

Coagulation Mechanism of Nucleation of Tabular Microcrystals at Double-jet Crystallization

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Abstract

Double-jet crystallization of AgBr is considered as non-equilibrium process where the homogenization of a supplying solution of AgNO₃ is accomplished in two stages: 1) mechanical grinding of initial drop of a solution up to extreme possible sizes, specified by construction and performance of crystallizer, 2) diffusion of reactants ions and derivation of AgBr molecules around a microdrops and local areas of super-saturation where primary nuclei of opposite charges are developed stimulated by an adsorption of determining a potential reactants ions.

The further changes are analyzed in terms of the coagulation model of the non-equilibrium disperse Smolukhovskiy-Mueller system and it is supposed, that the coagulation of two initial nuclei in two cases from four results in appearance of one nucleus of a tabular microcrystal (TMC) with one twinning plane (TP), coagulation (coalescence) of three ones results in appearance of the nucleus with two TP, etc. The product of a constant of coagulation velocity on a life time of non-equilibrium conditions is accepted as the quantitative characteristic of process of derivation of TMC nuclei.

The conditions of growth of TMC nuclei to the sizes used for obtaining micrographies are developed. Use of results of Hosoya and Urabe allowed to measure characteristic time of derivation of TMC nuclei. The research of dependencies of that time on gelatin concentration, pBr of the environment, temperature and concentration of AgNO₃ solution, supplying in a various points of crystallizer is conducted.

Introduction

The large number of the publications are devoted to the mechanism of nucleation and formation of tabular microcrystals (T-MC) of silver bromide. For a long time it has become clear, that T-MC will be derivated under conditions double-jet precipitation or recrystallisation fine grain emulsion for large surplus of halogen ions, owing to

formation of twin-planes (TP), but the mechanism remains obscure.

It is reasonably to believe that T-MC formation mechanism according to which TP will be formed as a result of coagulation of two and more primary nuclei. Models used by the majority of the authors of the publications are based on the following postulates:

1. The used reactor is the reactor of instantaneous ideal mixing.
2. The nucleation process in the reactor occurs after the homogenization will be completed, i.e. the origin nucleus appeared in a homogeneous solution.
3. It is supposed that despite of a homogeneity some areas with positive or negative ions surplus arise in the reactor.
4. In these areas the ions adsorption reaction rate is great but outside of them is small. Only in these conditions two nucleons can collaid, having various charges.

The conditions necessary for fulfilment of these requests contradict one another. Owing to the contradiction is very difficult to offer an adequate model of T-MC nucleation and to determine the quantitative characteristic of this process. Just thereof the contradictions, the share of T-MC is characterized as "small" or "high", that does not give actual submissions about dispersity of emulsions and about probability of coagulation process. In this connection the finding of a criterion of quantitative valuation of T-MC formations has large significance for understanding of the mechanism of this process.

This work is devoted to revealing of the T-MC nucleation mechanism and determination of the quantitative characteristic of this process.

Experiment

The AgBr microcrystals prepared by balanced double-jet precipitation. For revealing influence of main crystallisation parameters at the nucleation stage, pBr value varied from 1,2 up to 4,1; gelatin concentration changed from 7,5 up to

0,2 g/l; concentration of silver nitrate from 3 up to 0,1 mole/l; temperature at nucleation stage from 30 up to 60°C.

In all experiments at the nucleation stage was added 4,3 mmole of silver nitrate during 1 min (stage 1).

Obtained emulsion have hashed within three minutes (stage 2) and changed gelatin concentration up to 30 g/l (stage 3), temperature up to 60°C and pBr up to 2,0 (stage 4) and carried out T-MC growth. The conditions of growth reaction were selected to exclude possibility of nucleation of new crystals. At the growth stage 0,2 or more mole of silver nitrate was added.

Received T-MC controlled using electronic microscopy method. The selected upon termination of growth probe, stabilized by introduction of a solution 1-fenil-5-mercaptopotetrasol.

Turbidimetry measurements fulfilled with KFO-2. The probe stabilized by introduction of TAI solution.

Relative time of coagulation, τ , determined, using the M. Smoluhovsky equation of fast coagulation kinetics. The method of account is diskribed in [1].

Results and discussion

From thermodynamics positions double-jet precipitation device represents the system, which exchanges substance and energy with the external environment and consequently, may not considered as equilibrium state. In this system at the first stage, i.e. at nucleation stage, are formed colloidal particles and system represents non-equilibrium unstable colloidal system consisting of crystalline nuclei and gelatin clusters in water.

In any mixing device it can not give instantaneous homogenization of added reactants. According to this fact we shall consider the following model of origin of a solid phase.

