JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 45, Number 3, May/June 2001

Recrystallization of Isometric AgBr Microcrystals in a Gelatin Gel

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The investigation of kinetics of recrystallization (Ostwald ripening) of silver bromide microcrystals in gelatin was carried out. A theoretical model of the process of mass transfer between microcrystals during recrystallization was proposed and experimentally confirmed. Change of size of the crystals was monitored by a turbidimetric method. It was established that the rate of recrystallization is inversely proportional to distance between crystals in a gel and directly proportional to solubility of the dispersed phase. It was shown on model systems that the growth rate of large crystals is proportional to difference in size of large and fine crystals. It was also revealed that during recrystallization there is a change in growth rate of large crystals, which is caused most probably by change of habit of these crystals. The experimental approach allows study of the driving force and mechanism of recrystallization processes in more detail.

Journal of Imaging Science and Technology 45: 241–246 (2001)

Introduction

The photographic emulsions used in the technology of manufacturing silver halide photographic materials comprise silver halide microcrystals in the size interval of 50–1000 nm, which are dispersed in medium of a protective colloid (gelatin). Now the most widely used methods of synthesis of emulsions involve a controlled double jet crystallization and a physical ripening of the resulting fine grain emulsions. There is a common opinion that during double jet crystallization continuous nucleation of microcrystals of a silver halide takes place; these nuclei serve a centers for growth of larger crystals.[1] In the most perfect techniques of synthesis these two processes are divided spatially.[2] Thus the key processes during mass crystallization is the process of recrystallization, i.e. transformation of finer crystals into larger in closed (physical ripening) or open (double jet crystallization) systems.

As is known the process of mass transfer between colloidal particles of different size in the closed system is called Ostwald ripening. For the description of kinetics of this process now the approaches advanced by Lifshitz and Slezov, and also Wagner often are used (LSW theory).[3,4] This classical theory is usually used for description of physical ripening of silver halide microcrystals.[5,6] Accordingly it is necessary to pay attention to the experimental conditions, whereby the surface energy of a microcrystal depends both on its shape and on the concentration of halide ions in solution.[7] In most cases the experimental results are in good conformity with the LSW theory.

Unfortunately not all events occurring during recrystallization can be adequately described within the framework of LSW theory. It is known, for example, that during growth of tabular crystals by means of Ostwald ripening, the size increase of these crystals is accompanied by reduction in concentration of fine crystals instead of the expected reduction in their size[8] (see Fig. 1). It is difficult enough to explain the changes in morphology of final crystals in case of recrystallization in gelatin medium.[9,10] In our opinion, for elucidating the detailed mechanism of mass transfer during Ostwald ripening it can be useful to compare results of recrystallization in a solution (melted emulsion) and in a gel. In turn the revelation of the driving force for recrystallization would allow us to solve a wide range of both technological and fundamental problems of modern photographic and colloid chemistry. However until now, as far as we know, the research on recrystallization in gelatin medium (except with respect to transformation of the gel itself) has not been undertaken in systematic fashion, and attempts to establish laws of mass transfer under such conditions has not been undertaken. Therefore the purpose of our work was to understand the process of recrystallization in medium of a gelatin gel in the specific case of isometric AgBr microcrystals.

Monitoring the change of particle size during recrystallization represents great technological difficulty. The method that allows definition of an average diameter of the growing particles with minimal intervention in the system is spectral turbidimetry, based on the phenomenon of light scattering by colloidal systems.[11] The method of electron microscopy differs owing to its high labor input and is poorly suitable in this case because of possible parasitic processes of further recrystalliza-

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Original manuscript received September 10, 2000

