New Insights into the Mechanism of Precipitation of Silver-Halide Tabular Crystals Having {100} Major Faces

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Abstract

The benefits of the use of tabular silver halide grains in photographic materials is well known. Methods for the precipitation of tabular silverchloride grains have been reported since the early eighties. This type of silverchloride crystals has two parallel {111} crystallographic planes that need to be stabilized by a crystalhabit modifying agent (HMA). Because of its high affinity for silver ions, the use of an HMA may effect the efficiency of these grains in photographic emulsions.

Tabular grains having two parallel {100} faces are becoming more and more of interest since the {100} crystallographic planes are intrinsically stable for an FCC lattice.

On the basis of a conventional precipitation scheme for the preparation of tabular silverchloride crystals having two parallel {100} major faces, an overview will be given of the parameters that influence most the efficiency of every step in the precipitation of this type of crystals.

Starting from samples taken from different steps during the precipitation, and studied by STEM and SEM, a model will be proposed to explain the mechanism of the precipitation of said crystals.

The different experimental settings will be discussed in terms of supersaturation, local supersaturation and solubility referring to the proposed model.

Introduction

During the 80's the advantages of using tabular grains instead of cubic emulsions became clear and were intensively explored. These advantages are an improved speed-granularity relationship, increased covering power even at higher hardening degrees and an increased separation of intrinsic and spectral sensitivity. Tabular grains of this type are AgBr(I) crystals having two parallel {111} crystal faces.

During the 90's the benefits of using grains that are rich in chloride became evident. A more rapid developability was obtained and a more ecological processing could be performed.

The way to the combination of tabular grains and grains rich in chloride was obvious but not easy to take. The tabular grains rich in chloride and having {111} crystal faces are not stable. A crystalhabit modifying agent (HMA) is needed to overcome the instability in an aqueous environment. It was found however that this HMA can effect the speed of the emulsion and therefore degrade the efficiency of this type of crystals in photographic emulsions. Therefore the crystalhabit modifying agent must be washed away. This is however a critical and irreproducible step.

In the mid 90's the AgCl tabular crystals having {100} major crystal planes were introduced[1] as an alternative to stable tabular grains rich in chloride.

The formation process of this type of crystal is however totally different from the one forming tabular crystals having two parallel {111} faces. In the case of {111} tabular grains, the crystals are formed by inducing a double twin parallel to the {111} crystallographic orientation. These twin-plans lead to an enhanced lateral growth without an increased thickness growth. The {100} tabular grains do not have this type of stacking faults[2] so another type of mechanism must be on the basis of the formation of the {100} tabular grains.

This paper will try to give an explanation of how the crystals are formed and which parameters can have an effect on the efficiency of the formation process.

Experimental

Precipitation Scheme

In the following figure a typical precipitation scheme is illustrating the different steps in the preparation and formation of the tabular crystals rich in silverchloride and having {100} major faces. The scheme clearly illustrates a nucleation step (NS), a first physical ripening step (FR1), a first growth step (GS1) followed by a second physical ripening (FR2) and growth step (GS2).
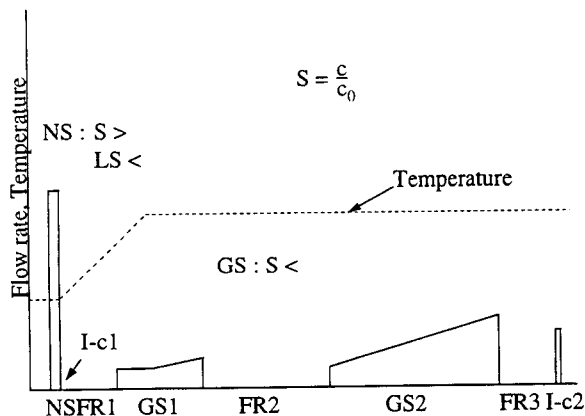

Figure 1: Typical precipitation scheme for the preparation of AgClI-100-Tabular Crystals taken from a patent issued in Europe on 961106.

An iodide conversion at the end of the precipitation (I-c2) may be possible after an optional third physical ripening step. During nucleation no iodide is present. After NS a solution of iodide is added to the reaction vessel (I-c1).

