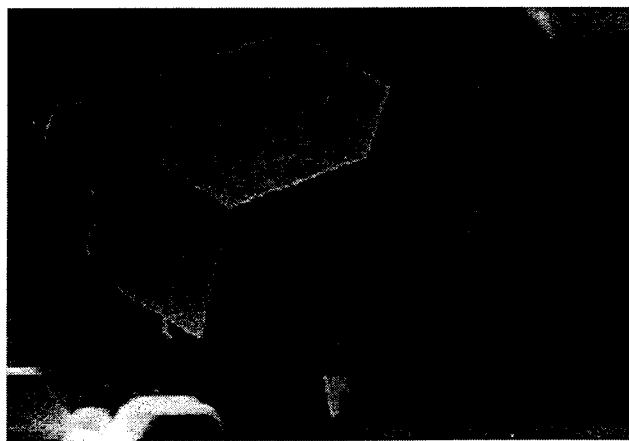


Figure 4. Single twinned crystal separated from the solution after two weeks. The rectangular shaped faces are $\{100\}$ faces and the other faces are $\{111\}$ faces. The bar represents 100 μm .

leaving a triangular shaped crystal behind. Such a crystal is completely bounded by $\{111\}$ faces and is therefore, not able of expressing preferential growth. After one month the large majority of the crystals were tabular. Thus, single twinned crystals will have a high chance of dissolving owing to the

physical ripening process. After two weeks the $\{100\}$ faces are not completely grown out of the crystal and the single twinned crystals can still be observed. After one month the $\{100\}$ faces are no longer present and the single twinned crystals will be dissolved.

Single twinned crystals were also observed by Marchetti^[10] and Millan et al.^[11] as triangular shaped crystals. Thus, for those crystals the $\{100\}$ faces were already grown out.

3.2 Etching experiments to observe the twin planes

Pure DMSO was found to be the best medium for etching tabular AgBr crystals to make the location of the twin planes visible. AgBr is poorly soluble in pure DMSO but becomes very well soluble when KBr is added. Etching of crystals in pure DMSO for about one minute made a clear groove visible on the crystal sides. The groove could be observed with a SEM. The position of the groove

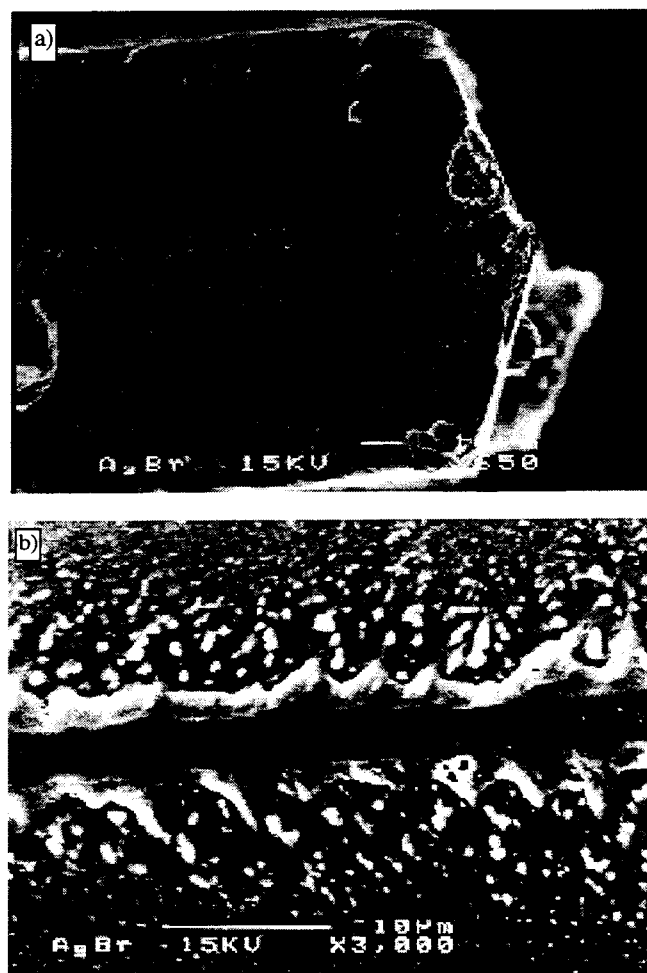


Figure 5. a) Etch line on the long crystal side of a group 3 crystal, the bar represents 10 μm , b) magnified picture of the etch line, the bar represents 10 μm