In the reactor with some mixing system containing bromide ions and gelatine clusters, the silver nitrate solution is added, and crushed in small drops with a size 1-10 μm depending on mixed rotation rate. Therefore, by analysis of the system it is possibly to consider that in the one reactant ions containing medium are held spherical drops of other reactant solution. The subsequent gomogenization is controled by mutual diffusion of ions of reactants and appearance of insoluble molecules.

The model, offered for the analysis, can be realized by the absence of mutual affection of separate drops divided one from another as in space and in time during all nucleations stage. The availability of such influence marks approach of stage of T-MC growth. The management of this transition, within the framework of a discussed model, implements decrease of concentration of a reactant submitted in the reactor or increase of reactor temperature to appropriate growth of dissusion coefficient.

In absence of drops mutual affection and by approximatly equality of drop volumes, the total number of nuclei in the given moment of time is equal to product of number of the nuclei which have arised near to one drop, on number of drops, that is weight of an added reactant.

Then, for want of constant conditions in reactor, the duration of nucleation stage should result in different sizes final MC because of different values of numerical concentration of nuclei at the beginning of growth stage. Under condition of $m_n \ll M_r$, where m_n and M_r - weight of a reactant entered at the stage of nucleation and growth, we shall receive a size of a T-MC at the end of growth, equal,

$$d = \frac{\text{const}}{\sqrt[3]{m_n^3}} \quad (1)$$

On a figure 1 the experimental data and settlement dependence which is indicative of justice of the stated offers are indicated.

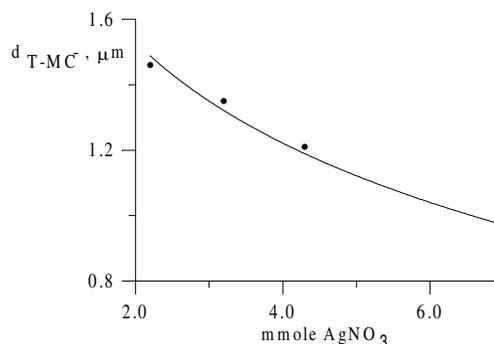


Figure 1. Mean diameter of T-MC at the end of the growth stages versus silver nitrate weight added in the nucleation stage

Thus, the derivation T-MC nuclei proceeds in a vicinity of one drop, which sizes are approximately equal 1-10 μm .

The satisfactory correspondence of data indicated on a figure 1, allows to evaluate sizes of T-MC nuclei at the end of nucleation stage.

For this purpose, besides the assumption of an invariance of numerical concentration of dispersible particles, we shall consider, that the nuclei have the spherical form, and T-MC at all stages are selfsimilar, i.e. have aspect $a_s = d/h = \text{const}$. Then

$$n_{T-MC} = \frac{Mv_m}{pd_{T-MC}^3} \cdot 4a_s = n_n = \frac{mv_m}{pd_n^3} \cdot 6, \quad (2)$$

where

$v_m = 29,0 \text{ cm}^3/\text{mole}$ - volume of one mole of a crystalline silver bromide.

In result we have

$$d_n = \frac{d_{T-MC} \sqrt[3]{m_n}}{\sqrt[3]{\frac{2}{3} a_s M_r}} \quad (3)$$

Believing $a_s = 15$, we shall receive $d_n = 95$ nm, and for want of $a_s = 30$ - $d_n = 75$ nm.

The obtained sizes of T-MC nuclei are represented largely overestimated. Besides the assumption of an invariance of numerical concentration contradicts numerous experimental and theoretical data.

For finding out a situation the measurements of sizes of dispersive particles by a method turbidimetric at three stages prior stage of growth and divided by the acts of exchange by substance or energy with an environment were conducted.

The probe took after stages 1,3 and 4. As a result we have received - 27 nm, 53 nm and 90-100 nm accordingly.

Despite of provisional concurrence of results of measurement of sizes of dispers particles in the beginning of stage of growth with estimated values, the assumption of an invariance of numerical concentration causes the reasonable doubts. These doubts may be destroyed if to assume, that proceeding in a vicinity of each drop processes result in derivation of two kinds of particles - unstable and stable. The stable particles are increased in sizes at the expense of dissolution of unstable particles.

Distinctive tag of a kind of a particle is the dissolution rate in the conditions, that it is possibly to connect with availability or absence crystalline edges. The last assumes availability of plane sites of a surface, where there is no influence of curvature on solubility.

As a rule, crystalline edge arises during growth, however it is impossible to consider a size of a particle as the defining reason of it occurrence.

