Abstract

AgCl(I) crystals with (100) surfaces are studied with conventional transmission electron microscopy (TEM) for their microstructure in relation with their growth habits. The crystals are prepared according to two different growth methods which give slightly different results. It is observed that the presence of dislocations of mixed character that end at only two of the six cube faces are in both cases responsible for the tabular growth, but the formation of these dislocations is different. In the first case a stacking fault is formed which is eliminated by dislocations. In the second case the incorporation of iodide impurities is at the origin of the formation of dislocations. For comparison the defects in AgBr (100) tabular crystals are studied. Again dislocations of mostly mixed character are responsible of the anisotropic growth, but they are much more mobile compared to dislocations in AgCl.

1. Introduction

If AgBr crystals are grown at high Br− concentration with respect to the concentration of silver, tabular crystals with (111) faces are formed. The anisotropic growth habit is due to the presence of usually two or three twin planes [1,2] parallel to a (111) plane, which are easily formed under this condition.

Applying the same procedure to make AgCl tabular crystals, gives rise to a few problems. Due to the high ionic charges, the (111) planes of AgCl are not stable in an aqueous environment, even at high concentrations of Cl−. Consequently no (111) planes can be formed. A solution to this problem is the addition of stabilizers. This, however, reduces the sensitivity of the emulsion and interferes with chemical and spectral sensitization [3].

To avoid the use of stabilizers a method was developed to grow tabular crystals with (100) surfaces [4]. Large (≈ 30 μm) flat AgBr crystals with (100) faces have been prepared for the first time by Mignot et al. in 1974 [5]. Brust and House [6] found a method to produce AgCl (100) tabular microcrystals. Both authors argue that no twin planes are formed and Mignot et al. suggest that screw dislocations are responsible for tabular growth, but only little experimental evidence is provided. Recently Oyamada et al. [7] have presented a growth mechanism for (100) tabular crystals. These authors state that the tabular crystals contain two dislocations which intersect in one corner of the crystal and that their direction is [310] or [130]. Although the Burgers vector is not explicitly determined, they conclude that the dislocations are screw dislocations, which induce the tabular growth. This, however, would mean that the Burgers vector is of the ⟨310⟩-type, which will be contradicted by our measurements and is also unlikely according to the literature [8].

In this presentation the nature of the defects present in AgCl and AgBr (100) tabular crystals is discussed based on a conventional transmission electron microscopy (CTEM) study.

2. Experimental procedures

The AgCl crystals are prepared at Agfa-Gevaert N.V. and two different growth methods are used to produce them. In both cases a double jet method of an AgNO3 solution and a KCl solution is used. The first method starts with a nucleation phase, followed by a physical ripening and finally a growth phase. The crystals grown in this way are in this paper referred to as type 1. The second method, referred to as type 2, also starts with a nucleation phase, after which a small amount of iodide is added. Afterwards there are three physical ripening phases each of them followed by a growth phase [9].

The AgBr crystals are prepared at Agfa-Leverkusen. A double jet method of an AgNO3 solution and a KBr solution is used. The nucleation phase, where small nuclei of AgCl are formed, is followed by a first growth phase with AgBr. Afterwards there are two physical ripenings at different pAg values and finally there is a second growth phase [10].
For the preparation of the specimens for TEM microscopy 50 µl of each emulsion is thinned in 50 ml of doubly distilled water. A drop of this solution is placed on a copper grid covered with a carbon foil and the water is evaporated. To avoid photolytic reaction the preparation of the specimen and the mounting in the microscope are done in a dark room under red light conditions.

The samples are studied with Philips CM20 and CM200 microscopes using a Gatan double tilt liquid nitrogen cooling holder. The results are obtained mainly by diffraction contrast observations. The temperature of the environment around the specimen during the study is kept at approximately 100K to minimize radiation damage.

3. Results for AgCl.

3.1 Characterization of the defects.

The two types of growth methods yield tabular crystals with a different defect structure and it appears that a different mechanism must be responsible for the defects.

When the crystals are fully grown to the desired size (= 1µm) the only defects that occur in both cases are dislocations. The number of dislocations in tabular crystals is limited and usually varies from 1 to 4. They mostly lie in a (001) plane parallel to the top surface of the crystal, although a small component along the [001] axis can not be excluded. During the observations the dislocations appear to be immobile and do not move under electron irradiation. However, it can not be excluded that the dislocations move during the growth process. Exceptionally a tabular crystal occurs with no defects at all. It is, however, impossible to decide whether there were defects present during growth which have disappeared or that the crystal was defect-free all through the process.

a) type 1 crystals

The Burgers vector of the dislocations is determined from diffraction contrast extinction conditions and two different types are found. If the top surface is referred to as a (001)-surface then most of the dislocations are extinct for a 111 and a 220 type of reflection, as shown in figure 1. The combination of the two extinction conditions always leads to a Burgers vector of the (110) type, parallel with the crystal surface. This result is not surprising since in crystals with a face centred cubic structure and in particular with a rock salt structure dislocations with an a/2[110] Burgers vector have the lowest energy [8] and are thus most likely to occur. The direction of the dislocation is mostly along [100] or [010] and it switches often between these two, as observed in figure 1. Also other directions are possible, but the dislocation line practically never runs along a [110] or [1 10] direction, which means that the dislocations are never pure screw nor pure edge dislocations but have a mixed character.

b) type 2 crystals

In this type of crystals only one type of dislocations occurs, which all lie in a (001) plane. From extinction conditions it follows that the Burgers vector is always of the a/2[110] type (the dislocations marked by arrows in figure 2). The main dislocation directions are [410] and [100], but practically never [110]. So all dislocations again have a mixed character. The shape of these crystals as seen in top view is rectangular. In one of the corners one often observes a small dislocation loop, from which
two dislocations originate: one goes to the opposite (100) side plane along a [140] direction and the other goes to the opposite (010) side plane along a [410] direction.

