

Formation of monodisperse hexagonal tabular microcrystals during growth of AgBr(I) lateral shells on a AgBr cores

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Introduction

The problem of improvement of quality of the registered image always was important for silver halide photography. One of the possible ways of the decision of a similar task is the optimization of properties of recording elements of a photosensitive layer - silver halide microcrystals. It was shown, in particular, that the resolution of a film is essentially increased a case of use in a layer of monodisperse hexagonal tabular microcrystals[1]. On the other hand, use of heterophase microcrystals of complex halide structure allows to optimize interaction of microcrystals with light and to make controllable the process of development in the greater degree[2].

Recently in a photographic science the significant successes were achieved in understanding of driving forces of formation of tabular microcrystals of different shape[3,4]. However for manufacture of a photoemulsion it is important to formulate the recommendations for realization of process of a mass recrystallization allowing to receive the microcrystals with the necessary properties. The existing decisions not always carry universal character. For example, use of growth modifiers for reception of hexagonal crystal results in essential delay of process of an emulsification. We undertook attempt to reveal the technological decisions allowing at the minimal change of process a crystallization to create hexagonal tabular monodisperse microcrystals of complex structure.

As object of research the tabular AgBr microcrystal with $AgBr_{0.96}I_{0.04}$ lateral shell was chosen[5]. For this system for formation of final hexagonal tabular crystals it is necessary to receive hexagonal core AgBr microcrystals and grew on them a monosize shell, or to achieve of the transformation of core microcrystals of any shape into hexagonal ones at a stage of growing of lateral shell. It was interesting also to try to solve a problem of increase of uniformity of tabular crystals by means of optimization of a stage of lateral shell growing.

Experimental

The manufacturing of tabular heterocontact microcrystals was carried out by a method of a recrystallization of fine emulsions. The initial fine emulsions of halide structure AgBr and $AgBr_{0.96}I_{0.04}$ were received by a traditional method of a control double jet crystallization. For reception of core tabular microcrystals the AgBr fine emulsion was subjected to a physical ripening at increased temperature at the presence of the silver halide solvents (KBr and KSCN). For creation of a lateral shell to an emulsion, containing core microcrystals and the silver halide solvent, the addition by one portion or gradually of fine emulsion of halide structure $AgBr_{0.96}I_{0.04}$ was made. The ripening was carried out until complete disappearance of fine microcrystals in system takes place. During a recrystallization the samples were taken for researches by a method of an optical microscopy.

Experimental results and discussion

Control of the shape of tabular crystals at a stage of core formation. Generally in case of creation of tabular microcrystals by a method of a recrystallization of fine emulsions the physical ripening will be carried out at increased temperature and presence of excess of bromide ions. However microcrystals, received in these conditions, can have both triangular, and hexagonal shape. For change of the shape of received tabular crystals it is possible usually to vary conditions of synthesis of a fine emulsion[1]. On the other hand, it is possible to achieve formation of hexagonal tabular crystals by a variation of recrystallization conditions.

Now it is supposed that the formation of triangular tabular crystals is caused by distinction in growth rate of adjacent lateral sides of these crystals. At presence of similar distinction the quickly growing lateral side becomes degenerate. In turn distinction in growth rate is caused by different amount of nonequilibrium surfaces (100) which forming side face[3,4]. The achievements of equalizing of growth rates of the lateral sides it is possible by realization of crystallization in conditions ensuring

equality of growth rates of surfaces (111) and (100). For this purpose it is possible:

- To carry out a crystallization at high pBr value[6];
- To use a retarder of growth of a (100) surface[7].

The second variant is less convenient, as thus in system the additional substations appear which are difficult to remove and which can complicate the further process of manufacturing of an emulsion layer. The first variant is deprived of this lack, however solubility of a silver halide with growth pBr is very quickly reduced, therefore the process of crystal growth is very strongly slowed down. Therefore for maintenance of acceptable speed of crystallization usually it is necessary to add the solvent of a silver halide, which has no modifying action on a shape of microcrystals (for example, thioethers or thiocyanates).

