Experimental Research of the Mechanism of Growth of Silver Halide Tabular Microcrystals

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Introduction

Recently the all-round research of the mechanism of growth of tabular crystals AgHal on model systems was carried out.[1,2] However mechanism of formation and growth of such crystals during manufacturing a photographic emulsion by a way of control double jet crystallization or physical ripening of a fine emulsion remains by a subject of discussion. The formation of tabular crystals can proceed not only in an emulsion, where the mobility of microcrystals is not limited, but also with aging of gelatin gel containing fine microcrystals.

The technique of reception of tabular crystals was offered by means of fine microcrystals recrystallization in gelatin gel.[3] In this case the fine emulsion was cooled down to the temperature of gel formation and was kept for 48-240 hours at the temperature 19±1ºC. The present authors investigated the influence of conditions controlling the solubility of silver halide on the process of tabular crystal formation in gel. It was shown that the efficiency of tabular crystal formation largely depends on the microcrystals concentration of the initial fine emulsion in gel. Also it was shown that the formation of tabular crystals proceeded at 19ºC, but they would not be formed at the temperature 10ºC even during long (more than 800 hours) aging.

Recently the investigation of formation of tabular crystals due to recrystallization process in gel was made.[4] The conception of tabular crystals formation[5] was used for interprets of received experimental date. It was shown that the most probable reason for the changes of the dispersion characteristics of resulting tabular crystals is the change of the number of particles, which can ensure the growth of this crystals on the coalescent mechanism. The conclusion was made that the initial fine microcrystals, which are situated within the range of an effective action of a tabular crystal nucleus, participate in the growth of a tabular crystal mainly by the coalescent mechanism. By this mechanism the tabular crystals can be formed quickly, but the mobility of microcrystals in gel is limited, therefor the movement of the microcrystals limits the growth rate. On the other hand, the mobility of ions in gel is high, but the growth rate by the ionic mechanism is small.

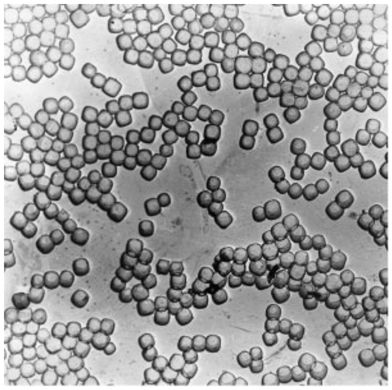
The possibility of the participation of an individual microcrystal in a coalescence process is determined by its size.[5] As a result of Ostwald ripening there is a change of the microcrystals size and owing to a high mobility of ions in gel the rate of this process depends on microcrystal concentration in a smaller degree. After a certain time interval the system does not contain microcrystals capable of providing the growth of tabular crystals by the coalescent mechanism. Then the growth of tabular crystals by the coalescent mechanism stops. Thus, the radius of the action of a nucleus is always limited by speed of a microcrystal movement in gel.

If the amount of nuclei is great, zones of their effective action are overlapped and all microcrystals of the fine emulsion can participate in growth by the coalescent mechanism. Then it is realized the average equivalent diameter of formed tabular crystals does not depend any more on the concentration of microcrystals of the fine emulsion and approaching the value of an average equivalent diameter of tabular crystals obtained by means of physical ripening. Thus, the final emulsion contains tabular crystals with high crystallographic uniformity, the share of isometric microcrystals being considerably reduced.

When reducing of the concentration of microcrystals in gel, the system in which the contribution of the coalescent mechanism can be up to zero level can be created. Under conditions, the transformation of nuclei into tabular crystals by the ionic mechanism is observed. However as the growth by the coalescent mechanism is impossible, the tabular crystals do not have advantages over isometric crystal as to growth rate. Therefore the mix of tabular and isometric microcrystals with approximately the same as a result of recrystallization is formed.

The realization of a crystallization process in the gel allows in the greater degree to control this process and to operate the relative contribution of the ionic and coalescent mechanism to formation of final crystals.[6]

In this paper the results of addition research of a recrystallization of silver halide microcrystals in the gelatin gel are submitted. The basic attention was given to study of the mechanism of growth of tabular crystals.