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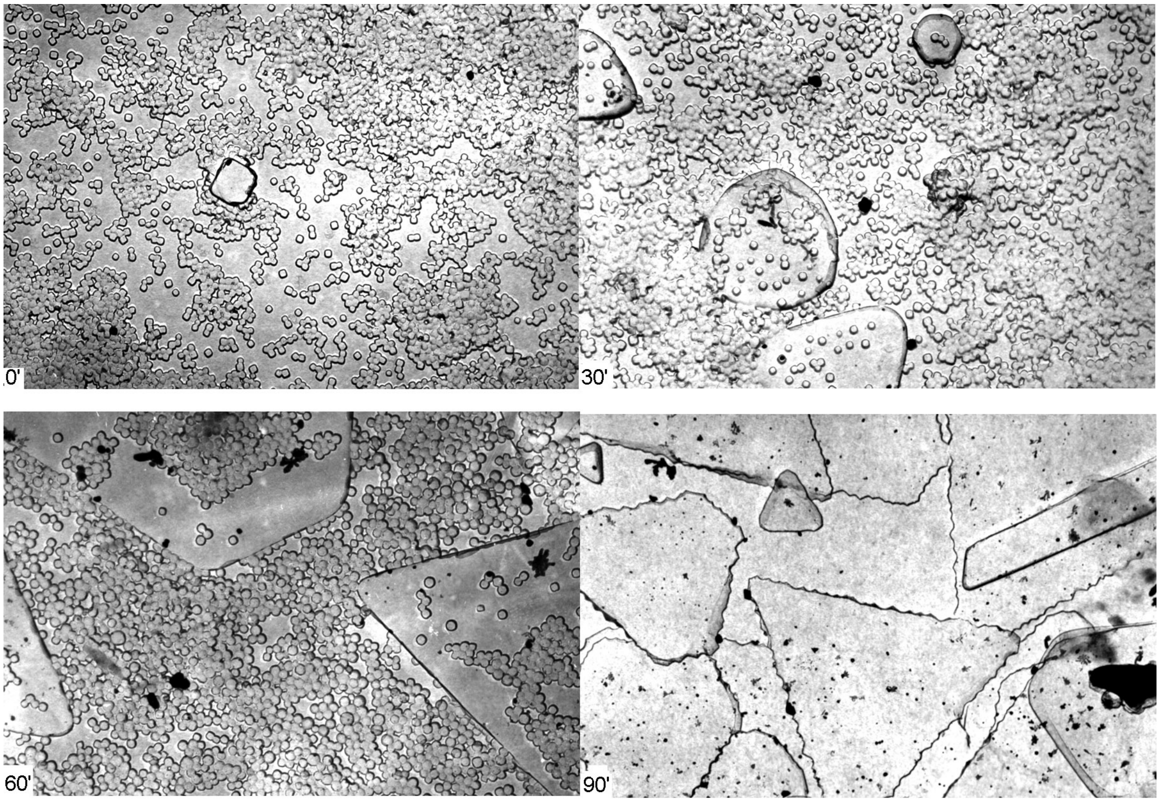

Figure 1. Electron microphotographs of carbon replicas of microcrystals formed during physical ripening of a fine grain emulsion. The ripening conditions are as follows: T = 60°C; pBr = 1.0; gelatin concentration 30 g/l; initial fine microcrystal concentration 3.5×10^{15} l^{-1}: 0' – initial emulsion (×6000); 30' – 30 minute physical ripening (×6000); 60' – 60 minute physical ripening (×6000); 90' – 90 minute physical ripening (×4000).

tion at the stage of preparation of replicas of the emulsion microcrystals.

The method of specific turbidity was widely used in modern research into processes of formation and growth of silver halide microcrystals.[12–14] However in all these investigations the size of microcrystals was in the domain of applicability of Rayleigh's law for light scattering by small particles. It is generally accepted that the equation of the Rayleigh is satisfied when the size of the light scattering particles does not exceed 0.1 λ, the length of a light wave.[11] Thus limiting size of crystals for research in the visible regime should not exceed 70 nm. On the other hand, the size of real emulsion microcrystals lies in the interval of 50–1000 nm for isometric microcrystals and 300–3000 nm for tabular microcrystals, i.e., mostly outside of regime of the Rayleigh equation.

Meanwhile following the more common laws of light scattering allows us to use a turbidimetric method for characterization of silver halide particles of large size. For example, Meehans and Beattie[15] used this method for study of processes of formation of microparticles of a silver halide sol. Pruss and co-workers[16–19] carried out detailed research of the phenomenon of light scattering by large silver halide microcrystals in a dry gelatin layer. However as the literature and calculated data frequently contradict each other, we found it necessary to carry out our own research into light scattering by silver bromide microcrystals.