Thus, in a vicinity of each drop the following processes proceed: diffusion interpenetration of reactants; chemical reaction of appearance of insoluble molecules; supersaturation growth and occurrence of nuclei of a crystalline phase; the adsorption of ions of reactants on a surface of particles accompanying not only increase of their sizes crystalline edges and occurrence, but also appearance of a charge, which sign is determined by distance from drop centre; diffusion of primary nuclei, then recrystallisation and coagulation.

As already it was marked, the edge appearance increases stability of a particle. Besides it, the availability of the crystalline planes is a condition of derivation T-MC-appearance, causing to increase growth rate and its anisotropy.

The average size of stable dispers particles is determined by local rate of supersaturation increase and processes of coagulation and recrystallisation. The local partial concentration depends on concentration, of an added reactant, and average partial concentration in the reactor, i.e. on drop dissipation rate and diffusion coefficient of dispers particles. The valuation of significances gives the following results. For drop by a size $10 \mu\text{m}$ and with concentration of a silver nitrate solution 1 mole/l in the medium with concentration of a bromide 10^{-2} mole/l (pBr 2) completion of response of recombination can pass in volume $10^2 V_d$. In this drop there is $5 \cdot 10^{-13}$ mole of substance, which in a solid phase takes volume $145 \cdot 10^{-13} \text{ cm}^3$, from which the particles

with $d = 25$ nm and volume $V = 7,8 \cdot 10^{-18} \text{ cm}^3$ will be obtained, that is in all $N = 2 \cdot 10^6$ pieces. Partial concentration for want of it of $n = 4 \cdot 10^{13} \text{ cm}^{-3}$.

For volume of the reactor equal 500 cm^3 used in our experiments we receive $n_n = 4 \cdot 10^{12} \text{ cm}^{-3}$ at the end of nucleation stage, i.e. the coagulation of dispersive particles is most probable in a vicinity of each drops.

Thus, offered in [1,2] method of quantitative valuation of efficiency of TP formation is applicable only to stable dispers particles. However availability of other particles does not change an essence of process. The determination of the quantitative characteristic has allowed to reveal influence of gelatin and silver nitrate concentration on relative characteristic time of coagulation (τ), which is the quantitative characteristic of TP formation (figure 2).

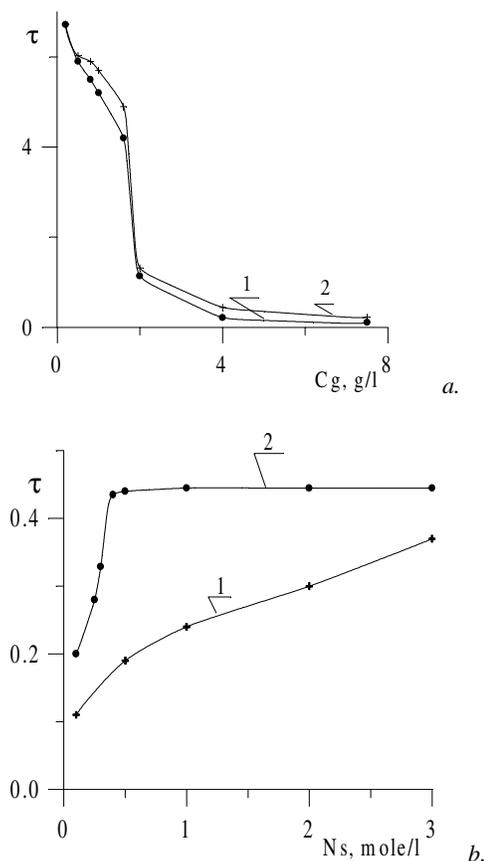


Figure 2. Relative characteristic time of coagulation (τ) versus a) gelatin concentration in reactor solution; b) silver nitrate solution concentration. 1 - added in centrum reactor; 2 - added in periphery reactor

The method of account τ , based on the M. Smoluchovsky equation of fast coagulation kinetics with attraction of data in [3], is in-depth indicated in [1,2].

On a figure 3 the dependence τ from concentration of bromide ions in the reactor is indicated. This dependence has a well resolved minimum [4] in interval pBr 3,2-3,4, that does not allow to connect the changing only with the supersaturations value. In our opinion, the character of

dependence is connected to critical growth rate (R_{cr}) of a side (111). This critical growth rate is investigated in [5] and is indicated on a figure 3.

As it is seen on a figure 3, the dependence of critical growth rate of a side (111) and τ from pBr are similar one another. Hence, the TP formation on (111) for want of pBr 3,2-3,4 proceeds with smaller probability owing to minimum growth rate of this side. The deviation from pBr 3,2-3,4 in the party of its increase or decreases increases critical growth rate of a side (111) and, as a consequence, probability TP formation.

