Growth Mechanism of Vapor-Grown Silver Crystals: Relation between Twin Formation and Morphology

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This study deals with the morphology and growth mechanism of multiply twinned Ag crystals grown from the vapor phase. Ag crystals were grown under sublimation conditions for small growth rates as a function of the driving force and sublimation temperature. At relatively low driving force and low temperature cubooctahedrons and single twinned crystals appeared. At higher driving forces also {111} tabular crystals (containing multiple parallel twin planes) and 5-fold twinned structures resulting in decahedrons, icosahedrons, and elongated decahedrons bounded by {100} sides faces, were observed together with other nonparallel twinned crystals. Increasing the driving force further led to tabular crystals with higher aspect ratios and different side-face structures; the preferential unidirectional growth of the elongated decahedrons was also increased. The growth mechanism of {111} tabular Ag crystals and other multiply twinned Ag crystals is for the first time studied in detail. The influence of the driving force and the ratio of the growth rates $G\{100\}$ and $G\{111\}$ on the morphology is examined. The preferential lateral growth of twinned Ag crystals is explained by a substep mechanism. The relation between vapor-grown tabular Ag crystals and tabular AgX (X = Cl, Br) grown from solution and from the vapor is discussed. The similarities in the growth mechanism give a new insight into the role the ionic character of AgX has in the twin formation.

1. Introduction

Much research has been done to study the different morphologies of Ag and other face-centered cubic (fcc) metals grown from the vapor on alkali halide surfaces.[1,2] These studies reveal a low threshold for twinning parallel to the {111} faces. Kimoto et al.[3,4] studied multiply twinned particles of Au produced by condensation in argon at low pressures. The sizes of these particles ranged from 10 nm to 1 μm. Two types of multiply twinned particles showed a nearly perfect 5-fold symmetry. The first is a decahedron composed of five tetrahedra that are connected with each other via twin planes parallel to the ⟨111⟩ directions. The other crystal is an icosahedron built up by 20 tetrahedra related through twin planes sharing a common central point. Both types of particles were bounded only by {111} faces. Kimoto and Nishida[3] studied fine smoke particles of several fcc metals and other metals. For Ag and Au they observed hexagonal shapes, multiply twinned crystals with 5-fold symmetry, and tabular hexagonal or truncated triangular crystals. The diffraction patterns of the tabular crystals showed anomalous intensities that they could not explain. Uyeda[5] found in comparable experiments for different fcc metals single octahedra that were more or less truncated, truncated triangular bipyramids (single twinned crystals bounded by {111} and {100} faces), thin tabular crystals with {111} top faces, decahedrons, and icosahedrons. The 5-fold and 3-fold symmetries were also found in silver clusters by Giorgio and Urban.[6,7] These clusters, with sizes of 1−8 nm, were condensated in argon gas cooled to liquid-nitrogen temperature. Techniques to stabilize and study small clusters, with sizes down

to 1 nm, of transition and noble metals have been developed in recent years (see refs 8 and 9 and references therein). Such small clusters of Au show besides the fcc, decahedral and icosahedral structures and also amorphous structures.[9]

Hayashi et al.[10] solved the structure of the thin tabular crystals discussed by Kimoto, Nishida, and Uyeda. They found that these flat truncated triangular and hexagonal plates had several parallel {111}-type twin planes. Recently, Gotoh et al.[11] studied in situ the vapor growth of twinned Ag crystals on a Mo(110) surface. They observed that a twin was formed on a {111} face of a cubooctahedron. A reentrant groove was present between two {111} faces intersecting at the twin plane. Owing to the reentrant corner mechanism, which acts as a step source, the {111} faces will grow out, leaving two {100} faces in a ridged configuration.

For the understanding of the growth mechanism of AgBr and other silver halide crystals, it is important to realize that despite the different nature of the species in silver halide (ions) and fcc metals (atoms) the large variety of morphologies for the two is the same. For AgBr (NaCl structure) the same morphologies, also containing {111}-type twin planes, have been found. {111} tabular AgBr crystals can be grown from precipitation in water,[12] by extractive crystallization in DMSO,[13] and from the vapor phase.[14] Tabular AgBr crystals are used in the photographic industry. The photographic process takes place around the surface of the crystal. Tabular crystals have a relatively large surface, and therefore, less Ag is needed for the same exposed surface as compared to block-shaped crystals.