Experimental

Emulsions containing AgBr microcrystals of various sizes and habit were made by standard methods of controlled double jet crystallization.[20] Recrystallization in a gelatin gel was carried out as follows. The emulsions containing microcrystals of different sizes were mixed. If necessary a water–gelatin solution was added to establish the required AgBr concentration. Then 1 M potassium bromide solution was added to the mix to provide the required pBr value. The sample was placed in a sealed container and quickly cooled in water to 10°C for gelation to occur. The resulting samples was stored at room temperature, 18 ± 1°C. After certain intervals of time a sample of an emulsion was melted at 40°C and the required amount thereof was placed in a volumetric flask and diluted with warm distilled water (35°C). Then turbidimetric characterization of the sample was carried out using either a Shimadzu UV-2100 spectrophotometer or PEC-56M photoelectrocolorimeter. The wavelength dispersion of the characteristic turbidity of the system was accordingly recorded. This experimental dependence was then compared with the theoretical, predicted on the basis of the mathematical model described below. On the basis of this comparison the estimation of the degree of conversion of the fine microcrystals and of the current size of the large microcrystals in the system was carried out.

Results and Discussion

Theoretical Model of Recrystallization Process

At the first stage we investigated light scattering by real AgBr microcrystals in the size intervals of interest. For this purpose a series of monodisperse emulsions was made. The microcrystal size was determined by scanning electron microscopy (SEM). The dependencies

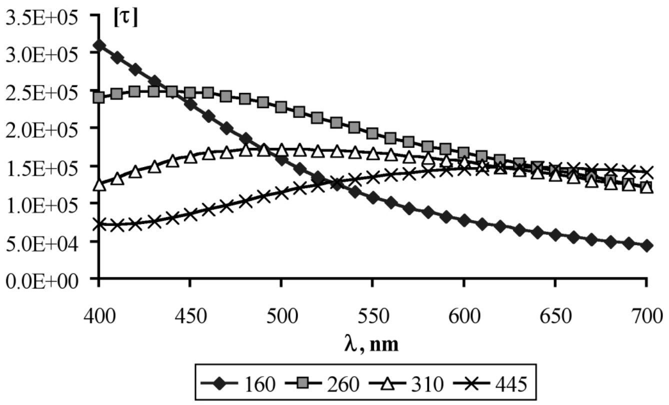

Figure 2. Dependence of the characteristic turbidity of the AgBr monodisperse emulsion on the wavelength of light. The digits in the legend correspond to the AgBr microcrystal size (nm).

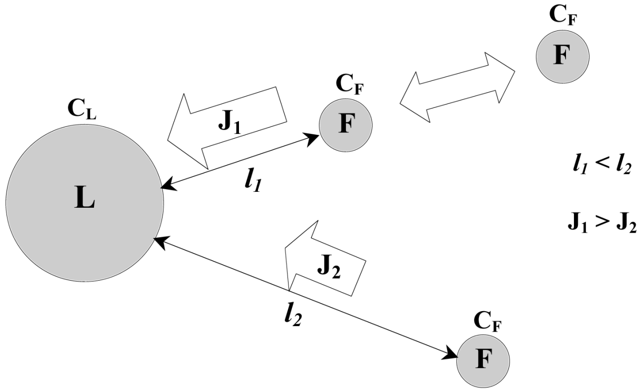

Figure 3. Schematic model of the mass transfer process between large (L) and fine (F) AgBr microcrystals in a gel, where J represents the rate of mass transport (Eq. 2), l represents the spatial separation of the microcrystals, and C is the concentration of soluble substance, i.e., AgBr, immediately above the microcrystal surface (Eq. 1).

of characteristic turbidity on the microcrystal size for different wavelengths were recorded. Representative experimental curves are presented in Fig. 2. On the basis of these data it was possible to account for change of turbidity during a recrystallization in a gel. The following theoretical model of process of recrystallization was used.

In the typical system there are two types of microcrystals of different size—large and fine. By definition the size of large microcrystals during recrystallization increases. The increase of mass of large microcrystals in the closed system is equal to the loss of mass of fine microcrystals. For simplicity of account we assume both emulsions to be monodisperse and their contribution to light scattering strictly additive. All microcrystals are also assumed to be perfect spheres.