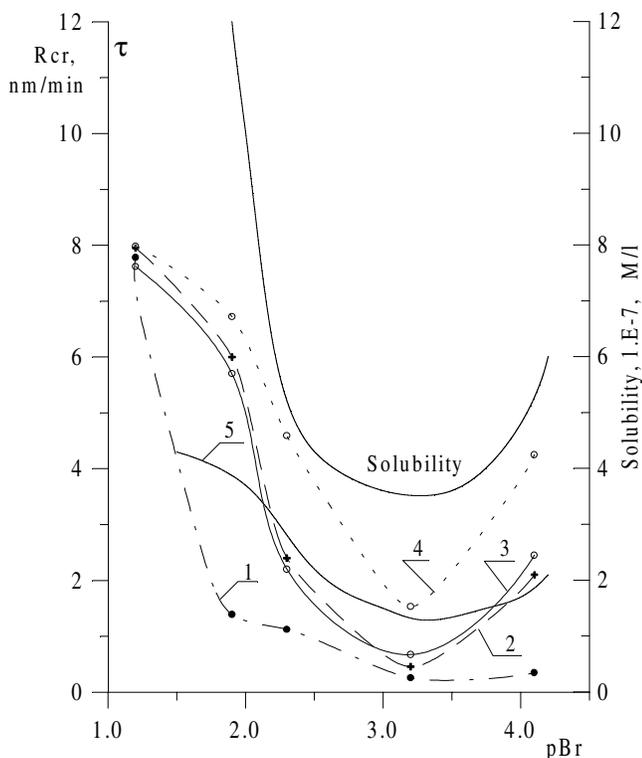


Figure 3. Relative characteristic time of coagulation (τ) versus pBr of the reactor medium at the nucleation stage. 1- $C_g=2$ g/l; $N_s=1$ mole/l; 2 - $C_g=1$ g/l; $N_s=1$ mole/l; 3 - $C_g=1$ g/l; $N_s=0.25$ mole/l; 4 - $C_g=0.2$ g/l; $N_s=1$ mole/l; 5 - critical growth rate of a side (111)

On a figure 4 is indicated temperature-viscosity dependence of τ . The reactor medium viscosity can be changed both temperature, and gelatin concentration. The increase of viscosity by changing of temperature results in growth τ , and the increase of viscosity by changing of gelatin concentration results in a falling τ .

The various character of these dependences shows, that temperature renders influence on primary nuclei appearance but gelatin concentration on the consequent process of their coagulation.

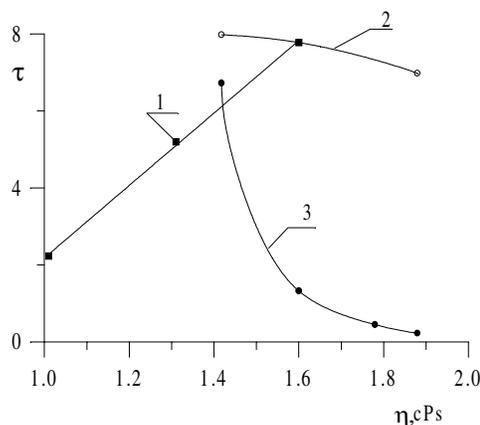


Figure 4. Relative characteristic time of coagulation (τ) versus viscosity of the reactor medium at the nucleation stage, changed 1- temperature increases, pBr 1,2; 2- gelatin concentration, pBr 1,2; 3- gelatin concentration, pBr 1,9

Conclusion

Thus, the results allow to conclude, that double-jet precipitation it is necessary to consider as non-equilibrium process in the open system.

On this basis the model of T-MC creation is offered, on which the nuclei appearance of a solid phase begins before homogeneity setting up and near to boundary of two solutions. This model has allowed quantitatively describe process of T-MC creation.

References

1. A.V. Medvedeva, A.G. Kotov, Zh. Nauch.Prikl.Fotogr., **45**, N 1, 3(2000).
2. A.G. Kotov, A.V. Medvedeva, Zh. Nauch.Prikl.Fotogr., **45**, N 1, 13(2000).
3. Y. Hosoya, S. Urabe, J.Img.Sci. and Technol., **42**, 487(1998).
4. A.G. Kotov, A.V. Medvedeva, Zh. Nauch.Prikl.Fotogr., **45**, N 2, 28(2000).
5. T. Sugimoto, Sci.Publications of the Fuji PhotoFilm Company, **30**, 28(1985).

Biography

Alexander G. Kotov is a Dr. of Sciences, Professor, of Laboratory of Physical-Chemical and Photographic Investigation, and the author 100 papers. His field of scientific interest includes radiation and photochemistry, scientific and applied photography, technology of photographic materials and optical recording materials.