3.2 Origin of the dislocations.

In order to investigate when and how these dislocations are formed, samples are studied that have been taken from the emulsion at different stages during the growth process. This also gives different results for the two types of crystals.

a) type 1 crystals
After the nucleation phase conventional TEM can not distinguish between the different nuclei. They are very small (less than 50 nm) and no defects are observed in these crystals. The shape of the crystals is cubic.

After the physical ripening most of the nuclei did not grow and still do not show any defect contrast. The crystals that did grow are also cubic and they all contain one stacking fault, but contrary to the crystals at the end of the growth process, no dislocations are found (figure 3a). The displacement vector for stacking faults in face centred cubic materials is $\frac{a}{6}\begin{bmatrix} 112 \end{bmatrix}$ and this is confirmed in the present crystals by diffraction contrast analysis.

In samples, taken from the emulsion after 10 to 20 minutes in the growth phase, the number of crystals with a stacking fault decreases. Moreover the stacking fault is not the only defect in those crystals anymore, but one or two dislocations are observed always related with the stacking fault (figure 3b). The directions of these dislocations are [100] or [010], but they can change direction when the crystal further grows. Crystals with a stacking fault and one dislocation have the shape of a needle (figure 3c), with the long side parallel to the dislocation.

The next step is the elimination of the stacking fault. It is known that a stacking fault can only end at the surface or at a partial dislocation. Moreover, the movement of such a partial dislocation causes the faulted area to enlarge or to reduce or even to disappear. So the formation of a partial dislocation and the subsequent movement to a side plane, can eliminate the stacking fault. Figure 3d shows that such a process is very likely to be the cause for the disappearance of the stacking faults in these samples. The stacking fault (SF) no longer runs from one side of the crystal to the opposite one, as in figure 3a-c, but seems to be partially eliminated at two places by the formation and subsequent movement of the indicated partial dislocations (PD). At the end of the process the partial dislocation also reaches the surface and disappears together with the stacking fault. This process will probably be very fast and a intermediate situation like in figure 3d is only rarely observed. However, we assume that most crystals undergo this process because when they are fully grown all tabular crystals contain exclusively dislocations as residual defects.

b) type 2 crystals
A totally different kind of process seems to be responsible for the formation of the dislocations in type 2 crystals. Crystals that are taken from the emulsion after the physical ripening or during the first growth phase have no stacking fault, but all crystals are very small and only during the first growth phase dislocations are observed. Once the dislocations are formed the tabular growth of the crystals proceeds. The direction of the dislocations does not change very much, except for a few short segments. The origin of these dislocations is related to the addition of iodide after the nucleation phase, which induces lattice strains because of their larger radius. To verify this, an emulsion is grown under the same conditions as for the second growth method but without the addition of iodide after the nucleation phase. The result is a serious decrease of the number of tabular crystals and the defect structure is similar to that of the crystals of type 1.

In order to correlate the presence of the dislocations more firmly with the tabular growth, the position of the nucleus in the fully grown crystal is determined. Crystals are grown according to growth method 2 but at three...
At the end of the growth process dislocations are the defects that occur in most crystals. From extinction conditions it was determined that the Burgers vector is again of the $\frac{a}{2}(110)$ type. The dislocation lines do not run as straight as in the AgCl-crystals, but, as shown in figure 5, they are stepped. However, they still lie in a plane parallel to the (001) top surface and end only at the side planes.

Another difference with AgCl is that the dislocations are much more mobile in AgBr. Dislocations in an AgCl microcrystal were not observed to move under electron irradiation, but in AgBr crystals they were. This could also explain why the dislocations are stepped.

In approximately a third of the tabular crystals, no defects were observed, but for a small dislocation loop in one of the corners of the crystal. This number is much higher than in AgCl emulsions. The most logical explanation for this is that the crystal during the growth process did contain dislocations that induced the anisotropic growth, but that, due to the higher mobility, the dislocations have moved out of the crystal at a later stage during the growth process.

The origin of the dislocations in AgBr crystals was not studied since no samples were taken from the emulsion during the growth process. It is therefore not possible to correlate the AgBr crystals with AgCl crystals of type 1 or type 2.

5. Discussion of the results related to tabular growth.

In the crystals studied, many indications are found that accelerated growth occurs at surface steps caused by defects. In crystals of type 1 after the physical ripening, the largest crystals are those that contain a stacking fault and their shape is cubic, which confirms that there is a step of equal height on all three faces. In the needle-like crystals, containing a stacking fault as well as one
Two different growth methods are developed to grow AgCl tabular crystals with (100) surfaces. For crystals resulting from growth by these two methods a limited number of mixed dislocations with mostly an $a/2[110]$ Burgers vector are responsible for the tabular growth. The origin and formation of the defects is different for the two types of crystals. In crystals of type 1 the first a stacking fault with a displacement vector of $a/3[111]$ is formed, while later during the growth process dislocations are formed always in correlation with the stacking fault. In a final step the stacking fault is erased by the formation and subsequent movement to the surface of $a/6[112]$ partial dislocations. For type 2 the dislocations are formed due to the incorporation of a small amount of iodide after the nucleation phase. They already originate in the early stages of the growth process and are not subjected to major changes anymore. For AgBr (100) tabular crystals also mixed dislocations with an $a/2[110]$ Burgers vector are responsible for the anisotropic growth, but the origin of the dislocations was not studied.

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