In this study we will focus on the growth mechanism of all (multiply) twinned Ag crystals. Tabular crystals, twinned

TABLE 1: Morphologies That Make up at Least a Few Percent of the Total Crystal Population, Observed in Two Regimes[a]

regime	morphology	percentage twinned crystals	furnace temp (°C)
1	cubooctahedral, single twinned	30−48	700−800
2 (low driving forces)[b]	cubooctahedral, single twinned, {111}	60−90	850
	tabular (ridged, mixed), decahedrons, icosahedrons, elongated decahedrons and needles		
2 (high driving forces)[c]	cubooctahedral, single twinned, {111}	>95	850−900
	tabular (mixed), needles		

[a] The percentage of twinned crystals for each regime and the sublimation (furnace) temperature are given. [b] Low driving force means that the crystals were observed close to the middle of the furnace where the temperature difference between the substrate and the furnace is small (first 8 cm on the substrate). [c] High driving force means that the crystals were observed close to the outside of the furnace where the temperature difference between the substrate and the furnace is larger (from 8 to 22 cm on the substrate).

crystals with 5-fold symmetry, and other twinned crystals were grown from the vapor. The growth conditions, however, were different from those used in the references on silver and other metals mentioned above. In the present study the material was sublimed instead of evaporated and the substrate temperature was relatively high, resulting in smaller to moderate driving forces or supersaturations and relatively small growth rates. Moreover, the substrate was given a temperature gradient in order to be able to study the crystal morphology and growth mechanism as a function of the driving force and the sublimation temperature. Thus the results obtained in earlier studies for the ionic crystals of AgBr can be compared with those of the metallic Ag crystals. The preferential growth rate (lateral for tabular crystals and unidirectional for needles) of the twinned crystals is explained by a substep mechanism based on the twin-lamella mechanism developed by Ming et al.[15−17]

2. Experimental Section

The experimental procedure is essentially the same as described for the growth of AgX (X = Cl and Br) crystals grown from the vapor.[14] A schematic diagram of the setup can be found in Figure 1 of ref 14. Ag crystals were grown in a sealed quartz tube. The tube was filled with 200 mg of pure (99.9%) Ag grains of approximately 1 mm diameter. The evacuated tube was sealed with a background pressure outside the tube lower than 10^{-6} mbar. No carrier gas was used. The observed morphologies turned out to be not very sensitive to the final evacuation pressure, and no further precautions were taken to avoid residual gas species or effects of surface oxidation. The growth experiments were performed for a period of 100−170 h. The sublimation (furnace) temperature varied between 260 and 60 deg below the melting point of Ag for the different experiments but was constant during each experiment. The crystals were grown on a quartz substrate. This substrate was a quartz wire with a diameter of 2 mm having the same length as the tube. The quartz tube had a length of 50 cm and a diameter of 9.0 mm. The tube was placed 35 cm in the furnace and 15 cm outside the furnace (room temperature). The substrate temperature in the furnace, therefore, had a gradient. In the middle of the furnace (at the position where the 200 mg of Ag was located) the substrate temperature is the highest (equal to the actual furnace temperature). The gradient across the substrate was estimated to be 1.5 °C/cm. The crystals grown on the substrate were located 3−22 cm from the middle of the furnace. Morphologies were studied as a function of the driving force (position on the substrate) and for different sublimation temperatures. After the growth experiments the quartz substrate and the tube were cut in parts and prepared for examination by scanning electron microscopy (SEM). The different crystals found on the substrate were also found at the same positions on the inner wall of the tube. With SEM we could find the
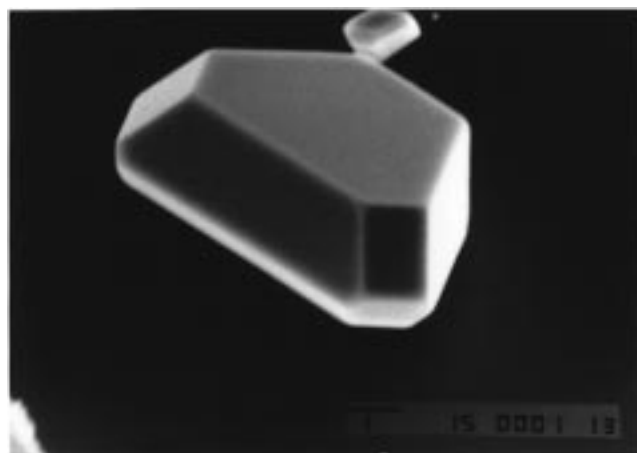

Figure 1. Single twinned Ag crystal. The small rectangular side faces are {100} faces; the other faces visible are {111} faces. The twin plane is parallel to the large {111} top face and is situated between the two faces on the crystal sides. The bar represents 1 μm.

precise positions of the different morphologies and reveal the side-face structure of the {111} tabular crystals and the elongated decahedrons. This was done by positioning the crystals perpendicular to the image and roughly measuring the angle between the faces and by judging the shape of the faces. Triangular- (or hexagonal-) shaped side faces were indexed as {111} faces and the rectangular-shaped ones as {100} faces. The vacuum pump was a Balzers TCP 1231 and the SEM used was a JEOL JSM-T300.

