Technical sciences

INFLUENCE OF IONIC BALANCE ON THE PROCESS OF MICROCRYSTAL AgBr (111) MATURING

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The research of the effect of photosensitivity level increase found in the process of maturing microcrystals AgBr with octahedron facets (111) without addition of sulphur containing additives (natural maturing) is carried out. It is stated that formation of sensitivity centres occurs during modification of AgBr (111) microcrystal form owing to difference of chemical potentials of microcrystal sides. Thus, the direct proofs of silver nature of sensitivity centres at maturing of AgBr (111) microcrystals in the conditions involved are obtained. The reasons of absence of natural maturing for AgBr microcrystals of a cubic facet (100) and flat AgBr (T-MC) microcrystals are discussed.

Introduction

The process of maturing of AgBr microcrystals (MC) was carried on at the value of pBr=3,0...3,2 (pBr=−lg[Br⁻]) regardless of the conditions of their production. However, the conditions of AgBr MC synthesis of different facet are distinctly different. So, octahedral, flat, and cubic microcrystals in the final stage are obtained at the values of pBr equal to 1,6; 2...2,5 и 3,2, correspondingly. In this connection there is a necessity to research the influence ionic balance change on the process of AgBr (111) MC maturing. The main factor of growth and modification of MC form is oversaturating. In the process of mass crystallization oversaturating is set by the velocity of reagent introduction into the reactor. For isolated reactor (without reagent introduction) a definite level of oversaturating is sustained due to ostwaldite maturing, in the case of homogeneous crystals it is done due to the difference of chemical potentials μ for different facets (hkl). In this case oversaturating is defined by the difference $\Delta\mu=\mu(h_1k_1l_1)-\mu(h_2k_2l_2)$, that results in the change of microcrystal facets and modification of surface. In this work the influence of the given process on the process of AgBr MC maturing of different facets has been studied.

Methods of experiment

To investigate the process of AgBr microcrystal maturing of different facets monodisperse emulsion on the bases AgBr (111) MC of sizes d=0,2...1,8 mkm, AgBr (100) microcrystals of sizes 0,2...1,0 mkm, as well as flat AgBr microcrystals produced in the conditions of controlled double-jet crystallization (CDC) and the method of physical maturing of fine-grain emulsion (FGE) were synthesized. To study the influence of production conditions, subsequent keeping in refrigerator and maturing conditions on the form and sizes of microcrystals, all MC were investigated by the method of electron microscopy (method of carbon replica). After synthesis MC were stored at T=5...6 °C during six months at pBr synthesis, as well as at the value pBr=3,0 for AgBr (111) MC and T-MC, and pBr=1,6 for AgBr (100) MC. The process of maturing was performed at fixed values of Br taken in the range of 1,6...3,2. To make the mechanism of photosensitivity centre formation more clear in the process of natural maturing of AgBr (111) MC the investigation of Gibbs-Thomson's effect influence (ostwaldite maturing) on sensitometric cha-

racteristics of AgBr (111) MC was carried out. In the experiment FGE (d=0,1 mkm) of different concentrations ($m_1<m_2<m_3<m_4$) were introduced into initial emulsion containing AgBr (111) MC with average equivalent size d=1,0 mkm, with subsequent mixture maturing during 4 h at 52 °C, pBr=3,0.

To research the photographic characteristics of photolayers the sensitometric method using sensitometer PSR-41 was applied. Exposition was made at colour temperature $T_{col.}$=5500 K and exposure 0,05 s. For all examined emulsion the sensitometric tests were carried out with determination of photosensitivity by $S_{0,85}$ criteria and fog level D_0. The sizes of AgBr MC were defined by the method of electron microscopy [1].

Results and discussion

In fig. 1 the typical data for the series of experiments in AgBr (111) (d=1,0 mkm), AgBr (100) and T-MC maturing without adding sodium thiosulphate to the solution at 52 °C, pBr=3,0 are presented. In fig. 2–4 the photomicrography of carbon replica of AgBr MC are presented after different techniques of treatment. In fig. 5 the results of photosensitivity changes in the process of natural maturing AgBr (111) MC when introducing fine-grain emulsive microcrystals (FGE MC) with sizes $d_{FGE\ MC}<d_{MC\ AgBr\ (111)}$.
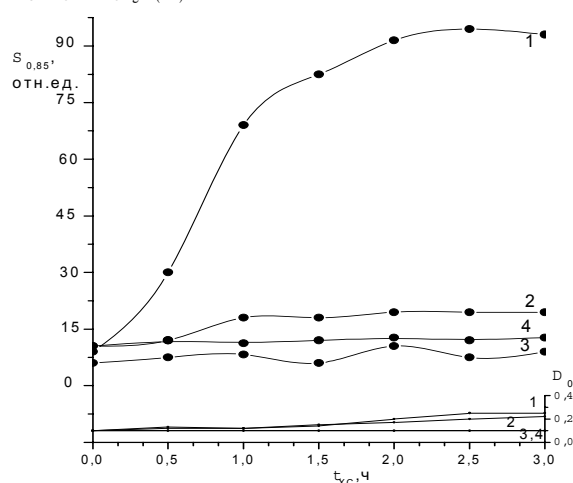

