The Influence of Silver Halide Crystal Thickness on Image Tone

W. Van Renterghem, D. Schryvers* and J. Van Landuyt

EMAT, Universiteit Antwerpen (RUCA), Antwerpen, Belgium

C. Van Roost and R. De Keyzer✦

Agfa-Gevaert N.V., Mortsel, Belgium

It is known that the neutral image tone of a developed photographic film becomes brownish when the thickness of the original silver halide tabular crystals is reduced. We investigate by electron microscopy to what extent the silver filament structure has changed and how it induces the shift in image tone. Therefore, two samples of AgBr {111} tabular crystals with average thicknesses of 160 nm and 90 nm respectively, are compared. It is shown that the dimensions and defect structure of the filaments are comparable, but that the 90 nm crystals result in a more widely spaced structure, which explains the shift in image tone on a qualitative level. The influence of the addition of an image toner, i.e., phenylmercaptotetrazole, on the filament structure is also investigated. An even more open filament structure of longer, but smaller filaments was observed.

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Introduction

During the development of a photographic film the growth of the silver nucleus is continued until the entire silver halide crystal is reduced to silver. The morphology is not a single crystal of silver, but an aggregate of spherical to filamentary particles at the location of the original silver halide crystal. The most widely used development method, which is also applied for this investigation, is chemical development. For this method the exposed film is brought into contact with a solution that does not contain a silver salt, but that selectively reduces the exposed crystals.[1] Initially the developing agent adsorbs on the grain surface and provides electrons to the silver nucleus, which becomes negatively charged.[2] New silver interstitials are attracted by the silver nucleus and are reduced to silver, allowing the silver nucleus to grow. Once the silver nucleus reaches a critical size, the reaction becomes autocatalytic. Oxidation of the developer occurs at the interface between the silver cluster and the solution, while reduction of silver ions occurs at the interface with the silver halide crystal. In this way the silver halide crystal is transformed into a silver crystal. The excess bromide ions diffuse into and are diluted by the solution.

The method and parameters of development influence the morphology of the silver filaments and the color of a developed photographic film, which is generally called the image tone. A blue-black color is esthetically more pleasing than a warmer colored image, but is not always obtained under the development conditions.[1]

There are several factors that influence the image tone. A first one is the particle size. The transmission and scattering color of silver hydrosols have been measured by Wiegel[3] as a function of particle size. It was observed that the transmission color changed from yellow, over violet, to grey-green as the particle size increased from 10, over 50, to 120 nm respectively. The scattering color changed from blue, over yellow-green, to red-brown for the same particle sizes. At the beginning of the 20th century, Mie[4] published a fundamental theoretical paper in which he computed the dependence of the absorption and scattering of spherical metal particles on the particle diameter, wavelength of the incident light, refractive index of the surrounding medium and the optical constants of the compact metal. Klein and Metz[5] applied the Mie equations to silver particles and found a good agreement between theory and experiment.

Apart from the particle size, other parameters are also important for the image color. Jones and Bird[6] calculated the effect of aggregation on the absorption behaviour of spherical silver particles and showed that the absorption peak shifts to longer wavelengths. Moreover, under most conditions a broadening of the absorption peak is also obtained, leading to a more neutral image color. The effect of aggregation decreases rapidly as the distance between the particles increases.

A third parameter is the particle shape. If it changes from spherical to ellipsoidal, the main absorption peak will shift to shorter wavelengths and a secondary peak

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✦ Fellow of IS&T

*Corresponding author: Tel: ++ 32 3 218 02 47; Fax: ++ 32 3 218 02 57; e-mail: schryver@ruca.ua.ac.be

appears at a longer wavelength.[7] As the ratio between the short and the long axis decreases, meaning that the particle becomes more needle-shaped, the main absorption peak will shift to shorter wavelengths and the secondary peak to longer wavelengths. A broad size distribution will therefore lead to a broader and smoother absorption peak resulting in a more neutral color.