3. Results

3.1. Observed Morphologies. We observed, depending on the sublimation temperature and the position on the substrate, two regimes in which different morphologies were found (see Table 1). The size of the observed crystals varied between 0.5 and 50 μm.

3.1.1. Morphology of Regime 1. Both cubooctahedral and single twinned crystals (see Figure 1) were observed in this regime. The shape of the cubooctahedral crystals varied. The single twinned crystal in Figure 1 is an example of a crystal having the maximal growth rate difference between the {111} and {100} face. Therefore, it is concluded that the growth rate of the {100} faces and the {111} faces was comparable in this regime. The conditions for this regime were low driving forces and low sublimation temperatures (see Table 1). In this regime the majority of the crystals had no twin plane.

3.1.2. Morphology of Regime 2 (Low Driving Forces). In the second regime, a rich variety of crystal morphologies was observed. All crystals were again bounded by {100} and {111} faces. A total of 45% of the total crystal population was made up of single twinned and cubooctahedral crystals. The ratio
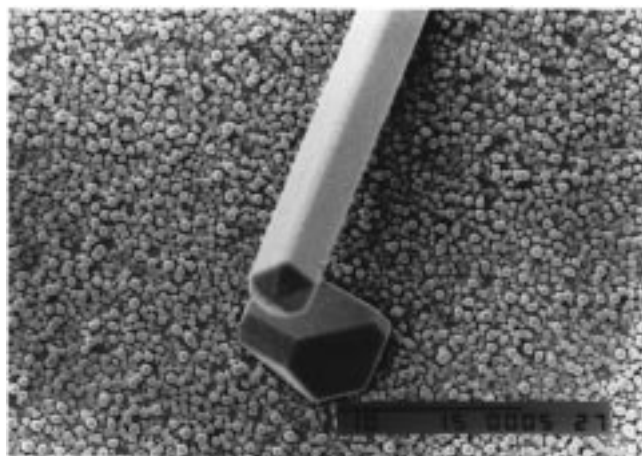
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Figure 2. Elongated decahedron appearing at the beginning of regime 2. The triangular top faces are {111} faces, and the side faces are {100} faces. The bar represents 10 μm.
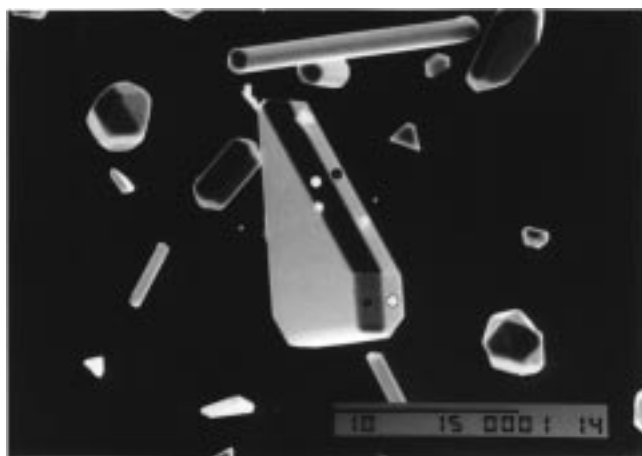

Figure 3. Tabular Ag crystal with a ridged side-face structure observed at low driving forces of regime 2. A crystal side contains two side faces, a {111} face (indicated with white circles) and a {100} face (indicated with black circles). The twin planes are located between the side faces parallel to the large {111} faces. The bar represents 10 μm.
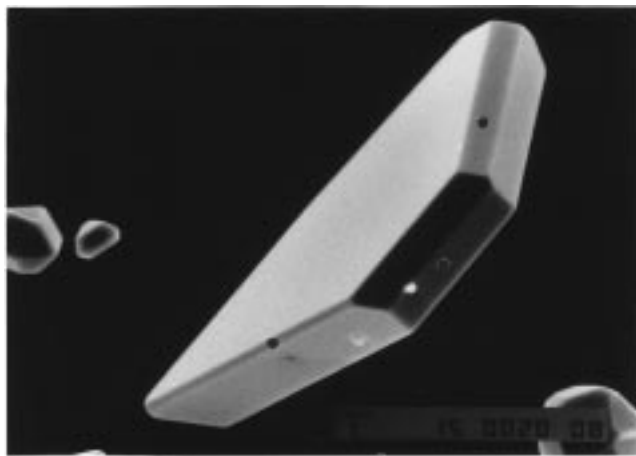