In Fig. 3 the theoretical circuit of interaction of large (L) and fine (F) crystals in gel medium is presented. The mass transfer in the system occurs through diffusion of the soluble substance. The driving force for mass transfer is the difference in concentration of the dissolved substance at the surface of large and fine microcrystals, which is determined by the Gibbs–Thomson equation[11]:

$$C_r = C_\infty \exp\left(\frac{2\sigma V_m}{RTr}\right) \qquad (1)$$

where C_r is the solubility of a particle with radius r, C_∞ is the solubility of macro particles, σ is the specific surface free energy, R is the universal gas constant, and T is absolute temperature. According to this equation the concentration of the dissolved substance near the surface of fine crystals is higher than near the surface of large ones. The presence of a concentration gradient results in a diffusive flow, according to Fick's first law[11]:

$$J = -D\frac{dC}{dx} \qquad (2)$$

where J is the amount of the dissolved substance which passes through a unit of surface in a unit of time, D is the diffusion coefficient for the dissolved substance and dC/dx is the concentration gradient of the dissolved substance.

As all particles in a gel are motionless, the mass transfer can take place only between adjacent crystals. However mass transfer between the adjacent crystals of identical size is impossible owing to absence of a concentration gradient. If the neighbors are the large and fine crystals, the diffusive flow of the dissolved substance must be from Eq. 2 inversely proportional to distance between them (see Fig. 3). Therefore in the case where the limiting step is the diffusion of components of the dissolved substance, the growth rate of large crystals will be inversely proportional to distance up to the nearest fine crystal.

On the basis of this model we expect that during recrystallization the growth of large crystals will be accompanied by reduction of concentration of fine crystals, but that the size of small crystals will change insignificantly. Insofar as the size of crystals does not change, it is possible simply to use the initial values of a characteristic turbidity and to scale them to obtain the current $[AgBr]_F$ concentration. In turn the current concentration at a given moment in time is equal to the initial concentration minus that corresponding to the loss of mass spent for growth of the large microcrystals. This loss can be designated as Δ[AgBr]. It is obvious, that the mass of large microcrystals increase by the same value Δ[AgBr].

The size of the growing, larger microcrystals can then be expressed through this increase. However for this purpose it is necessary to know the initial concentration of large microcrystals, which can be calculated using the formula:

$$N_L = \frac{V(AgHal)_L}{V(MK)_L} = \frac{6[AgHal]_L}{\pi d_L^3 \rho(AgHal)} \qquad (3)$$

where $V(AgHal)_L$ is the total silver halide volume in large microcrystals, $V(MK)_L$ is the average volume of one large microcrystal, $[AgHal]_L$ is the concentration of silver halide in large microcrystals (g/l), d_L is the initial diameter of the large crystals (cm), and ρ(AgHal) is the density of a silver halide (g/cm^3). The value of N_L is a constant, insofar as the number of large microcrystals does not vary during recrystallization. Therefore the

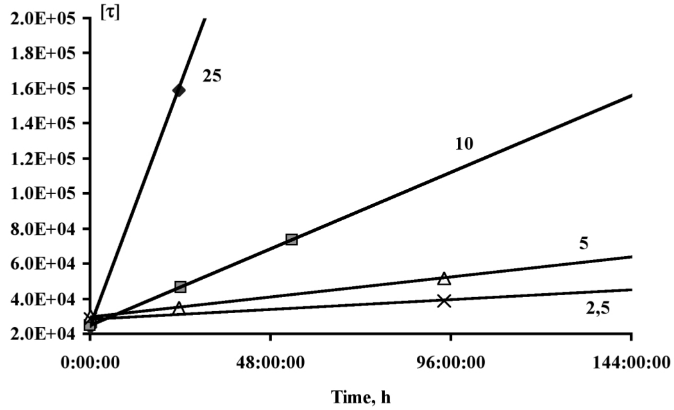

Figure 4. The experimental dependence of characteristic turbidity (λ = 490 nm) on time of recrystallization of a fine emulsion in a gel. The size of the fine crystals is 65 nm, pBr = 1.0, gelatin concentration = 4 % wt. The line labels correspond to the silver concentration in the system (g/l).

average diameter of large microcrystals at the any moment of a recrystallization can be calculated according to expression:

$$d_L = \sqrt[3]{\frac{6([AgHal]_L + \Delta[AgHal])}{\pi N_L \rho(AgHal)}} \qquad (4)$$

Given an average diameter and calibration of specific turbidity for average size of the particles, it is possible to calculate the contribution of large microcrystals to the total turbidity of the system. Thus, it is possible to determine a theoretical turbidity of system for any degree of conversion of fine microcrystals. By comparing theoretical dependence of turbidity with the experimental results, it is possible to estimate the current degree of conversion in the system and consequently, the average diameter of large microcrystals. From a series of experimental points the dependence of the average size of large microcrystals on time, i.e., kinetic curve, can, in turn, be estimated.