Impurities incorporated in the silver particles can have a considerable effect on the optical constants and hence on the absorption peak. One mechanism is the reduction of the electron mean-free-path in silver by the action of contaminants, like sulfur, or by lattice defects.[8] An increase of the concentration of impurities or lattice defects will again lead to a broader and smoother absorption peak. The adsorption of impurities at the surface is also expected to modify the image tone, because it deforms the electronic energy levels at the surface.

A final influencing factor is the environment of the silver particles. The absorption behavior will be different if the particles are encapsulated in water or gelatin. This is due to the difference in refraction index, n = 1.33 for water and 1.5 for gelatin. To a first approximation an increase of the refractive index of the environment shifts the absorption peak to longer wavelengths.[9] Combining all previous effects will also lead to a more neutral image tone.

Fortunately, for conventional photographic films a neutral blue-black color is generally achieved, except in the case of ultra-fine grain materials. Also, using tabular crystals, a neutral tone is achieved if the crystal thickness is above 200 nm. In populations of thinner crystals the image tone is too brownish, but until now the influence of the thickness of the crystal on the filament structure and hence on the image tone has not been investigated. More neutral tones can be obtained by changing the development parameters, mostly by adding contaminant particles to the developer. This process is called toning and the reactants are called toners. Some toners change the morphology of the silver particles, while other toners modify the surface energy levels of the silver or introduce new energy levels.[8] The exact mechanism of toning is not always understood, but it acts on one or more of the above mentioned processes.

A second important parameter of the developed film is the covering power (*CP*). The covering power is defined[10] as the ratio D/M of the optical density of the developed film (D) to the mass of silver in grams in an area of 100 cm^2. A high value for *CP* means that the amount of silver is more efficiently used to build up the optical density. *CP* is inversely proportional to the size of the undeveloped silver halide crystal if the projective area is larger than 0.04 μm^2. For large tabular crystals the *CP* is approximately inversely proportional to the crystal thickness.[11] However, an increase in covering power will lead to a loss in neutrality of the image tone. Both properties impose conflicting demands on the development process. To obtain a more neutral image tone, larger or more compact silver particles are required, which means that a higher amount of silver is necessary. The covering power, on the other hand, is maximized if the amount of silver is lowered. Therefore, optimal conditions have to be found. The estimated maximal *CP*[11] for a silver deposit in gelatin is 350 cm^{2}mg^{-1} while the maximal *CP* for a neutral deposit is only 50 cm^{2}mg^{-1}.

In this study, the chemical development of tabular silver bromide crystals with {111} surfaces will be investigated. When the thickness of the tabular crystals is varied, a shift in image color and covering power is obtained. It was also investigated to what extent morphological differences and differences in defect structure of the silver filaments can account for these shifts.

Experimental

Two samples of silver bromide {111} tabular crystals with average thickness of 90 nm and 160 nm are investigated. To distinguish between the two populations, the crystals will from now on be denoted by their thickness. The conventional parameters for obtaining a homogeneous population of tabular crystals have been applied and details, including the chemical and spectral sensitization, can be found in the patents of Verbeeck *et al.*, the 90 nm crystals correspond with example 3,[12] and the 160 nm crystals with emulsion B.[13] After the growth of the crystals, they are chemically sensitized for 4 hours at 50°C introducing S, Se and Au^{3+}. The concentrations of the sensitizing elements in the 90 nm and 160 nm crystals are respectively 1.29×10^{-5} mol/mol Ag and 1.075×10^{-5} mol/mol Ag for S, 8.31×10^{-6} mol/mol Ag and 8.31×10^{-6} mol/mol Ag for Se and 5.93×10^{-6} mol/mol Ag and 4.45×10^{-6} mol/mol Ag for Au^{3+}. Then the crystals are spectrally sensitized using a green sensitive, azacyanine, dye. Finally the gelatin dispersion of the crystals is coated on a PET film.