Figure 4. Tabular crystals with a mixed side-face structure observed in regime 2. Owing to the relatively higher growth rate, the {100} faces (indicated by black circles) on the crystal sides are smaller than the {111} side faces. Especially, the {100} face on the lower side in the figure does not touch the region of the twin planes in the middle of the crystal. The bar represents 1 μm.
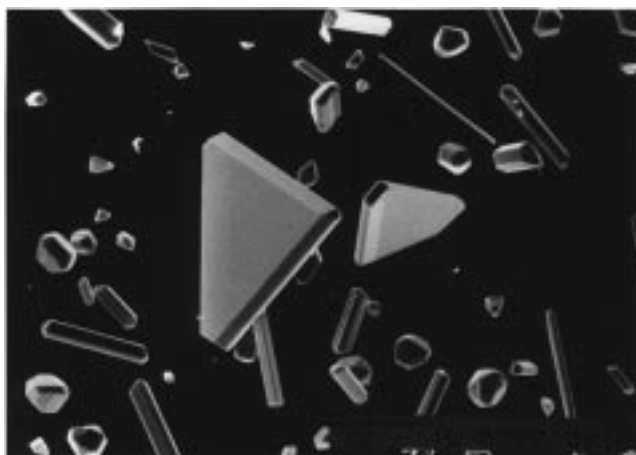

Figure 5. Overview of the crystals at the beginning of regime 2. The tabular and needle-shaped crystals can express preferential growth and therefore have larger sizes than the other cubo-octahedrons and single twinned crystals. The bar represents 10 μm.

between the occurrence of single twinned versus cubooctahedral crystals was increased to over 60%. The 5-fold twinned crystal morphologies consisted of decahedrons, icosahedrons, and elongated decahedrons. The elongated decahedrons are bounded by {100} side faces and {111} top faces (see Figure 2). This morphology was also observed for Ni crystals by Melmed and Hayward[18] and later by Gillet and Brieu.[19] The 5-fold twinned crystals made up around 10% of the total crystal population. The {111} tabular crystals, which made up around 8% of the observed crystals in this regime, were bounded by two large {111} top and bottom faces (see Figures 3 and 4). Two possible side-face geometries for tabular crystals were observed in this regime. A crystal side of the first side-face structure consists of a {100} and a {111} face in a ridged structure, as depicted in Figure 3. For the other geometry the {100} side faces were partly grown out of the crystal habit (Figure 4). This results in relatively large {111} side faces and small {100} side faces. The needle-shaped crystals (30% of the total crystal population) are the earlier discussed elongated decahedrons or other needles without a 5-fold symmetry. The majority of the needles without 5-fold symmetry had the same morphology as was observed for AgCl needles grown from the vapor phase.[20] The other needles also had this morphology; only one or more extra twin planes (parallel to the growth direction) were present. From

Figure 5 one is able to see that the tabular and needle-shaped crystals can express preferential growth and are therefore larger than the other crystals (twinned or not). The preferential growth that can occur owing to the presence of twin planes will be described furtheron. The last group of crystals in this regime was made up of multiply twinned crystals having a morphology that was rarely observed (in some cases merely once). Most of the multiply twinned crystals had a small separation between the twin planes but for some of these crystals the separation could be observed. An example of a rarely observed crystal was the tetrahedrally shaped one (see Figure 6). This shape was not previously observed for Ag, but some smoke particles of the fcc metal Yb had the same shape.[21] Goessens et al.[22] observed the same morphology for AgBr crystals. They found that the defect structure of these tetrahedrally shaped crystals consists of two nonparallel (111)-type twin planes enclosing an angle of 70.5°.

3.1.3. Morphology in Regime 2 (High Driving Forces). For the highest driving force in the second regime, that is, at the positions corresponding to the largest temperature difference between the furnace temperature and the substrate temperature, the large majority of the crystals appeared. There were {111} tabular crystals and needle-shaped crystals and to a lesser extent
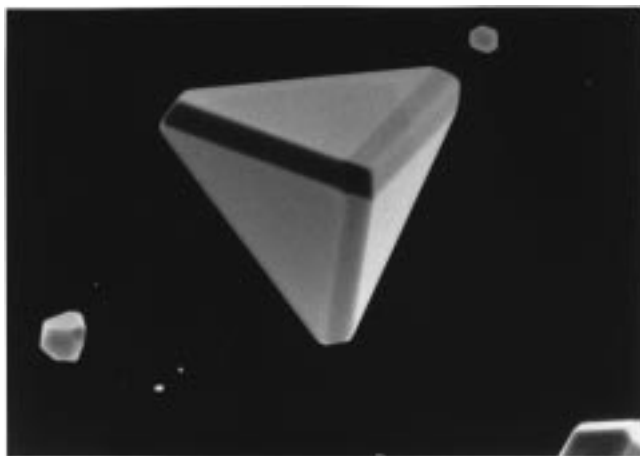
Figure 6. Tetrahedrally shaped Ag crystal observed in regime 2. The defect structure of this crystal is determined to consist of two nonparallel (111)-type twin planes enclosing 70.5°.[22] The size of the crystal is 5 μm.