Precipitation Parameters

Growth Step

Looking at the precipitation scheme presented in Figure 1, it is clear that a lot of parameters can be changed to optimize the number of {100} tabular grains with a certain aspect ratio and to minimize post-nucleation.

However, from all the experiments it appeared that during the growth steps the supersaturation S must be kept very low (see figure 1) to prevent the formation of new nuclei. The most effective parameters to keep the supersaturation low are low flow rates during the growth steps, high temperature ramps, high growth temperatures and vigorous stirring of the reaction medium.

However conditions of high solubility (e.g. high excess of chloride) during growth may lead to cubic (thickness) growth.

Since the growth steps need to be performed at very low supersaturation, an insufficient number of nuclei is formed during the nucleation step. If more nuclei were present more precipitation sites would be available, which would increase precipitation efficiency.

Understanding the initial formation of the crystals is therefore very important. Therefore, the parameters influencing the nucleation and formation of the tabular germs were investigated.

Nucleation Step

During nucleation a high supersaturation is needed to form enough nuclei. However the local supersaturation must be kept low to minimize {100} crystals having a single twin plane in the {111} crystallographic orientation.

To obtain optimal conditions we found that the type and amount of gelatin used during nucleation is of major importance.

Low temperatures are of course a condition to obtain high supersaturation leading to more precipitation sites. Since during growth a high temperature is needed, a temperature ramp must be included. This temperature ramp between NS and FR2 is however very critical. It was found that the homogeneity of the emulsion was highly improved when this ramp was set high, but a high ramp also leads to a growth of thickness of the crystals.

The most important parameter however to obtain the best results (high number of thin tabular crystals and low post-nucleation) was I-c1. It was found that when the precipitation scheme (Figure 1) was followed but no I-c1 was performed no tabular crystals were obtained. Also the way in which I-c1 was performed leads to tremendous differences in the number of tabular grains. The amount of iodide used in I-c1 is also very important.

Physical Ripening Step

In the formation of tabular crystals having parallel {111} twin planes one physical ripening step is performed to resolve all non-twinned crystals. This is a very efficient way to increase the number of tabular grains because the difference in growth speed between twinned and non-twinned crystals is very high. As shown in the scheme of figure 1 at least two physical ripening steps are required. Both are necessary but are performed for different reasons. The classical Ostwald ripening step (as in twinned tabular crystals) corresponds to the second physical ripening step.

Relation between the number of nuclei and the amount of iodide during I-c1

From the former experiments we concluded that the number of nuclei formed during nucleation is important but that the iodide conversion after the nucleation is even more important. However, if the number of nuclei is changing, the amount of iodide during the conversion step must be changed also since more conversion sites are present.

Therefore an experiment was set up to determine the relationship between the flow rate during nucleation, the percentage of Ag precipitated in NS and the amount of iodide used in I-c1.

It is clear that the number of nuclei increases when the amount of silver precipitated during NS is increased. When the amount of silver is kept constant but the flow rate is increased, the number of nuclei also increases since the supersaturation is increased. Both the thickness and the diameter of the tabular grains are influenced.

The amount of iodide offered during conversion on the formed nuclei has an influence on the amount of tabular grains and on the thickness of the grains.

In both cases where thin tabular grains were formed, post-nucleation appeared. Only at an optimal number of nuclei and an optimal iodide concentration thin tabular grains with no late nucleation were obtained.

Results and Discussion

Nucleation and Growth Model for the 100 Tabular Grain AgClI grains

Since this type of grains has no twin planes[2] another type of stacking fault must be the reason for the anisotropic growth of these crystals.

By means of scanning transmission electron microscopy it was found that at least two dislocations are responsible for the anisotropic growth.

Our experiments suggest that iodide is responsible for the introduction of this stacking fault. The nuclei grain size must therefore be responsible for the thickness of the resulting crystals. With this knowledge (the types of dislocations) we can describe a model where diameter and grain thickness can be controlled independently of each other to obtain the correct grain dimensions needed for the desired photographic applications.

References

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2. Brust, *IS&T's 49th Annual Conference*, 35 (1996)