A standard procedure is used for the exposure of the crystals. A combination of 20 12 W lamps generates white light. A diffusing screen is placed over the lamps to allow homogeneous illumination. Because the crystals are covered with a green sensitive dye, a filter having a bandpass centered on 535 nm, which corresponds with the green part of the visual spectrum, is used. The intensity of the light after passing trough the spectral filter is 1.56×10^{17} photons/m^{2}s. To further control the intensity of the incident light, a carbon neutral density filter is placed between the spectral filter and the photographic film. Filters with different densities correspond to different regions of the sensitometric curve. All films were illuminated at D_{max}, which corresponds with lowest intensity of the incident light at which the maximal optical density of the developed film is reached.

For the development of the crystals, the commercially available Agfa G138I developer with starter is used. It contains 266 mmol/l hydroquinone and 7 mmol/l Phenidone™ as active elements, a buffer, a pH controller, a stabilizer and anti-fog elements, but no added toning agents, and develops both the surface and internal latent images. This is a very fast developer and less than 30 s are required for total development. To slightly reduce its activity the developer is diluted 5 times, the development remaining very fast. For the investigation of the effect of an image toner, phenylmercaptotetrazole with a concentration of 3.9×10^{-5} mol/l was added to the Agfa G138I developer as a toning agent.

For the sample preparation of the TEM investigation, the developed film is dissolved in a solution containing trypsin, which is an enzyme that breaks down the gelatin. The silver and silver halide crystals will sink and the remaining liquid can be removed. Next, 15 ml of distilled water is added at a temperature of 42°C for the dilution of the sample. Finally a drop of this mixture is deposited on a TEM grid and the water is evaporated.

To avoid radiation damage all steps of the sample preparation are performed under red light conditions, and even exposure to the red light was limited as much as possible. The totally developed crystals are no longer sensitive to radiation and no special precautions are

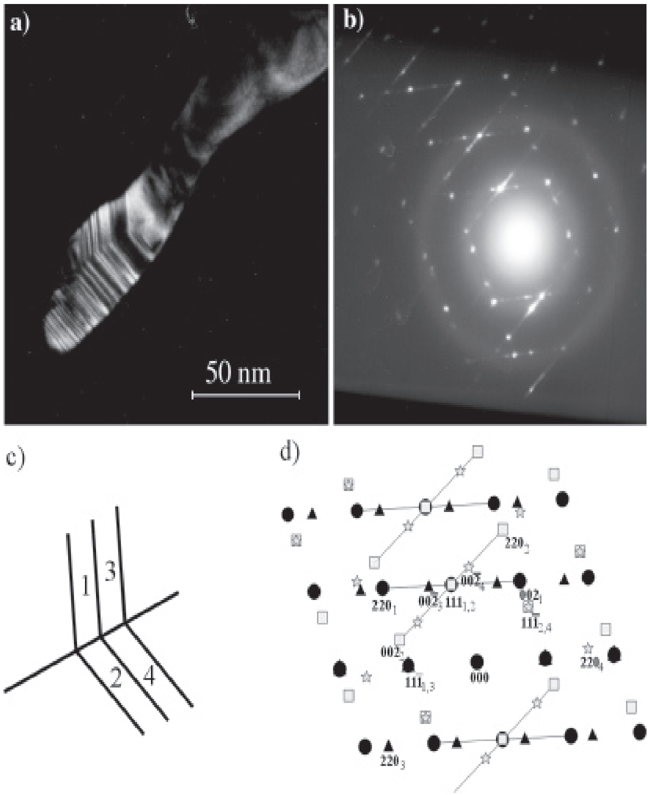

Figure 1. (a) Dark field image of a filament containing a large number of twins. b) Corresponding diffraction pattern proving the presence of four twin-related variants and c) and d) schematic representations of the location of the twinned variants and the diffraction pattern.

necessary any more. The CTEM images were obtained with a Philips CM20 and CM200 microscope and the HREM images were obtained with a JEOL 4000EX top-entry microscope.