Figure 7. Needle and tabular crystals observed at high driving force in the second regime showing large aspect ratios. The side-face structure of the tabular crystals is mixed. The small horizontal side face is a {100} face (visible on the top of the front crystal side). The bar represents 10 μm.

single twinned crystals. The difference in sizes between crystals that have preferential growth (tabular and needles) and the other crystals was further increased. All observed single twinned crystals were only bounded by {111} faces. This indicates that the growth rate of the {100} faces as compared to the {111} faces was further increased as the driving force increased. For AgBr and AgCl crystals grown from the vapor phase it was also observed that increasing the driving force leads to a relatively higher growth rate for the {100} faces.[14] The morphology of the needle-shaped crystals was not clear enough to determine because of the high aspect ratio (see Figure 7) for all tabular and needle-shaped crystals in this regime. The separation between the twin planes could not be observed. For other (rarely observed) multiply twinned crystals no separation between the twin planes could be observed with SEM either.

3.2. Tabular Crystals. *3.2.1. Number of Twin Planes.* For the majority of the tabular crystals we could not determine the separation between the different twin planes. Therefore, we assume that twin planes were formed during or shortly after the nucleation stage. If in cubooctahedral crystals a twin plane is present parallel to the [111] direction this results in a rotation over 60° of the top with regard to the bottom of the crystals. A crystal side is then no longer built up of a {111} and a {100}

face but contains either two {100} or two {111} faces in a ridged structure (see the single twinned crystal in Figure 1). A second twin plane will therefore give, owing to the rotation of 60°, the same morphology as a single cubooctahedron (neglecting the faces between the twin planes). Three nucleation twin planes will give the same morphology as a single twinned crystal (neglecting the structure between the twin planes) and so on.

Over 90% of the tabular crystals show a morphology of a flat cubooctahedron or a flat octahedron. This means that these tabular crystals have an even number of twin planes (probably two). The rest of the tabular crystals have an odd number of twin planes (probably three, as will be explained furtheron). In all cases the nucleation twin planes are parallel to the large top and bottom faces and extend throughout the crystal. They are confined to a small region in the middle of the crystal.

3.2.2. Side-Face Structures. We observed two kinds of side-face structures for the tabular crystals as a function of the driving force and the growth temperature. At the lowest growth temperatures and driving forces, tabular crystals were observed with a ridged structure (see Table 1). These crystals have the morphology of a flat cubooctahedron for which the {100} and {111} side faces touch the region where the twin planes are located, that is, in the middle of the crystal (see Figure 3). The aspect ratio of these tabular crystals was between 4 and 13.8 with an average of 7.5. For the second group of tabular crystals the {100} faces on the crystal sides were relatively smaller (see Figure 4). The {100} faces no longer touch the region of the twin planes in the middle of the crystal. The aspect ratio of these, what we call, mixed tabular crystals was between 6.5 and 60 with an average of 18.5.

4. Discussion

4.1. Twinning Mechanism. *4.1.1. Twinning Mechanism of 5-Fold Crystals.* Five-fold twinned crystals (decahedrons and icosahedrons) have attracted attention of different research disciplines.[23] Five-fold twinned crystals are observed for a variety of fcc metals and NaCl-type compounds. The formation of twins in those crystals can proceed according to different mechanisms.[23] Ino[1,2] observed that multiply twinned crystals, nucleated on a (100) NaCl substrate, are already formed in the earliest stage of nucleation in which the thickness is less than 5 Å, that is, before the beginning of appreciable coalescence of nuclei (overgrowth of neighboring nuclei). Therefore, it seems that multiply twinned particles do not result from coalescence but are formed in the nuclei themselves. Yagi et al.[24] observed the growth process of multiply twinned particles of Ag and Au, on a (001) MgO substrate, using in-situ SEM. They found that multiple twin planes could be formed by successive twinning and also by nucleation of twinned particles followed by equilateral growth. They also observed that multiple twinned particles can rearrange themselves after overgrowth. This indicates that twin planes can also be formed by overgrowth. Gillet[25] found, using electron diffraction and electron microscopy, evidence that small clusters first have an icosahedral shape and contain a noncrystallographic packing. Giorgio and Urban[6,7] found an equal distribution of icosahedra and cubooctahedra for 4−8 nm size Ag clusters using high-resolution electron microscopy (HREM). Martin et al.[26,27] found, with photoionization time-of-flight mass spectrometry, small clusters of Na, K, Ca, and Mg. They also found indications that these clusters have an icosahedral shape. These clusters grew with a layer by layer growth mechanism to sizes at which the clusters transformed into a 5-fold twinned structure with an fcc stacking. Bovin and Malm[8] observed such structural changes in Au

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clusters using high-resolution transmission electron microscopy. The HREM images of Au clusters of a few nanometer size were studied theoretically by Ascencio et al.,[9] showing fcc, decahedral, icosahedral, and amorphous structures.