corresponds to that of the expected location of the twin planes (see figure 5). The crystal sides of group 1 were etched much faster than the long crystal sides of group 3 (figure 5). The short crystal side of group 3 was etched the fastest. For this side the etch time was always too long to give a clear etch line. This could be caused by the presence of {100} side faces. These faces are present on the short crystal sides of group 3 and on all crystal sides of group 1 crystals (figure 1). Those faces are the faster growing and therefore, also faster dissolving faces.

Thus, the positions of the twin planes could be made visible by etching although the number of twin planes could not be deduced. This indicates that the distance between the twin planes is very small ($\ll 1\mu\text{m}$)

4. Discussion

Goessens et al.^[12] have studied the defect structure of mixed (AgBrI) tabular crystals grown from precipitation. The crystals contain a AgBr core and a AgBrI shell with a maximum of 20% I. They observed in the shell stacking faults and sometimes edge dislocations. In the core and in the shell they observed in 5% of the examined crystals another not well-defined type of dislocation.

During the crystal growth the supersaturation varies. During the precipitation the supersaturation is very high and drops to almost zero in the physical ripening stage. Ming et al.^[8] Jin et al.^[13] and Li et al.^[14] studied, with Monte Carlo simulations, the growth rate of a B-type twin lamella structure, a stacking fault and a screw dislocation as a function of the supersaturation.

A B-type twin lamella structure is a {111} side face with two parallel twin planes. Between the twin planes a rough growing {100} face is present. This B-type twin lamella structure is comparable with our side-face structures that have preferential lateral growth. For high supersaturation, like in the precipitation stage, the B-type twin lamella structure had a higher growth rate than that of the stacking fault and the screw dislocation. For a low supersaturation, like in the physical ripening stage, the growth rate of the B-type twin lamella structure was higher than that of the stacking fault but lower than that of the screw dislocation.

Thus, tabular crystals can contain stacking faults because their growth rate is during the whole growth smaller than that of the substep mechanism. Thus, a stacking fault has no significant influence on the shape of the crystals.

However, tabular crystals probably do not contain screw dislocations. If for example a cubo-octahedron or a single twinned crystals would contain a screw dislocation, it would be able, during the physical ripening stage, to express a faster growth rate than the tabular crystals. Thus, this crystal would not dissolve in the physical ripening stage. However,

the large majority of the observed crystals were tabular crystals after the physical ripening stage.

5. Conclusions

The morphology and growth mechanism of the single twinned crystals have been clarified with the earlier proposed model to explain the growth mechanism of {111} tabular crystals. A single twinned crystal is not able of expressing preferential lateral growth. It grows out to triangular shaped crystals that dissolve again in the physical ripening process. This again illustrates that tabular crystals must contain at least two parallel twin planes.

With chemical etching we were able to visualize the position of the twin planes. These results were in good agreement with our proposed model. We were not able to determine the number of twin planes. This gives an indication that the twin planes are close together and thus, are formed during the nucleation stage.

The growth rate of the substep mechanism was compared with a stacking fault and screw dislocation to get insight into the defect structure of the tabular crystals. The substep mechanism is the most effective during the precipitation. In the physical ripening stage the growth rate of the substep mechanism is smaller than that of the screw dislocation mechanism but higher than that of the stacking fault mechanism. Therefore, we conclude that stacking faults can be present in tabular crystals but the presence of screw dislocation can be discarded, owing to the long physical ripening process.

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