Tabular Crystals Nuclei Generation during Mass Crystallization

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Abstract

The investigation of influence of double jet synthesis conditions on formation of tabular microcrystals nuclei has been carried out. As varied parameters the concentration of gelatin, pBr value, concentration and rate of introduction of reagent solutions have been used. The original technique of definition of a share of tabular crystal nuclei among microcrystals of fine emulsion has been applied. The expressed influence of concentration of entered reagent solutions on process of formation of tabular microcrystals nuclei has been revealed. On the basis of the received data the new theoretical model of process of generation of tabular microcrystals nuclei during a mass crystallization has been developed.

Introduction

Tabular silver halide microcrystals or -crystals are widely used in modern photographic materials. Despite intensive research during last 30 years, a great number of problems concerning the processes of formation and growth of these microparticles during mass crystallization are to be solved. The problem was discussed in[1,2].

As is known, a specific characteristic of tabular microcrystals is the presence of one or several internal two-dimensional defects of the crystal structure parallel to the large faces of the crystal[3]. These defects are commonly identified with twinning planes. The appearance of defects on side faces of tabular crystals is considered to result in their fast anisotropic growth in the lateral direction[2]. However, the mechanism of the appearance of these defects is not clear so far. According to a more traditional point of view, the formation of twin planes can be due to a high level of supersaturation near a large face of a tabular crystal[4]. The counter-argument is the formation of additional twin planes on already existing tabular crystals is not observed even under the conditions of high supersaturation in the system during mass crystallization in the course of the preparation of silver halide photo emulsions. Making an attempt to resolve the contradiction, a group of Dutch researchers supposed[5] that embryos of a new layer on a growing large face in a twin position should less stable than in a regular position. Therefore, additional twinning planes are not formed any more as soon as a rather large surface area of main planes of tabular crystals results.

Within the framework of an alternative model it is supposed that the formation of two-dimensional defects could be caused by the aggregation of newly formed particles[6,7]. The aggregation (coalescence) model was paid a great attention to after Antoniades and Wey had shown an unambiguous connection between the intensity of aggregation processes and the amount of tabular crystals formed during the controllable double-jet crystallization[8]. This was confirmed by a number of independent researches[9,10]. Finally, Hosoya and Urabe showed that tabular crystal embryos could be formed even when rather large AgBr microparticles (~100 nm) aggregate, however, this becomes possible only in the absence of gelatin[11]. Therefore, the aggregation of very small newly formed particles must be the only way of the formation of tabular crystal embryos when synthesizing the photo emulsions by the double jet technique. On the basis of the data on the distance between twin planes in tabular crystals[12] and the experimental data of Antoniades and Wey it can be assumed that the diameter of these particles does not exceed 20-40 nm.

Unfortunately, the study of aggregation processes resulting in tabular crystal embryos during the double jet crystallization in a greater detail, is complicated by a number of difficulties. On the one hand, the interpretation of the data of turbidimetric investigations is hindered when the bimodal distribution (isometric particles and embryos) exists[13]. On the other hand, the electron microscopic studies of dispersion characteristics require a rather accurate preparation of materials because of low colloid stability of the analyzed system and parasitic processes of aggregation and Ostwald ripening at the stage of replica preparation.

However, there are some other approaches to studying the aggregation processes. Larichev and Kagakin[9] suggested the technique based on the investigation of dispersion characteristics of tabular microcrystals obtained by the physical ripening technique of fine emulsions. Specific particles, in addition to common isometric particles, were shown to be formed when synthesizing fine emulsions by the double jet method. These particles during subsequent physical ripening at the increased temperature and low pBr (~1,0) play the role of tabular crystal embryos. In this process all other common isometric crystals are the materials for growing the tabular crystals. Therefore, after the process of physical ripening is completed, only tabular crystals remain in the system.