In conclusion, small clusters can nucleate with different structures and even transitions from one structure to the other are observed. Once these nuclei become larger, the icosahedral structure becomes unstable and probably is transformed in a 5-fold twinned fcc crystal. The morphologies of these crystals are small decahedrons, small icosahedrons, and elongated decahedrons.

The structures with less than five nonparallel twin planes are stable and grow out to, respectively, cubooctahedrons or octahedrons, tabular crystals, tetrahedra, and needles.[14,20,22]

4.1.2. Twinning Mechanism of Tabular Crystals. In contrast to 5-fold twinned crystals, the twinning mechanism of tabular fcc metal crystals is not extensively studied. However, for AgBr (NaCl type) the mechanism of twinning of the commercially important tabular crystals is studied in great detail. Two mechanisms that explain the formation of the parallel twin planes have been proposed. Twin planes can be formed due to coalescence of microcrystals in aqueous solutions.[28,29] In the other mechanism twin planes are formed if the supersaturation on the {111} surface is high enough to form twin planes.[30,31] At these supersaturations twinned two-dimensional nuclei can grow out to a complete twinned layer. Another coalescence mechanism, in which neighboring crystals nucleated on a substrate coalesce during their growth, was proposed by Yagi et al.[24] for fcc metals. However, for Ag crystals, grown on the quartz substrate, no specific orientation and no specific faces parallel to the substrate were observed (Figure 5 shows the random orientation of the crystals). Thus, the chance that well-defined twin planes are formed by coalescence is small. Another possibility for the formation of twin planes is that noncrystallographic clusters appear in the nucleation stage, analogous to the 5-fold twinned crystals. A cluster can have a noncrystallographic packing that at larger sizes would transform into an fcc structure with parallel twin planes. The presence of clusters would indicate that the distance between the parallel twin planes is fixed. For AgBr tabular crystals different distances between the twin planes were observed with transmission electron microscopy.[32] For tabular Ag crystals the distance between the twin planes was in most cases too small to be observed with SEM (<0.1 μm). Occasionally, we could observe the separation between the twin planes (see Figure 8). This indicates that the distances between the twin planes for Ag are not fixed either. Thus, the possibility that parallel twin planes are formed by a noncrystallographic packed cluster is not likely.

According to the concept of Jagannathan,[30] twinning can occur above a certain critical surface supersaturation. So, if twinning was only caused by the bulk driving force, one would expect a continuous formation of twin planes at constant driving force. In our experiments we have seen that increasing the driving force (being in our experiments the temperature difference between the furnace and the substrate) leads to more twinning (see Table 1). For tabular crystals the twin planes were mostly formed during the nucleation (nucleation twin planes). However, during the experiment the driving force was constant. Thus, the chance of forming twin planes (at constant driving force) decreases with increasing crystal size. Another indication for this crystal size dependence is given by the observation of tabular crystals with large separations between the twin planes. Those tabular crystals appeared only at the beginning of regime 2. At the high driving force of this regime, where the preferential
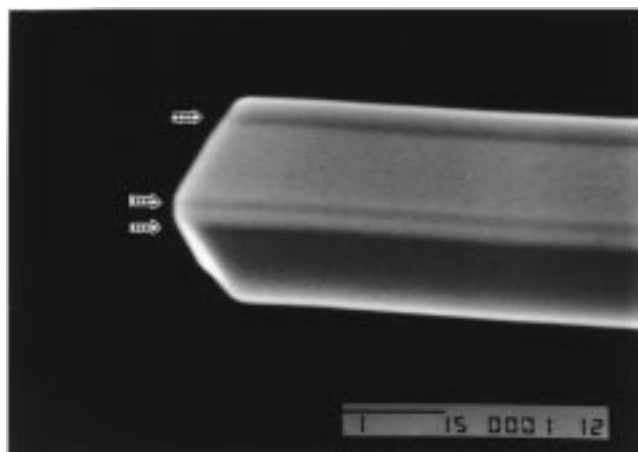

Figure 8. Side-face structure of a {111} tabular crystal observed in regime 2. The twin planes are marked with arrows. In most of the crystals the separation between the twin planes could not be observed. From the morphology of this crystal, it is concluded that the twin planes are single twin planes. The bar represents 1 μm.