Fig. 1. *The dependence of sensitivity and fog level on time of natural maturing: 1) AgBr (111) MC; 2) AgBr (111) T-MC synthesized by CDC method; 3) AgBr (111) T-MC synthesised by the method of physical maturing of fine-grain emulsion; 4) AgBr (100) MC*

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As it is evident from the data presented in fig. 1, for AgBr (111) MC there observes the increase of photosensitivity in the process of maturing without addition of sodium thiosulphate. This effect was called by the authors [2] a natural (or spontaneous) maturing. Probably, sensitivity centres formed in the given conditions have a purely silver nature as during maturing photographically active additives including sulphur-containing ones were not added. For all other microcrystals changing the level of photosensitivity in the process of maturing in comparison with the initial sensitivity was not observed except for T-MC obtained in the conditions of controlled double-jet crystallization. For these crystals a slight increase of sensitivity was observed. One can point out that sometimes the level of sensitivity for AgBr (111) MC achieved 120...150 units, which is comparable with the values of sensitivity obtained in the conditions of ordinary chemical maturing of corresponding systems.
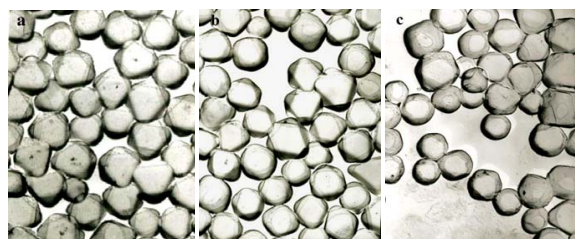
Fig. 2. *Photomicrography of carbon replica of AgBr (111) MC, d=0,7 mkm: a) initial microcrystals of octahedron facets; b) changes of form in the process of natural maturing, $t_{mat.}$=2 h; c) change of MC form in the process of natural maturing, t=4 h*
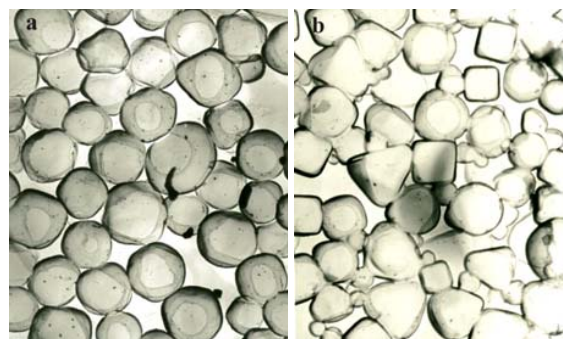

Fig. 3. *Photomicrography of carbon replica of AgBr (111) MC, d=0,7 mkm: a) natural maturing with addition of fine-grain fraction (d=0,1 mkm), t=2 h; b) natural maturing with addition of fine-grain fraction, t=4 h.*
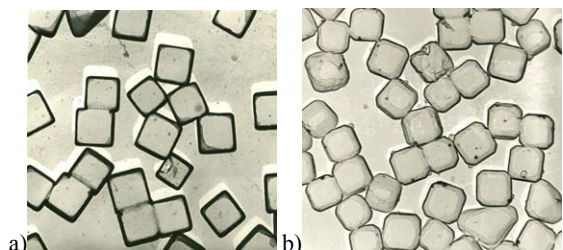
Fig. 4. *Photomicrography of carbon replica of AgBr (100) MC, d=0,8 mkm: a) initial microcrystals; b) 3 months of keeping at pBr=1,6, T=5 °C*

The analysis of photomicrography of MC carbon replica obtained (fig. 2, 4) shows that in the process of na-

tural maturing and keeping the change of form and microcrystal facets takes place. It manifests itself as smoothening away the edges and tops of octahedron at the times of maturing up to 2 h (fig. 2, b) and formation of nearly spherical and cubic form at 4 h. of maturing (fig. 2, c).
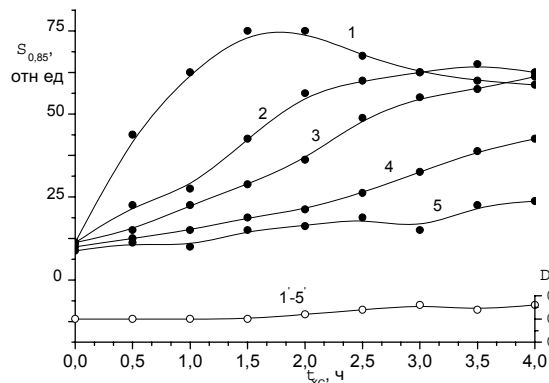
Fig. 5. *The dependence of photosensitivity $S_{0,85}$ (1−5) and fog level D_0 (1'−5') on time of natural maturing of AgBr (111) MC, d=1,0 mkm (1, 1') and with addition of AgBr FGE in different concentrations: m_1 − 2, 2'; m_2 − 3, 3'; m_3 − 4, 4'; m_4 − 5, 5'*