The equivalent diameter of resulting tabular microcrystals shows the quantitative ratio between common silver halide particles and tabular crystal embryos in a fine emulsion. The more the share of embryos is, the less is the diameter of final tabular crystals. Therefore, having analyzed the dispersion characteristics of the tabular crystals formed during the physical ripening of fine emulsions synthesized under different conditions, it is possible to establish the interrelation between the conditions of crystallization of a fine emulsion and the share of tabular crystal embryos in it. This technique was used for our research aimed at finding out the influence of double jet crystallization conditions on the formation of tabular crystal embryos.

The Model of Tabular Crystal Formation Process During Mass Crystallization of AgHal

Our experimental data allowed us to develop the model of the process of a new phase particle formation when synthesizing photographic emulsions by the controllable double jet crystallization method. It consists in the following.

In our opinion, there must be, at least, three zones with various properties inside the reactor (see. Fig. 1). For standard conditions of photo emulsions synthesis (e.g., fine emulsions) a greater part of the reactor space is occupied by the zone with an excess concentration of bromide ions. It is in this zone where the electrode systems for the control of pBr (pAg) value are usually placed, and where the concentration of excess bromide ions during the synthesis of photo emulsions is kept unchangeable.

Since the added silver nitrate solution cannot be instantly neutralized, the second zone with a nonzero dimension and with silver ion excess is formed in the vicinity of the point of its introduction into a reaction mix. And, finally, the third zone appears on the boundary of these two zones where a chemical reaction between Ag^+ and Br^- ions proceeds (the reaction zone or the phase formation zone). The last zone extent cannot be too large because of a very high rate of the reaction between ions in solution. Taking into account the requirements of material balance and also the data on an average rate of liquid movement in the reactor it can be assumed that the diameter of a sphere corresponding to the reaction zone does not exceed a few centimeters.

Our experimental data and the contradictory data in[14-16] on the maximum rate of the introduction of the reagents resulting in intensive aggregation, confirm the conclusion that the dimension of the reaction zone does not depend on the flow rate of an injected reagent solution, and is determined, first of all, by hydrodynamic conditions in the reactor. Within the framework of the suggested model, it is possible to give a new interpretation of the experimental data on the contribution of various crystallization conditions into the formation of tabular crystal embryos. But, it is necessary to take into account the fact that newly formed AgBr particles participate in the Brownian (thermal) motion, and in the movement of the liquid in the reactor (turbulent diffusion). The latter influences the rate of spreading the reaction zone and rate of increase in the distance between particles.

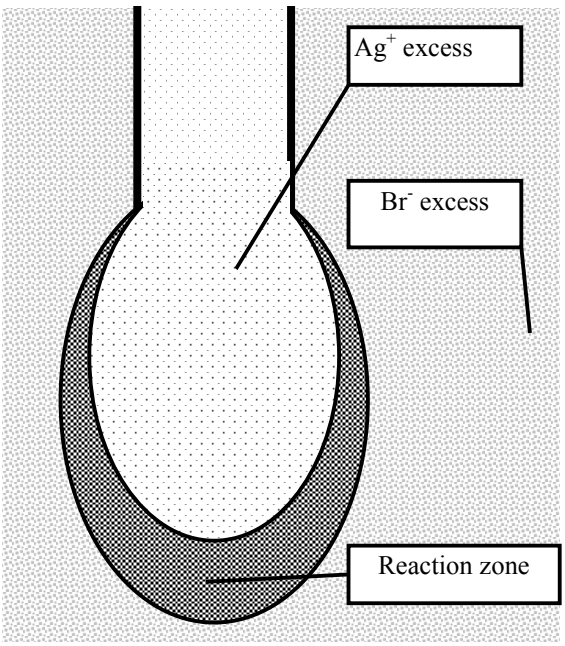

Fig. 1. *The distribution of different zones when introducing the silver nitrate solution into a reaction mix (the solution containing a bromide ion excess).*

The aggregation resulting in the embryo formation of tabular and twin grains occurs between the newly formed particles in the reaction zone. The frequency of collisions, is likely to be rather large, however, not every contact of particles results in their aggregation. Therefore, a necessary condition for irreversible aggregation is to keep a high volumetric concentration of ultra-fine interacting particles for a rather long time.