Recrystallization of Individual Monodisperse Emulsions

It was experimentally shown that the recrystallization of a monodisperse emulsion containing large (~300 nm) AgBr microcrystals does not result in a change of its dispersion characteristics. The spectral dispersion of light scattering for this system remains constant over a long period of time. By electron microscopic analysis we find that there is a change of a shape of the crystals from cubic to octahedral, however, even though their size does not vary. It was also shown earlier that, as a result of recrystallization of a fine emulsion in a gel, either tabular crystals or mix of tabular and isometric crystals, could be formed depending on the concentration of the microcrystals.[10] The theoretical account of the change of turbidity in a given system is complicated, as the exact number of nuclei (centers of growth) is not known. However, for a usual fine emulsion it is generally not too great. We find a linear dependence of turbidity on the degree of conversion of microcrystals of a fine emulsion (even in the initial stage of recrystallization) can in this case be observed.

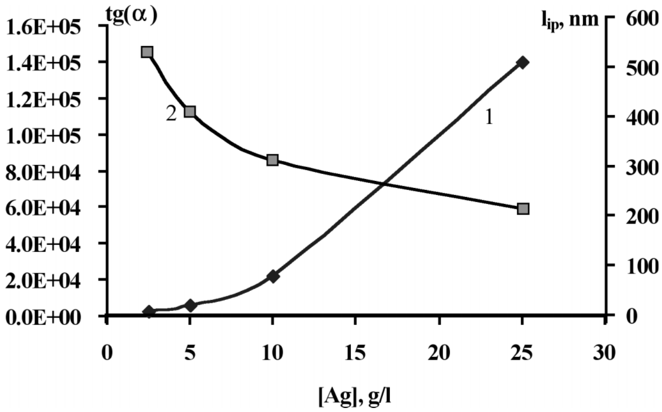

Figure 5. Dependences of the slopes of the kinetic lines (1, tg(α)) and interparticle distance (2, l_{ip}) on the silver concentration in the system.

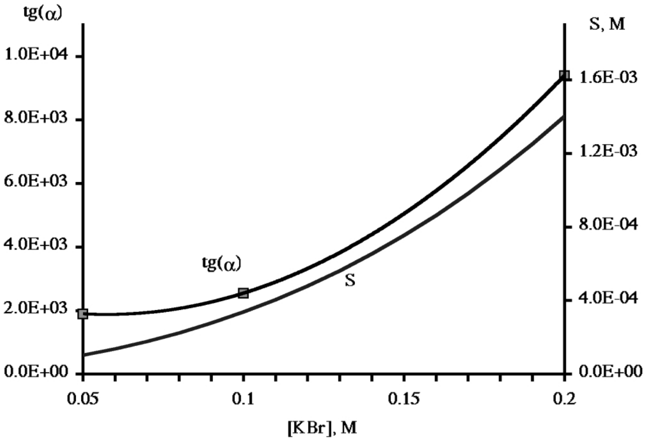

Figure 6. Dependences of the slopes of the kinetic lines (tg(α)) and the solubility of silver bromide (mol/l) on the KBr concentration in system.

Therefore as a kinetic curve it is possible to use the dependence of turbidity on time for an appropriately chosen wavelength. In Fig. 4 the similar dependencies for a number of systems at various AgBr concentrations are presented. It is possible to see that the rate of the process of recrystallization depends on the concentration of microcrystals in the system. The change of rate of recrystallization is in good conformity with our expectations based on the change of distance between microcrystals (see Fig. 5).

A series of experiments with variation in concentration of excess potassium bromide was carried out also. The results are presented in Fig. 6. In this case the change of rate of recrystallization is in good conformity with the change of solubility of silver bromide.