The Philips CM200 Microscope is equipped with a SIS digital camera that has been used for the quantitative measurement of surface areas. For these measurements the grey scale images recorded by the camera are transformed into black and white images using the local threshold method.[14] This method applies a combination of two filters. A first filter is a threshold filter that converts a pixel into a white or black pixel if its grey value is higher or lower than a certain threshold. The threshold is set manually depending on the overall brightness of the image. The second filter compares the pixel value with the average value of the surrounding pixels and avoids differences in background intensity within one image which would lead to a local bad conversion. After the conversion to a black-and-white image, the number of white pixels is counted. It was checked visually that the combination of the two filters gives good results for the separation of the open area and the filament area. A relative precision of 5% is obtained.

Results

Defect Structure

The defect structure of silver filaments of partially and totally developed crystals has been investigated with conventional as well as high resolution TEM. The majority of the defects that have been observed are planar defects, while hardly any dislocations are present. In a large number of filaments a series of parallel twins are observed, all lying on {111} type planes. For example, in Fig. 1, a dark field image (Fig. 1(a)) of a filament containing a large number of parallel planar defects and its corresponding diffraction pattern (Fig. 1(b)) are shown. The dark field image was taken in the 111 reflection that is common to variants 1 and 2.

Usually only one series of parallel twins, resulting in two variants, is formed, but in the filament of Fig. 1, four twin related variants are formed. Their presence can be deduced from a diffraction pattern that is oriented along a $[1\bar{1}0]$ zone. Twinning on the (111) plane results in a variant that is also oriented along the $[1\bar{1}0]$ zone. The diffraction pattern generated by this twinned variant contains the same types of reflections as the first variant, but mirrored with respect to the [111] axis perpendicular to the twin plane. Twinning on the $[11\bar{1}]$ plane results in a third twin-related variant again oriented along the $[1\bar{1}0]$ zone. A fourth variant with the same orientation can be obtained by twinning on the $[11\bar{1}]$ plane of the second variant.

A diffraction pattern containing 4 twin related variants all oriented along a $[1\bar{1}0]$ zone is shown in Fig. 1(b) and schematically represented in Fig. 1(d). The variants denoted by the subscripts 1 and 2 are twinned on the (111) plane which corresponds with the single twin plane in the centre of the filament parallel with its longest side. The other two variants, with subscripts 3 and 4 are twinned on the $[11\bar{1}]$ planes of the variants 1 and 2, respectively. These planes indeed correspond to the large number of parallel interfaces enclosing an angle of 70.5° with the first interface.

Not all reflections belonging to the third and fourth variant are recognizable in Fig. 1(b), because they are overlapped by streaks of diffuse intensity. According to kinematical diffraction theory,[15] which is correct for determining the spot position and shape, the presence of multiple parallel defects results in the smearing out of the intensity of a reflection in the diffraction pattern in a direction perpendicular to the defect plane in real space.

The dark field image in Fig. 1(a) was taken using the [111] diffraction vector that is common to the first and the second variant. Therefore, both halves of the filament contain bright variants and the high number of parallel twins appears as the alternating bright and dark areas. The twins in each variant stop at the interface and do not always continue into the other variant.

For a more detailed investigation of the defects, a high-resolution study is performed. An example of a silver particle is shown in Fig. 2. Although the image is taken from another silver filament, the same atomic stacking at the twins as in the case of Fig. 1(a) can be deduced. All twin planes are indicated by the letters T and the different variants are marked by the numbers 1 to 4 in Fig. 2(a). In the enlargement of Fig. 2(b), it can be seen that four twin-related variants are present and all are oriented along a [110] zone. The two parallel twin planes, between variants 1 and 3 and variants 2 and 4, are separated by only 5 atom layers, which corresponds with a distance of 1.6 nm. Several filaments have been investigated and in many cases it was found that the distance between two twin planes is less than 2 nm.

