

Three Stages in Formation of Silver Halide T-crystals, Created by a Method of a Physical Ripening of Fine Emulsions

Timothy A. Larichev and Eugenie I. Kagakin
State University of Kemerovo, Kemerovo, Russia

Abstract

The process of T-crystals formation includes at least three stages, and the absence though by one of them makes occurrence of T-crystals impossible. These stages are nucleation, transformation of nucleus into a T-crystal and growth of T-crystals.

Introduction

The silver halide T-crystals have wide application in modern photographic materials. However till now there is no conventional opinion on such crystal's process of formation and growth. Only rather recently was shown the importance of coalescence processes at the first stage of T-crystals formation^{1,2}. There is open the question on driving forces of a mass transfer at the stage of T-crystals growth. For example, idea about the dependence of the T-crystals form from amount of twin planes has not confirmed³. Recently the concept, explaining occurrence of T-crystals different forms by presence of different amount of surfaces (100) and (111) on their lateral sides was offered⁴. However while this idea has fail of general support. In particular, not clearly, why at presence of sides (111) the speed of lateral growth of T-crystals at pBr=3,0 was reduced up to a minimum. That's why the research of the AgHal T-crystals formation mechanism attracts steadfast attention of the explorers.

Experimental

We use a method of a physical ripening of fine emulsions as a method of reception of photoemulsion AgHal T-crystals. In our experiments we try to determine interrelation of the received T-crystals dispersion characteristics with conditions of initial fine emulsion synthesis and with conditions of a physical ripening realization.

At the first stage by a control double jet crystallization the fine silver halide emulsion (size of microcrystals—less than 0.1 microns) is received. Then this emulsion subjected to a physical ripening under control conditions (pBr value, temperature, presence and concentration of silver halide sol-

vents and other additives). A physical ripening is conducted up to complete disappearance of initial fine emulsion microcrystals. The dispersion characteristics of received T-crystals are estimated on microphotos of carbon replicas of photoemulsions samples, received on an electronic microscope UMVE-100.

Experimental Results and Discussion

On the basis of received experimental date we have come to the conclusion that process of silver halide T-crystals formation includes, at least, three stages:

- Formation of a T-crystal "nucleus";
- Transformation of "nucleus" into a T-crystal;
- Growth of the T-crystal.

Each of this stages has the peculiarities, but at the same time, the absence though by one of stages makes process of T-crystals formation impossible. We shall consider these stages in more details.

Formation of a T-crystal "nucleus"

It is impossible to explain process of occurrence and growth of T-crystals during a physical ripening of fine emulsions without attraction of the "nucleus" concept. Really, how among all close on the size microcrystals some of these crystals begin heavily and anisotropically to grow. It is obvious, that the part of microcrystals of fine emulsions should differ on the properties from common crystals. The share of these "nucleuses" and, hence, dispersion characteristics of T-crystals, are determined by conditions of fine emulsions synthesis, instead of conditions of a physical ripening realization.

Investigations of the last years have shown, that the formation of particles, distinguished on properties from common fine emulsions microcrystals, proceeds mainly at the coalescence of generated crystals¹. Was shown, that than the condition of fine emulsion crystallization is closer to ideal and the above concentration of gelatin, the will be less in this fine emulsion formation of growth centers - T-crystals "nucleuses"².

Transformation of "Nucleus" into a T-crystal

As is known, formation and the growth of T-crystals occur only in certain conditions⁵. Therefore the occurrence of "nucleuses" is first, but not unique stage necessary for T-crystals formation. Was shown, that the kinetic dependence of T-crystals average size change during fine emulsion physical ripening is expressed S-shape⁶.

The presence of induction period is caused by presence of a stage of the primary T-crystal "nucleus" transformation into a T-crystal, and the most probable mechanism of a mass transfer is ion diffusion through a solution. The T-crystals formation even at presence of T-crystals "nucleuses" does not occur in conditions, when the ionic growth is retarded.

As an example it is possible to demonstrate comparative results of a $\text{AgBr}_{0.96}\text{I}_{0.04}$ fine emulsion physical ripening at the presence of bromide ions excess ($\text{pBr} < 1,5$) and at the presence of potassium thiocyanate. A ripening of silver bromide fine emulsion results in formation of T-crystals in both cases⁷. However the AgBr(I) T-crystals will be formed only at low pBr value. At the presence of potassium thiocyanate and at $\text{pBr} > 2,0$ physical ripening AgBr(I) fine emulsion does not result in T-crystal formation, though the formation AgBr(I) lateral shell proceeds without complications at presence in system core AgBr T-crystals. Other words, it is blocked not the process of growth AgBr(I) T-crystals, but the stage of "nucleus" transformation into T-crystals.