Thus, the factors that facilitate the aggregation, include the crystallization conditions contributing to the increase in local supersaturation (it results in the growth of the concentration of newly formed particles and the decrease of their size), the decrease in the concentration of a protective colloid (gelatin) and the rate decrease of turbulent diffusion in solution (it enables to keep the concentration local particles at a high level for a long time interval).

The present model makes it possible to give a qualitative interpretation of the experimental data on the effect of crystallization conditions on the formation of embryos of twin and tabular crystals during double jet emulsification:

Varying the pBr value in a reaction solution. The increase in concentration of bromide ions in the reactor should result in the acceleration of a neutralization process of silver ions added into the reactor. As a result, the surface of the reaction zone should be reduced. Following Dolgonosov[17], it can be assumed that the phase formation area for lower pBr values shifts to the interface of solutions. As the amount of newly formed particles remains

approximately constant, partial concentration in the reaction zone increases, which promotes a more effective aggregation (the formation of tabular crystal embryos).

Varying the concentration of added reagents. The increase in $AgNO_3$ concentration at > 0,5 M when the reaction zone dimension is constant results in a high concentration of newly formed particles and to the increase in the share of formed units. The increase in the amount of tabular crystal embryos for a low concentration of reagents is accounted for by the fact that the aggregation between ultra-disperse particles becomes possible not only in the phase formation zone, but throughout the reactor as well. Since the growth of particles under these conditions proceeds slowly, microcrystals (20-30 nm) are accumulated in the system. These particles can effectively aggregate with each other, as they possess high mobility by virtue of their small size and their concentration is rather high. Besides, forces of electrostatic repulsion between such small grains are rather weak; macromolecules of gelatin cannot hinder much their aggregation since they form looplike structures with the diameter of loops about 40-50 nm in an adsorbed state.

The increase in the initial volume of the reaction mix is similar to the decrease in the concentration of reagents. In the former case, ultra-disperse particles when circulating throughout the reactor, do not often get into the reaction zone, i.e. their growth is limited. Hence, under these conditions the number of particles in the system capable of forming a tabular crystal embryo during aggregation again increases. It gives rise to, in many respects, the problems of scaling, i.e. the use of the emulsification technique employed in the installations of small volumes in industry. As one of the versions of solving the above problem, it was suggested to use cascades of reactors of smaller volume instead of big reactor[18]. Another version is to use continuous reactors where the phase formation is carried out under the same conditions[19].

Varying the reagent introduction rate. In this case more intensive aggregation can take place only when the geometrical dimension of the phase formation zone does not change. Then, increase in the reagent introduction rate plays the same role like increase in the concentration of added reagents.

Varying the temperature. Varying the temperature is one of the basic ways of governing the dispersion characteristics of resulting grains. Increase in temperature results in the growth of an average size of newly formed particles. When the molar reagent introduction rate is constant, this is equivalent to decrease in partial concentration in the phase formation area, which, in its turn, reduces the efficiency of aggregation as well. Besides, the growth of the particle size reduces their mobility, increases electrostatic repulsion and makes aggregation prevention on the part of adsorbed gelatin macromolecules more effective. That is why, temperature increase usually results in the reduction of the share of tabular.

On the basis of the above-mentioned, it can be to asserted that the model suggested in the present paper, though it is of a qualitative character, allows us to provide an explanation for a wide scope of problems, available at the present moment, concerning the formation of AgHal tabular crystals during mass crystallization.

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Biography

Timothy A. Larichev was born in Tomsk (Russia) on May 9, 1964. In 1986 graduated from the State University of Kemerovo, Chemical Department. Since 1988 he works on Kemerovo State University's Inorganic Chemistry Chair. Doctor of Chemistry since 2002. Field of research is the mass crystallization processes of silver halides. He is the author of more than 50 scientific publications.