lateral growth of the tabular crystals is faster, such crystals were not found. Faster lateral growth will increase the crystal surface and thus decrease the chance of forming additional twin planes. The same size (and driving force) dependence was found for AgBr and AgCl tabular crystal grown from the vapor phase.[31]

We will try to explain the crystal size effect by looking closely at the growth of a small and a large crystal. Both crystals will be placed in a supersaturation where twin planes can be formed. On both crystals there is a chance of forming a "twinned" critical two-dimensional nucleus. We assume that the chance of forming a twinned critical nucleus is smaller than the chance of forming a correctly stacked nucleus and the growth rate of the twinned nucleus is lower because the energy for the twinned nucleus is higher. If a twinned nucleus has been formed on a small crystal, the chance is high that it will grow out and form a full growth layer, because we assume that this growth process is relatively fast as compared to the formation of additional critical two-dimensional nuclei. A larger surface, on the other hand, has more chances of containing more two-dimensional nuclei at the same time. When a twinned and a regularly stacked island meet, the latter is favored because of the lower energy and the twinned island will evaporate. Thus, small {111} faces have a larger chance of forming a complete twinned layer.

In conclusion, the concept that twin planes are formed by a layer by layer growth mechanism is for tabular Ag crystals the most likely one. This mechanism is more generally valid as it can also be applied to AgBr and AgCl tabular crystals grown from the vapor phase. The difference with the 5-fold twinned crystals is that the latter probably originate from real icosahedral structures that become unstable on further growth. The resulting 5-fold twinned crystals have single twins, showing no preferential growth.[33] Tabular crystals originate from nuclei with a single twin, followed by a second parallel twin, resulting in fast lateral growth, as will be explained in the next section.

4.2. Growth Mechanism of {111} Tabular Ag Crystals. Hayashi et al.[10] examined, for several fcc metals, which {111} tabular crystals contain multiple parallel twin planes. However, they did not study the side faces of the tabular crystals. For AgX (X = Cl, Br) also tabular crystals, containing multiple parallel twin planes, were found.[14] The {111} tabular AgBr crystals studied contained two or three twin planes parallel to the [111] direction.[32,34,35] The side-face structure of the tabular crystals was revealed by Bögels et al.[36,37] for tabular crystals

grown from DMSO and later by Hosoya and Urabe[38] for tabular crystals grown with the industrial precipitation method. The majority of the {111} tabular crystals have two twin planes. Owing to the separation of some 50 nm between the twin planes SEM is not suited to observe the side faces between the twin planes. For tabular Ag crystals the same side-face structures were observed as for tabular AgBr crystals.[36] From our morphology determination we conclude that over 95% of the tabular crystals contain an even number of twin planes (probably two). If the driving force was increased, the side-face structure changed from ridged to mixed and the aspect ratio of the tabular crystals increased. In the following we will explain the growth mechanism of tabular crystals and the effect of changing side-face structures for a higher driving force.

The lateral growth model (substep mechanism[36]) is based on the twin-lamella mechanism developed by Ming et al. for fcc structures.[15−17] The model, built up of spheres as growth units, assumes that the fastest growth takes place at the position where an adatom incorporated on the surface has the maximal number of nearest neighbors. An adatom incorporated on a {111} face has three and on the {100} faces four neighbors. Therefore, we assume that the growth rate of the {100} faces is higher than the growth rate of the {111} faces. In the substep mechanism the relatively fast growing {100} faces are "the motor" for the preferential lateral growth. These faces are capable of producing substeps (with four or five nearest neighbors) at the position of the twin planes on the adjacent {111} side faces. These substeps will form steps on the {111} faces and thus increase the growth rate of the whole crystal side. In other studies, the substep mechanism is explained in more detail for the same side-face structures of AgBr tabular crystals.[36,37]

For the ridged tabular crystals (Figure 3) appearing in the second regime, two side-face structures are possible (neglecting mirror images): a {100} face between the twin planes and the other a {111} face. From the shape of the cubooctahedrons (observed at the same position as the ridged tabular crystals) we know that the growth rate of the {100} faces is somewhat higher than the growth rate of the {111} faces. At the position of the twin plane an adatom incorporated there has four or five neighbors. This indicates that the twin planes themselves, together with the faster growing {100} face, can act as a step source and thus increase the growth rate of the whole crystal side.