On the other hand, if solutions of silver nitrate and potassium bromide by double jet enter in a reaction vessel, in which the fine emulsion there is, supporting a condition of a crystallization at a level, ensuring growth of existing microcrystals and absence new formation of crystals, and then to subject received emulsion to a physical ripening, it is possible to note essential change of a T-crystals growth kinetics. In this case the duration of T-crystals formation is much reduced, and it is impossible to allocate induction period on kinetic dependence. The probable reason of this phenomenon is transformation of "nucleuses" into T-crystals during reagent addition.

Growth of T-crystals

In the most simple case, when the physical ripening of fine emulsion will be carried out in presence of bromide ions

excess, the change of a ripening conditions (pBr value, temperature, concentration of fine emulsion microcrystals, gelatin concentration) does not influence to the T-crystals dispersion characteristics and form, and adjusts only duration of T-crystals formation process⁶. The resulting emulsion usually contains T-crystals both triangular, and hexagonal form, and also T-crystals with intermediate forms (triangles with cut off corners). In these conditions T-crystals size and form distribution is determined only by conditions of fine emulsion synthesis².

Logically to assume, that the distinction on properties, resulting to formation of a T-crystal of one or another form, is available already for T-crystals "nucleuses". However an opportunity to operate the T-crystals forms by varying of fine emulsions physical ripening conditions is available.

For example, if to carry out a ripening at the presence of potassium thiocyanate and at pBr value little then 2.0, the final emulsion will contain a usual T-crystals with various forms. However if the physical ripening will be carried out at pBr value more then 2.0, essential changes are observed. Among T-crystals received in these conditions T-crystals of the hexagonal form prevail⁷. The share of hexagonal crystals can yet be increased, if to carry out a physical ripening at the high pH value, or at the presence of SV-105 surface-active agent (see. Figure 1). The similar effect was received at realization of a fine emulsion physical ripening at the presence of TAI⁸. It is necessary to note, that the precise tendency to transformation of triangular T-crystals to hexagonal ones is observed at AgBr(I) lateral shells growth on AgBr core T-crystals⁹, while the AgBr lateral shells growth in the same ripening conditions does not result in essential change of forms distribution.

In our opinion the general reason, causing formation hexagonal T-crystals in all these cases is relative retardation of growth by diffusion mechanism. Such retardation can be caused by increase of gelatin retarding action at pH increase, or presence of the stabilizer, such, as TAI, or reduction of a silver halide solubility, as in case of AgBr(I) lateral shell growth. The similar process can be caused by presence of some surface-active agents (as SV-105), which can be adsorb by a silver halide surface. The not adsorbing on AgHal surface-active agents (for example "Carbowax") do not influence on the T-crystals forms.