From the CTEM images only the presence of twins was deduced, but from the HREM investigation it is clear that also stacking faults on the same {111} plane as the twins are formed. The stacking fault in Fig. 2(a) and enlarged in Fig. 2(c), has a displacement vector of

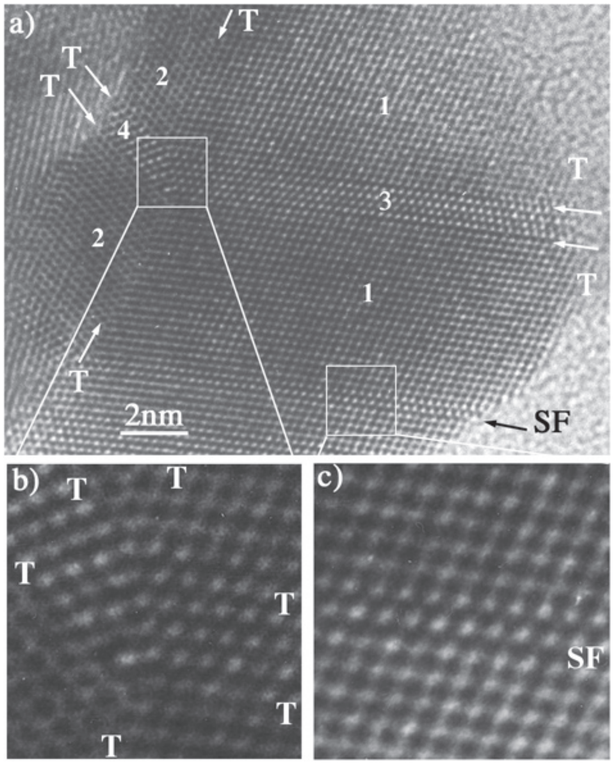

Figure 2. HREM image of a silver filament containing multiple twins (T) and one stacking fault (SF). b) and c) are enlargements of the intersection of the twins and of the stacking fault. The locations of the enlarged regions in the silver particle are indicated by the white squares.

a/3[111], which corresponds to the normal, low energy stacking fault in materials with a f.c.c. unit cell. From the image it was deduced that it is an extrinsic stacking fault, which means that an extra plane is added to the normal stacking and results in a stacking sequence of *abc**b**abc*.

The defect structure is not related with the type of sample. In all three samples a large number of filaments containing the present series of parallel twins and stacking faults are observed. The fraction of filaments that contain defects was not determined accurately, but a rough estimate shows no differences in the concentration between the different samples.

Filament Structure

Influence of the Thickness of the Crystals. The color of a developed film is expressed by the image tone (*IT*) value, which is the optical density D_r of the film measured through a red filter under the condition that the value of D_b, the optical density measured with a blue filter, equals 2.[12,13] A neutral image tone corresponds to a value for *IT* of 2. A lower value leads to an undesirable red-brown color, and a value below 1.97 is considered unacceptable for a high quality film. The IT values for the 160 nm and the 90 nm crystals are 1.95 and 1.84, respectively. Although both values are below the limit of acceptable quality, the 160 nm crystals are clearly more neutral than the 90 nm crystals.

Typical examples of totally developed 160 nm and 90 nm crystals are shown in Fig. 3. These images have been introduced into a digital system through a calibrated microscope using a digital camera. This allows the accurate measurement of the filament dimensions and provides images for direct digital processing. The lengths and widths of the filaments have been measured manually. As a result of the overlap, only 65 to 90 randomly selected non-overlapping filaments belonging to at least 10 different crystals were measured. For the width of the filaments it could be verified that the measured values are typical for all filaments, because there is always some part of the filament that is not or almost not overlapped by other filaments. For the length of the filaments this could not be verified, but because of the random selection of filaments lying near the edge as well as in the centre of the developed crystals, it is reasonable to assume that the measured average length is representative for all filaments. These measurements show that the dimensions of the silver filaments are comparable for both samples. The average thickness of the filaments is 30 nm in the 160 nm crystals and 25 nm in the 90 nm crystals, while the average lengths are 70 nm and 66 nm respectively.