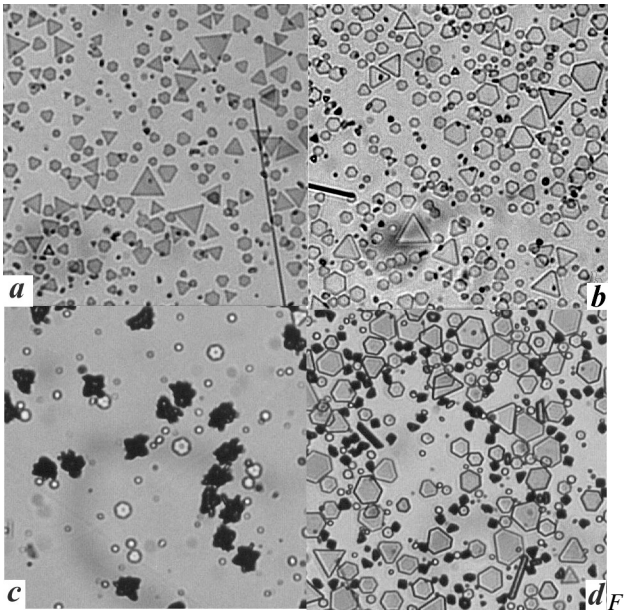

Figure 1. The microphotos (x400) of AgBr tabular crystals formed as a result of recrystallization of the same fine emulsion. The physical ripening conditions:
a. - [KBr]=0.1 M;
b. - [KBr]=0.01 M;
c. - [KBr]=0.001 M, [KSCN]=0.1 M;
d. - [KBr]=0.001 M, [KSCN]=0.01 M.

We carried out the comparative research of a process of formation of AgBr tabular microcrystals by a method of a recrystallization of a fine emulsion in various conditions. In figure 1 the optical microphotos of the received crystals are presented. Thesis crystals were created as a result of a physical ripening of the same fine emulsion. The realization of a recrystallization at the presence of significant excess of bromides ions (pBr=1) results in formation of mainly triangular tabular crystals with a high degree of polydispersity. If to carry out a ripening at pBr=2, the share of hexagons among final crystals is a little increased; however polydispersity remains on a former high level. Besides in this case process of a recrystallization proceeds by extremely low speed because of reduction of solubility of a silver bromide (see Figure 1b).

For acceleration of process of a recrystallization the solvents of a silver halide, such as, for example, potassium thiocyanate can be used[8]. However too large excess of KSCN can result in conversion of a silver bromide to silver thiocyanate (see Figure 1c). We can't to achieve the improvement of uniformity of received tabular crystals even at use of potassium thiocyanate in concentration exceeding extreme allowable (when process conversion begins) (see Figure 1d).

Control of the shape of tabular crystals at a stage of growth of a lateral shell. Generally at growing of AgBr(I) lateral shell even at bromide ion excess there is a change of the triangular crystals into hexagonal ones[5]. The probable reason of this phenomenon is the change of an energy condition of a growing side face, i.e. reduction of distinction in surface energy of (100) and (111) faces. However such tendency not has enough for transformation of all without exception growing crystals into correct hexagons. In figure 2a the microphotos of subjected to "differential dissolution"[5] tabular crystal with lateral shell are submitted. The growing of a lateral shell on the initial polydisperse and polymorph AgBr emulsion was carried out at excess of potassium bromide. It is possible to see the expressed tendency to transformation of triangular tabular crystals to hexagonal ones, however formation of a lateral shell proceeds non-uniformly. It results in increase of polydispersity.

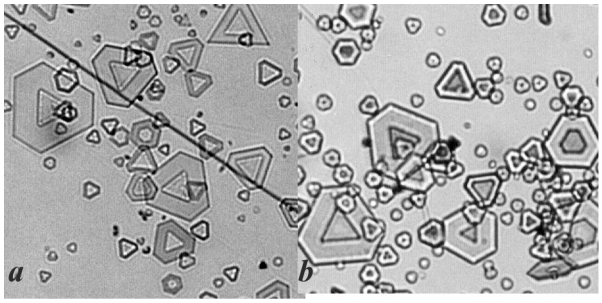

Figure 2. The microphotos (x400) of AgBr/$AgBr_{0.96}I_{0.04}$ tabular crystals after differential dissolution. The conditions of lateral shell growing:
a. - [KBr]=0.1 M;
b. - [KBr]=0.05 M, [KSCN]=0.03 M.

We undertook the attempt to reveal conditions of realization of a lateral shells formation, ensuring equal growth rate. For this purpose the experiments on growing of shell at the presence of potassium thiocyanate were carried out. The microphotos of the received tabular crystals subjected to differential dissolution are presented in figure 2b. It is possible to see that in this case essential increase of uniformity of final tabular crystals does not occur. Also it was revealed that the growth of a lateral shell is accompanied by partial conversion of silver

bromide of core to AgBr(I). The basic reason of this phenomenon is thickness growth of a tabular crystal at high pBr value and presence of potassium thiocyanate.

The experiment on research of influence of introduction rate of fine $AgBr_{0.96}I_{0.04}$ emulsion on uniformity of received lateral shells was carried out also. The introduction was carried out by two ways: in splash manner and gradually with use of the pump. The received tabular crystals are presented in figure 3. In this case the expressed influence of manner of introduction of a fine emulsion on uniformity of resulting lateral shells it is not revealed.