Recrystallization of Mixtures of Microcrystals with Large Difference in Size

In this case, because of the essential difference in solubility during recrystallization, there is a growth of large microcrystals and dissolution fine ones. The theoretical account is facilitated by the circumstance

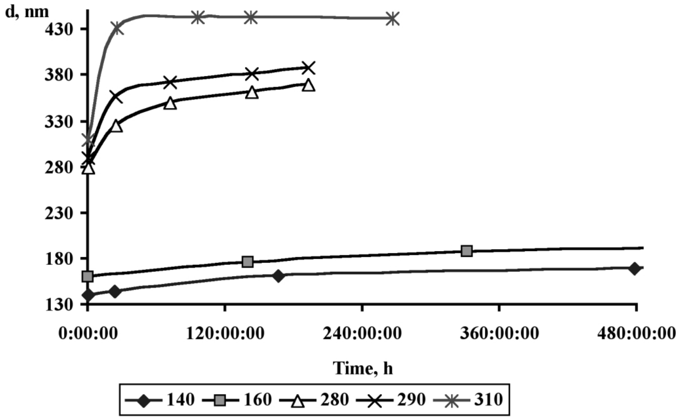

Figure 7. The increase of large crystal size during recrystallization. The mass ratio of large and fine crystals is 1:2, pBr = 1.0, total silver concentration in system = 1.7 g/l, size of fine crystals = 65 nm, gelatin concentration = 4 % by wt. The digits in the legends correspond to the initial large crystal size (nm). The 160 nm crystals initiallly had octahedral habit; all other crystals initially had cubic habit.

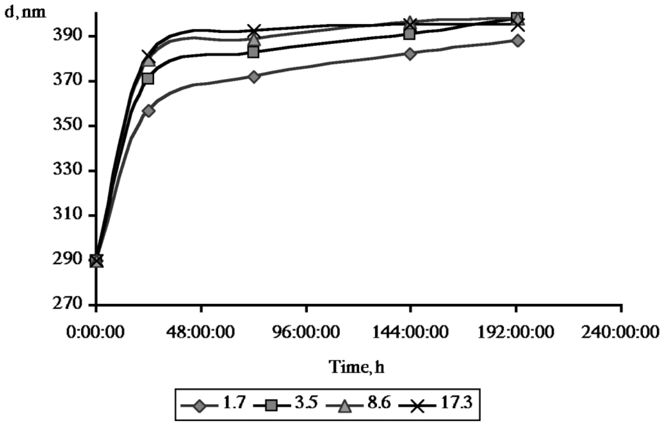

Figure 8. The increase of large crystals size during recrystallization. The mass ratio of large and fine crystals is 1:2, pBr = 1.0; the initial size of large crystals – 290 nm, size of fine crystals – 65 nm, gelatin concentration – 4 % wt. The digits in legend correspond to total concentration of silver in system (g/l).

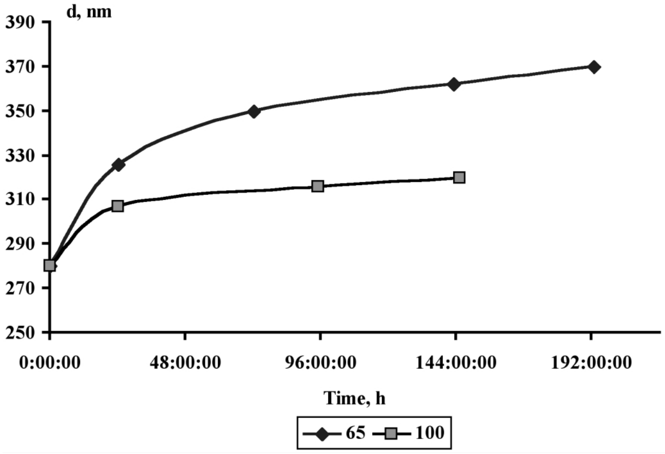

Figure 9. The increase of large crystal size during recrystallization. The mass ratio of large and fine crystals is 1:2, pBr = 1.0, the total silver concentration in system – 1.7 g/l, initial size of large crystals – 280 nm, gelatin concentration – 4 % wt. The digits in legend correspond to fine crystals size (nm).

that the concentration of large crystals in system is constant. We investigated the recrystallization of systems containing microcrystals of a fine emulsion along with larger microcrystals of cubic or octahedral habit. In Fig. 7 the comparative data on change of the size of large microcrystals during recrystallization for cases of the different initial size of these crystals are presented. It is possible to see that the speed of a recrystallization is proportional to the difference in a size between the fine and large microcrystals.