At a higher driving force the growth rate of the {100} faces is increased as compared to the {111} faces. This is also observed for mixed tabular crystals (Figure 4) as the {100} faces adjacent to the tabular face are already partly grown out of the crystal habit. These little {100} faces cannot increase the growth rate of the crystal side.[37] For the mixed tabular crystals two side-face structures are possible (neglecting mirror images): again, one with a {100} face and the other a {111} face between the twin planes. The crystal side with the {100} face present between the twin planes can increase the growth rate of the two adjacent {111} side faces by supplying substeps for these faces. Due to the relatively faster growing {100} face as compared to the {111} face, the aspect ratio of those crystals will be higher than that of tabular crystals with ridged side-face structures. Crystal sides with a {111} face between the twin plane can only have preferential growth at the position of the reentrant corner (four neighboring atoms) and therefore will have lower growth rates and therefore a lower chance to be observed.[37]

Thus, according to the substep mechanism, an increasing relative growth rate of the {100} faces leads to higher aspect ratios and side-face structures in which the {100} faces are (partly) grown out. This is in good agreement with our observations.

4.3. Growth Mechanism of Twinned Needles. Gillet and Brieu[19] studied Ni particles with icosahedral and decahedral shapes. They found that the decahedral crystals often have an elongated shape. They observed that these crystals were built up by five {111} top and five {111} bottom faces connected with five elongated {100} side faces. Melmed and Hayward[18] observed whiskers of Ni, Fe, and Pt. The morphology of the whiskers is the same as found for the elongated shapes of Gillet and Brieu.[19] Skillman and Berry[39] studied a rich variety of multiple twinned AgBr crystals. They also observed decahedrons and needles of decahedrons bounded by {100} side faces.

We observed decahedrons (pentagonal bipyramids), icosa-hedrons and elongated decahedral crystals for Ag in regime 2. The preferential growth of the elongated decahedral crystals can be explained by the angular misfit that produces a gap between the tetrahedral subunits of 7.35°. Melmed and Hayward speculated that growth of whiskers occurs owing to the angular mismatch that can cause a nonvanishing step at each twin boundary. We observed a groove at some elongated decahedrons along one twin plane; this groove was also observed for AgBr crystals.[39] This indicates that the major part of the angular mismatch is located at only one twin plane. A nonvanishing step or another step source, like a rough growing face, can be located in that region. Steps on a {111} face can grow onto the other top faces while the {111} top faces are connected via twin planes[36] and therefore increase the growth of the entire needle top.

The other needles observed in the second regime contain also nonparallel twin planes. Those needles were bounded on their top and sides by {100} and {111} faces. The majority of these needles had the same morphology as AgCl needles grown from the vapor phase. The growth mechanism of this needle was also explained, on the basis of the substep mechanism, in another study.[20]

5. Conclusions

A rich variety of morphologies is found for Ag crystals grown from the vapor phase. Twinning together with the preferential lateral growth owing to the substep mechanism explains this rich variety. The twinning of tabular Ag crystals grown from the vapor is probably caused by twinned two-dimensional nuclei, which can grow out to form a twinned layer. This will only occur when the supersaturation is above a critical value and the crystal size is small. Thus, the chance of forming twin planes is decreased with increasing crystal size. This crystal size dependence explains why the twin planes are only formed during the nucleation stage. The coalescence mechanism is not very likely to form twin planes in Ag crystals.

The 5-fold crystals probably originate from icosahedral clusters that become unstable at a certain size and transform to 5-fold twinned fcc crystals. The twins are nonparallel single twins showing no preferential growth.

All morphologies and shapes were also observed for AgBr crystals grown from different crystallization techniques. The morphologies of the {111} tabular crystals were the same as observed for AgBr and AgCl crystals. With the substep mechanism we were able to explain the preferential growth of the tabular crystals in different circumstances. The effect of relatively higher growth rates of the {100} side faces leads to higher aspect ratios and side faces for which the {100} faces are partly grown out of the crystal habit. The similarity between

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the fcc metals and the NaCl structures implies that the substep mechanism is generally valid. The substep mechanism also explains the different needle morphologies for which nonparallel sets of {111} twin planes together with the substep mechanism determine the morphology. Finally (multiply) single twinned crystals and single crystals showed no preferential growth.

The twinning mechanisms of (tabular) Ag, (tabular) AgBr, and AgCl crystals are very analogous. This gives a new insight into the twinning mechanism and the role played by the charge for AgBr and other NaCl structures. Although the charges in the ionic crystals are expected to play a role in the formation and stability of twin planes in these crystals, the morphologies observed are essentially the same as for fcc metal crystals. Therefore, we conclude that the role of these charges is of minor importance for the formation of twins and for the preferential growth owing to the substep mechanism. This minor role has been an assumption in our study of the substep mechanism in earlier papers.[36,37] To study the validness of this assumption in further detail, we intend to study the morphology of molecular (noncharged) fcc crystals.

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