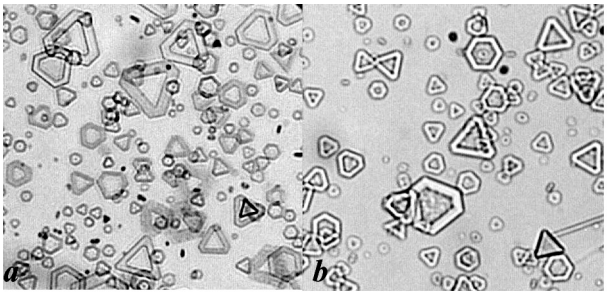

Figure 3. The microphotos (x400) of AgBr/$AgBr_{0.96}I_{0.04}$ tabular crystals after differential dissolution. The conditions of lateral shell growing:
a.- [KBr]=0.1 M, gradual fine emulsion addition;
b. - [KBr]=0.1 M, splash fine emulsion addition.

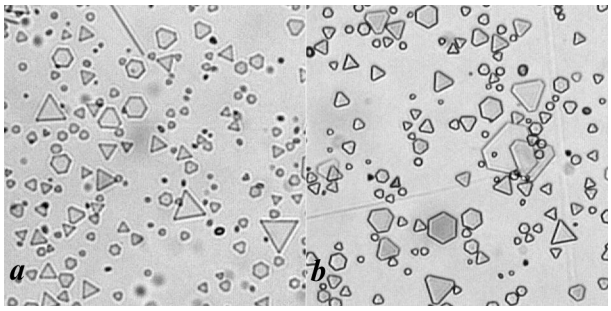

Figure 4. The microphotos (x400) of AgBr tabular crystals:
a. - After long physical ripening ([KBr]=0.05 M, [KSCN]=0.05 M);
b. - Same as (a) after AgBr fine emulsion addition.

For investigation of the reasons of conversion of a core part of tabular crystals the research of influence of presence of potassium thiocyanate on growth of thickness of these crystals was carried out. The core AgBr emulsion with tabular crystals was subjected to a long physical ripening at presence of KSCN. An influence on the dispersion characteristics (change of the shape, the change of thickness) was revealed not (Figure 4a). However after addition in system of a fine AgBr emulsion the expressed growth of thickness and transformation of the shape of tabular crystals took place (Figure 4b). Then latter in system to lower concentration of potassium thiocyanate and to carry out growing of $AgBr_{0.96}I_{0.04}$ shell at the presence of excess of bromide ions, the appreciable conversion of the core AgBr part does not occur (figure 5).

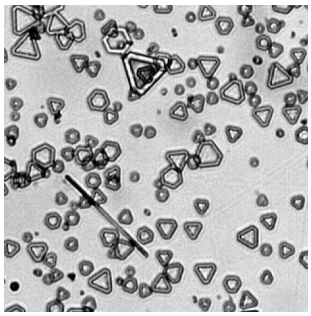

Figure 5. The microphotos (x400) of AgBr/$AgBr_{0.96}I_{0.04}$ tabular crystals after differential dissolution. The AgBr core was made in a manner similar Figure 4b. The conditions of lateral shell growing: [KBr]=0.1 M, [KSCN]=0.01 M.

On a base of our experiments it is possible to make conclusion that the reception of monodisperse heterophase tabular microcrystals at use of the polydisperse core AgBr emulsion is impossible. Therefore main attention at manufacturing of tabular crystals is necessary to focus on optimization of process of reception of primary nucleus of tabular crystals.

References

1. M.Saitou, S.Urabe, K.Ozeki, U.S.Patent No. 4,797,354 (1989).
2. Yu.A.Breslav, *J. Sci. Appl. Photogr. Cinematogr. (in Russian)*, **33,** 243 (1989).
3. R.V.Mehta, R.Jagannathan, J.A.Timmons, *J. Imag. Sci. and Techn.,* **40,** 77 (1996).
4. Y.Hosoya, S.Urabe, *J. Imag. Sci. and Techn.,* **42,** 487 (1998).
5. E.I.Kagakin, Yu.A.Breslav, T.A.Larichev, A.I.Mochov, *J. Sci. Appl. Photogr. Cinematogr. (in Russian)*, **36,** 353 (1991).
6. Y.Hosoya, T.Tani, *J. Imag. Sci. and Techn.,* **40,** 202 (1996).
7. A.K.Tsaur, M.Kam-Ng, U.S.Patent No. 5,210,013 (1993).
8. T.A.Larichev, E.I.Kagakin, *J. Sci. Appl. Photogr. (in Russian)*, **41**, No.4, 1 (1996).