On the basis of our theoretical model the mixed system of two monodisperse emulsions with a large difference in size may be described as follows. The number of small microcrystals in our case greatly exceeds the number of large isometric ones. In the case of uniform, stochastic distribution in a gel these small microcrystals form a three-dimensional network with more-or-less equidistant points, in which large microcrystals periodically appear. On the other hand, large microcrystals principally have fine microcrystals as their nearest neighbors, whereas the fine crystals can have both large, and fine particles as nearest neighbors. Mass transfer between neighboring fine microcrystals proceeds with a slow rate because the concentration of dissolved substance near the surface of these microcrystals is essentially uniform from crystal to crystal. Thus, the concentration of the dissolved substance is constant at any point of space between the fine microcrystals.

Fast mass transfer occurs only where large and fine microcrystals are neighbors. The flow of the dissolved substance can then be described on the basis of Fick's law (Eq. 2). In the event that the growth rate of a crystal is limited by diffusion, the rate of mass transfer will be directly proportional to difference in solubility of the microcrystals and is inversely proportional to distance between these interacting crystals. If, however, the limiting step is surface reaction then the growth rate will be not dependent on the distance between microcrystals.

The dependence of grain size on time in the case of a large difference in size between interacting crystals can conditionally be broken into two steps (see Fig. 8). In the first stage the fast growth rate of the large crystals depends on the concentration of fine microcrystals, i.e., is inversely proportional to the distance between small microcrystals. In the second stage the slower growth rate does not depend on distance between microcrystals and is proportional only to difference in size between large and fine crystals. In turn the difference in size between large and fine microcrystals also influences the rate of recrystallization. This situation is illustrated in Fig. 9. As expected, with a decrease in the size difference (solubility distinction) the rate of the recrystallization process is reduced too.

We propose to explain the presence of two stages by probable morphological changes occurring to large crystals. During the first stage the growth rate of large crystals seems to be limited by a diffusion of the dissolved substance, and, hence, depends on the pathlength of diffusion. This process proceeds until, as a result of growth, the (100) surfaces of the large crystals will be replaced with (111). After that the growth rate of the large crystals becomes limited by surface reaction,[7] and becomes independent of distance between interacting crystals. The increase in mass of crystals corresponding to this transition depends on the relative ratio of (100) and (111) surfaces in the initial crystal. In other words, it depends on amount of a silver halide necessary for transformation of a primarily cubic crystal into a correct octahedron. For large cubic microcrystals the ratio of (100) surfaces to (111) is great, therefore the distinction between the first and second stages of growth is clearly expressed. On the contrary for cubes of the small size this ratio is close to unity; therefore in this case kinetics of growth of cubic (140 nm) and octahedral (160 nm) crystals appear practically identical (see Fig. 7).

Summing up, it is possible to demonstrate that the method of recrystallization in a gel provides very rich opportunities for research on the mechanism of growth of silver halide microcrystals of various forms, size and shape under different conditions. Further research in this area could help us to understand many until now unclear details of the process of mass crystallization.

Conclusions

The investigation of the recrystallization processes for silver bromide microcrystals in a medium of gelatin gel was carried out. The theoretical model of interaction of adjacent microcrystals in gel suggests dependence of the rate of recrystallization on interparticle distance, which we found experimentally. Deceleration with distance increase is conditioned most likely on the decrease of diffusion between neighboring crystals with increasing separation. Observable increase of recrystallization rate with the increase of bromide ion concentration in a system reflects an increase in silver bromide solubility. It was also shown on model systems that the growth rate of large crystals is proportional to the difference in sizes of the large and fine crystals. It was revealed that during the course of recrystallization there is a change of growth kinetics for large crystals, related most likely to a change in habit of these crystals.

The experimental data are in good agreement with the proposed theoretical model. On the other hand the data on dependence of recrystallization rate on interparticle distance contradicts classical LSW theory. It is possible to suppose that in the case of common Ostwald ripening the interparticle distance influence is masked by constant microcrystal motion due to agitation and Brownian motion. Our experimental approach allows us to study the driving force and mechanism of recrystallization processes in more detail.

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