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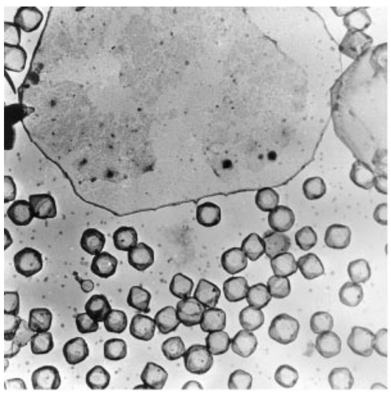

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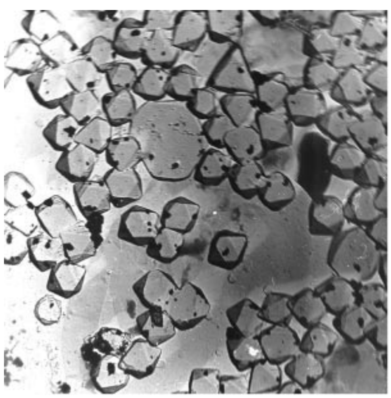

c

Figure 1. The micrographs of coal replicas of microcrystals after recrystallization in gel: a – cube crystal (600 nm); b – mixture of cube and fine crystals (fine crystals concentration $1*10^{17}$ l^{-1}); c - mixture of cube and fine crystals (fine crystals concentration $3*10^{16}$ l^{-1}).

Experimental Results and Discussion

Growth of Isometric Crystals in the Gel.

The processes of a recrystallization in a mix of emulsions with cubic crystals AgBr with the average size of 600 nm and with fine crystals $AgBr_{0.96}I_{0.04}$ with the average size of 50 nm were investigated. During experiments the constant quantitative ratio between crystals of various types was constant and only total concentration of particles in system was changed.

Is shown that recrystallization of an emulsion with cubic crystals in the gelatin gel at pBr=1.0 does not result in essential changes of its dispersion characteristics (see Figure 1a). Though in these conditions the surface (100) is nonequilibrum, the shape of crystals does not change almost. Thus in system, in which distinction in solubility of crystals is small, the processes of a recrystallization practically do not take place.

The intensive recrystallization is observed at presence in the gel of crystals, with significant size difference. It was established, that at high concentration of microcrystals (more than $1*10^{17}$ l^{-1}) the significant growth of isometric crystals is observed, but simultaneously there is a formation of tabular crystals of halide composition presumably $AgBr_{0.96}I_{0.04}$ (Figure 1b). Thus initial microcrystals of a fine emulsion are disappear via two simultaneous processes. The size of final tabular crystals practically does not differ from the size of tabular crystals received at a recrystallization of the fine emulsion in absence of isometric crystals.

At low concentration of microcrystals (less than $5*10^{16}$ l^{-1}) the growth of isometric crystals proceeds with high efficiency, though a little slower. However the tabular crystals in these conditions practically is not formed (Figure 1c). Thus, the result of a recrystallization for isometric crystals in a small degree depends on distance between particles in the gel. In our opinion it testifies that the growth of isometric crystals proceeds mainly on the ionic mechanism.

Growth of Tabular Crystals in the Gel.

At high concentration of microcrystals of a fine emulsion in the gel growth already of existing tabular crystals and the formation of new tabular crystals proceeds without complications. In result the mix of tabular crystals with lateral shells $AgBr/AgBr_{0.96}I_{0.04}$ and tabular crystals $AgBr_{0.96}I_{0.04}$ is formed. It is necessary to note that at growing of lateral shells the shape of crystal change from triangular to hexagonal.

It is believed that the high speed of lateral growth of tabular crystals is caused by presence of a nonequilibrum surface (100) on their lateral sides. This surface does not degenerate in conditions of a low supersaturation of reactionary environment, that corresponds to conditions of physical ripening or recrystallization in the gel. Thus, the tabular crystal should create in the gel around of itself stable in time field with an essential gradient of concentration. It, in turn, should cause higher growth rate of tabular crystals on the ionic mechanism in comparison with isometric, as the growth of isometric crystals results in degeneration of fast-growing surfaces (100).

In practice at low concentration of microcrystals in the gel (less than $5*10^{16}$ l^{-1}) the efficiency of formation of tabular crystals is considerably reduced. In these conditions the speed of lateral growth becomes comparable with growth rate in thickness. It is necessary also to note, that is not observed changes of the shape of tabular crystals from triangular to hexagonal, as in case of high concentration of fine crystals. The given phenomenon can be explained by reduction of amount of crystals of a fine emulsion capable to provide growth of tabular crystals on the coalescent mechanism. In these conditions the tabular crystals have not advantages on growth rate before isometric.

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