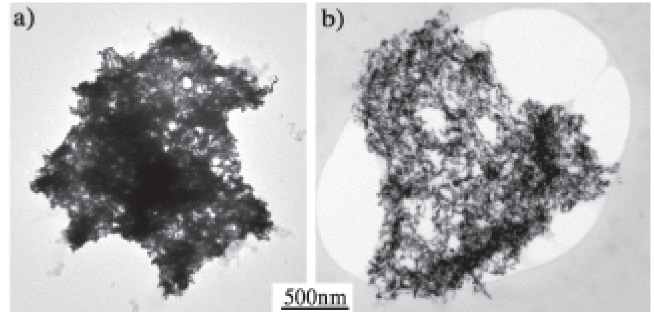

Figure 3. (a) TEM image of a totally developed 160 nm crystal. b) Similar image of a 90 nm crystal.

The major difference, however, is the surface area covered by the filaments. Moreover, in the 160 nm crystals there is more overlapping of the filaments, leading to the darker regions in the TEM-images of Fig. 3. This is already obvious from the visual information, but was also quantified by calculating the ratio of the open areas within the contours of the crystal to the total surface.

In order to measure the surface coverage, the grey scale images are transformed into black and white images using the local thresholding method, as described in the Experimental section. Next, the ratio of the open area to the total surface area is calculated. In this way it was found that for the 160 nm crystals on the average 10% of the projected area is not covered by silver filaments, whereas for the 90 nm crystals 30% is not covered.

Addition of an Image Toner

In the literature it is reported that the addition of certain impurities to the developer results in a more neutral image tone.[8,16] Two types of tone modifiers are generally applied. The first type consists of molecules, mostly organic molecules, that adsorb on the silver filaments. The second method is based on the incorporation of contaminants in the silver filaments. The exact mechanism is not yet understood, but it is assumed that the tone modifiers either change the morphology and aggregation of the filaments[16] or influence the optical constants or energy levels to give a more neutral absorption.[6]

To increase the image tone of the 90 nm crystals phenylmercaptotetrazole is added to the developer. This

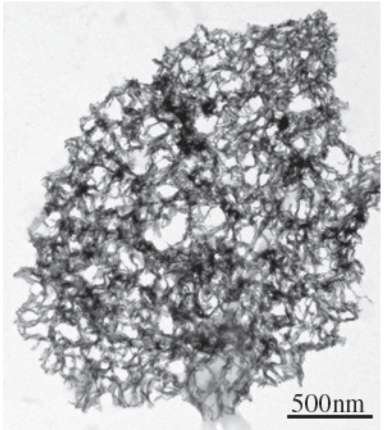

Figure 4. TEM image of a totally developed 90 nm crystal using a tone modifier.

TABLE I. Summary of the Most Important Properties of the Filament Structure for the 160 nm Crystals and the 90 nm Crystals With and Without Toner.

	160 nm crystal	90 nm crystal	90 nm with toner
image tone	1.95	1.84	1.91
filament width	30 nm	25 nm	16 nm
filament length	70 nm	66 nm	90 nm
width/length	2.7	3.2	5.1
open area	10%	30%	38%

leads to an increase of the image tone to a value 1.91, which is better than without toning but still not very good. We investigated to see if the addition of this tone modifier has any influence on the defect structure, morphology and aggregation of the silver filaments.

Figure 4 shows a typical image of a totally developed 90 nm crystal using the tone modifier. The average ratio of the open area to the total surface of the crystal was measured using the same procedure as described above. This measurement showed that using the image toner 38% of the crystal consists of open area.

Also the dimensions of the silver filaments were measured and compared with the crystals developed without toner. The result is that the average width of the filaments is smaller. The image tone filaments have an average width of 16 nm, while the filaments without toner are 25 nm wide. The length of the filaments, on the other hand, is longer when using the image toner. The average length is 90 nm with image toner and 66 nm without image toner. Consequently, the length to width ratio is larger and also the variance of this ratio is larger.

The most important observations about the filament structure and the image tone for the different samples are summarized in Table I.