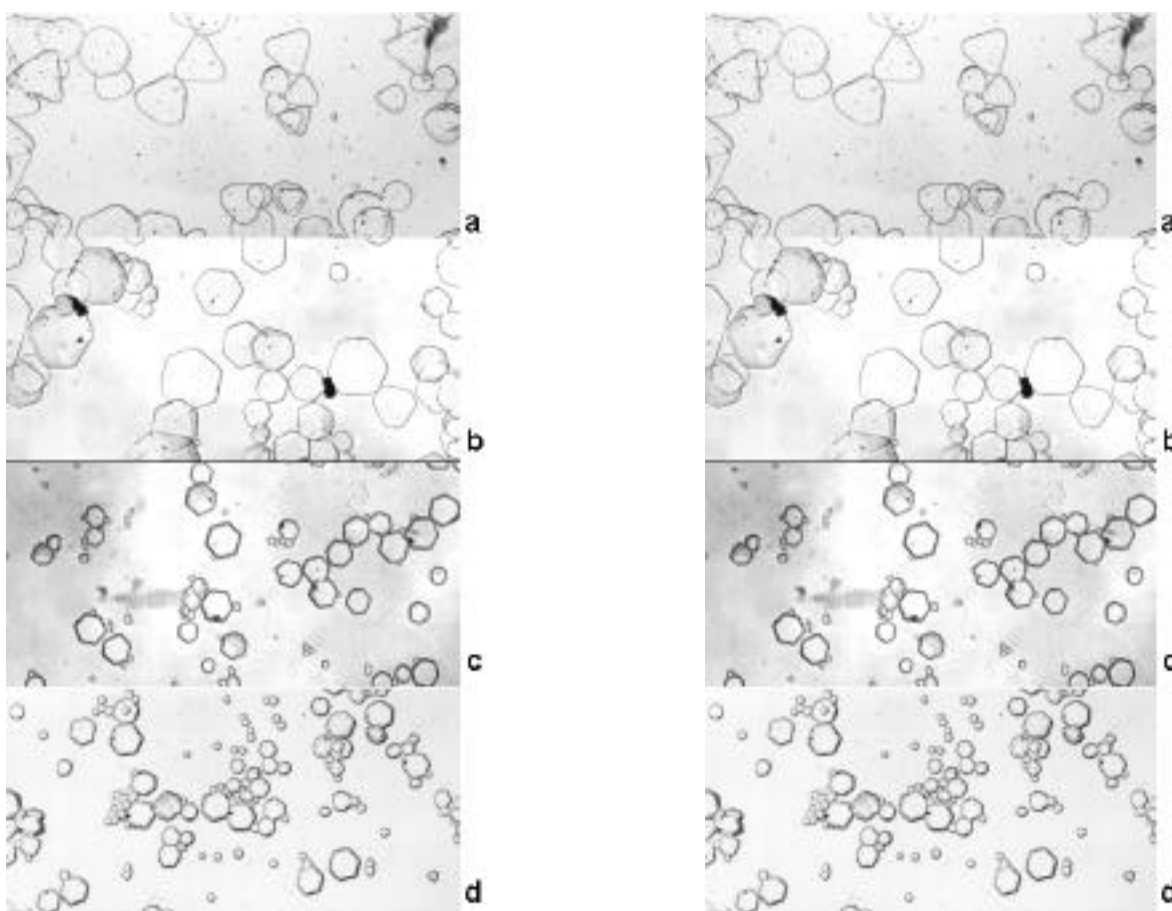


Figure 1. Microphotographs of carbonic replicas of emulsion AgBr T-crystals ($\times 6000$). The fine emulsion physical ripening conditions are:

a - $pBr=1.1$;

b - $pBr=2.5$, $[KSCN]=0.04$ mol/l, $pH=6.0$;

c - $pBr=2.5$, $[KSCN]=0.04$ mol/l, $pH=10.0$;

d - $pBr=2.5$, $[KSCN]=0.04$ mol/l, $pH=6.0$, $[SV-105]=1\%$.

Presence of modifiers results in that the growth rates of separate lateral sides of T-crystals become equal. By other words, advantage in growth rate of separate sides, resulting to formation of triangular T-crystals, disappears. It is possible to show, that there is the fast transformation all T-crystals without exception to correct hexagons in conditions of equalization of separate side's growth rates.

On the other hand, it is known, that at lateral shells growth by physical ripening of fine emulsions the essential influence can render the size of fine emulsions microcrystals⁶. So, the formation of identical shells on all core T-crystals is observed by use of AgBr fine emulsion with the average microcrystals size 0,05 microns, and forms distribution between triangular and hexagonal crystals remains practically constant. If the size of fine emulsion microcrystals to increase up to 0,09 microns, there are the essential changes. First of all, a process of T-crystals majority growth is sharply slowed down. However on thicker T-

crystals the lateral shell formation occurs with high former speed and the overwhelming majority of such crystals gets the form of correct hexagons.

A conclusion was made on the basis of the observable phenomena that the mass transfer at silver halide T-crystals growth comes true, at least, on two mechanisms: diffusion through a solution and coalescent. The growth on the diffusion mechanism depends on a crystallographic type of surfaces, forming T-crystals lateral side. Therefore both triangular, and hexagonal T-crystals are formed at prevalence of growth on the diffusion mechanism depending on a type of T-crystals "nucleus". The coalescent mechanism of T-crystals growth becomes determining in case of ionic growth retarding (including the decrease of a solubility of fine emulsion microcrystals at increase of their size). The growth rate on the coalescent mechanism does not depend on crystallographic peculiarities of lateral sides of T-crystals and hexagonal T-crystals form irrespective of a "nucleus" type.

However the large importance gets geometrical conformity of growing lateral side of T-crystals and fine emulsion microcrystals in case of growth on the coalescent mechanism. The growth on the coalescent mechanism becomes impossible at absence of this conformity. The presence of a isometric microcrystals plenty is frequently observed in conditions of strong retarding of ionic growth and this crystals do not built in growing T-crystals even at a long physical ripening (see Figure 1).

The dissolution of remaining isometric crystals can be carried out, if to remove effect of retarding (for example - by changing of pH value). But the growth of T-crystals separate sides will again proceed with different speed, and a result emulsion, containing non-uniform on size and form T-crystals, will be received. It is necessary to use fine emulsions with the extreme small size of microcrystals (no more than 0.02 microns) at the stage of T-crystals growth to avoid occurrence of a such situation.

What it is possible to wish to the explorers, working up on the problem of reception of photographic emulsions with the maximum uniformity on the size and form? In our opinion the basic attention should be concentrated on perfection of fitting and technology of fine emulsion with T-crystals "nucleuses" synthesis, to have an opportunity to receive "nucleuses" only of triangular, or only of hexagonal T-crystals. In this case the success is guaranteed and practically does not depend on realization of further operations of photoemulsion synthesis.

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