Discussion

The presence of twins and stacking faults in crystals can have an influence on their growth and morphology. For example, the two-dimensional growth of AgBr (111) tabular crystals is the result of the formation of twins in the crystal nuclei.[17] In the silver filaments investigated here no relation could be established between the presence of defects and the morphology of the filaments. In fact, the majority of the defects lie almost perpendicular to the longest side of the filament, which means that growth occurs almost perpendicular to instead of along the defects. One explanation is related to the specific filament growth conditions. As a result of the chemical development, the silver atoms are delivered by the silver halide crystals and are incorporated at the interface with the silver filament.[18] As a consequence, no silver can be incorporated at permanent surface steps on the side edges of the filament. A second reason is that at a high growth speed, i.e., there is a high driving force, new silver atoms can deposit anywhere on the surface and the influence of surface steps is reduced. The high driving force is also favorable for the formation of defects, certainly in silver crystals where the formation of twins or stacking faults on a {111} type of plane requires only a very limited energy. The large number of defects formed on a {111} plane furthermore indicates that growth preferentially occurs on these planes.

Furthermore, it was shown that the defect structure and the dimensions of the silver filaments formed during the development of the 160 nm and the 90 nm crystals are comparable and, therefore, cannot be responsible for the difference in image tone. The major difference is the surface area covered by the filaments. The development of the 90 nm crystals show in projection a much more open structure compared with the 160 nm crystals. As explained in the introduction, the aggregation of silver particles leads to a more neutral image tone and therefore it is reasonable to assume that this difference in surface coverage could account for the shift in *IT*-value. Unfortunately, as the result of the complex filament structure, it is at this moment not possible to quantify the effect of the surface coverage and it cannot be calculated if the surface coverage alone can account for the observed difference in image tone.

The reason for the difference in surface coverage is probably entirely due to the difference in thickness and thus in volume of the original crystals. The silver for the filaments has to be delivered by the silver halide crystals. Therefore in the case of the 90 nm crystals only about half the amount of silver is available to cover the same surface area. It was measured that the dimensions of the silver filaments are comparable and therefore the shortage of silver must result in a more openly spaced filament structure.

The addition of an image toner to the developer leads to a slight improvement of the image tone. As was mentioned in the introduction, the image toner can have an effect on the optical constants or energy levels to give a more neutral absorption.[8] This investigation however focuses on the morphology of the filaments. Because the size of the original crystals has not changed, it can be expected that the same surface area is not covered by silver as for the development without toner. The measurements showed that 38% of the surface is not covered, which is slightly higher than for the crystals developed without image toner, but it is still within the experimental uncertainty. The filaments themselves have a higher width to length ratio. Therefore, this investigation shows that the addition of an image toner has a limited effect on the filament morphology and consequently it can have only a limited effect on the image tone. Unfortunately, because of the complex filament structure, it is not possible to calculate the image tone and only qualitative arguments can be given.

Conclusions

It was observed that the image tone of chemically developed AgBr {111} tabular crystals with an average thickness of 90 nm and 160 nm shifts from 1.84 to 1.95 respectively. Therefore, the defect structure and morphology of the filaments of both types of sample have been investigated and their influence on the image tone is evaluated.

The CTEM investigation showed that in many filaments a large number of parallel twins are formed on the {111} type planes. The distance between the twin planes is often only 1 to 2 nm. From the HRTEM investigation it can be deduced that also stacking faults on the same {111} type planes with a displacement vector of the a/3⟨111⟩ type are formed. These defects do not determine the morphology of the filaments, but their existence indicates that growth occurs on the {111} planes. They have been observed in all samples and can therefore not account for the difference in image tone.

It was furthermore shown that the filaments of both samples have similar dimensions, but that the filaments formed from the 90 nm crystals cover a smaller fraction of the surface than those of the 160 nm crystals. A more compact filament structure leads to a more neutral image color and, on a qualitative level, this observation can indeed account for the difference in image tone. The influence of an image toner, phenylmercaptotetrazole, on the filaments of the 90 nm crystals was also investigated. This leads to an increase of the image tone from 1.84 to 1.91. It was shown that a slightly smaller fraction of the surface was covered, while the filaments themselves were longer and narrower. It was concluded that the image toner has only a limited effect on the filament morphology.

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