The increase of oversaturation in the solution by means of addition of fine-grained emulsion in the process of natural maturing of AgBr (111) MC results in increase of velocity of MC form modification. Microcrystals of spheric form appear already at maturing times t=2 h, but at 4 h of maturing there appear microcrystals of cubic facet (fig. 3). As it follows from the obtained data presented in fig. 5 (curve 1) without FGE addition a sixfold growth of photosensitivity with maximum at 1,5 h of maturing at fog level $D_0<0,1$ is observed. Introduction of fine-grain emulsion to the reactor results in slowing down the process of natural maturing and decrease of photosensitivity level (fig. 5, curves 2−5). It means that the velocity of Br⁻ and Ag⁺ ion precipitation formed at solution of fine MC on the surface of AgBr (111) MC is more than the velocity of passing into solution of low-coordinated facet (111) ions and their carrying over high-coordinated lattice points on the surface (100). At the same time microcrystal maturing at pBr=1,6...2,5 does not virtually result in modification of ArBr (111) MC form and formation of sensitivity centres. When keeping AgBr (111) MC even during 6 months at 5 °C and pBr=3,0 the change of microcrystal facet and increase of fog level in the process of spontaneous maturing are observed. All the results permit to confirm that in order to form sensitivity centres in the conditions of AgBr (111) MC natural maturing a definite level of oversaturation in reactor solution is necessary. Define the value of oversaturation in the reactor following way:

$$\Pi=\frac{[\text{Ag}^+][\text{Br}^-]}{\text{SP}},$$

where [Ag⁺], [Br⁻] − silver and bromine ion concentration in reactor, SP − product of AgBr crystal solution. Thus, excess of silver and bromine ions in the emulsion with AgBr (111) MC can appear for the following reason. It is known that up to definite sizes the microcrystals being in equilibrium with the environment take the form with the

minimum energy of the surface. This concept was formulated by Gibbs-Woolf in the form of the relations:

$$\sum_i S_i \gamma_i = \min, \quad \text{or} \quad \frac{\gamma_1}{r_1} = \frac{\gamma_2}{r_2} = \frac{\gamma_i}{r_i} = \frac{kT}{2V_m} \ln \frac{C}{C_0},$$

here S_i, γ_i, r_i – square i-facet, free energy of i-facet surface and the distance to i-facet from crystal centre (normal line to i-facet), correspondingly; V_m – MC volume in molar units, k – Boltzmann constant, C – solution concentration, C_0 – solubility at crystallization temperature.

As applied to the data presented in fig. 2, 3, the change of r_{111} and r_{100} mean the change $\Sigma S_i \gamma_i$ in line with the solution conditions. In this case oversaturation on solution containing microcrystals depends naturally on size distribution of microcrystals. Therefore, the more significant the process of recrystallization is, the less homogeneous is the distribution due to Gibbs-Thomson effect (Oswald maturing. It means that the process of natural maturing depends essentially on oversaturation, i.e. there is a threshold value Π_{thres}. In this case, if the value of oversaturation in Π solution is sufficiently more or less Π_{thres}, centre sensitivity formation at maturing occurs less effectively. For cubic microcrystals the solution conditions correspond to $\Pi \ll \Pi_{thres}$ at natural maturing and formation of sensitivity centres is not observed.

In fig. 2, 3 one can point out some forms of MC in the process of modification: octahedral, cubic octahedral (tetradecahedrons with different relation of facet squares (111) and (100)) and cubic. All the mentioned forms can be obtained varying the concentration of Br⁻ in solution or maturing AgBr (111) and MK AgBr (100) MC at definite temperature and pBr=3,0 and 1,6, correspondingly. As stated above, in our experiments the spherical MC form was also observed which had not mentioned in the works before. The relation of normal lines to MC facets change for the forms enumerated in the following range:

In the scheme the evolution of AgBr (111) MC form with time keeping in conditions pBr=3,0 is presented. Tetradecahedrons of (1) and (2) types differ in square relation S_{111} and S_{100}. For type (1) – $S_{111} > S_{100}$ (fig. 2, b); for type (2) – $S_{100} > S_{111}$ (fig. 3, b). Transfer from tetradecahedron of type (1) to type (2) and appearance of MC spherical form depends on temperature and concentration of gelatine.

The change of chemical potential of facet (111) μ_{111} can be defined as the change of free surface energy $G = S_{111} \gamma_{111} + S_{100} \gamma_{100}$ (S_{hkl} – square of corresponding facet, γ_{hkl} – free facet energy hkl) changing one mole of substance to the direction r_{hkl} (r_{hkl} – normal lines to facets hkl) [3]:

$$\mu_{hkl} = \left(\frac{\partial G}{\partial n}\right) = \left(\frac{\partial G}{\partial n_0}\right)_{hkl} = V_m \left(\frac{\partial G}{\partial r_{hkl}}\right) \cdot \left(\frac{\partial r_{hkl}}{\partial \upsilon}\right) =$$

$$= V_m \left(\frac{\partial G}{\partial r_{hkl}}\right) \bigg/ \left(\frac{\partial \upsilon}{\partial r_{hkl}}\right),$$

where n_0 – the number of substance moles participating in recrystallization, V_m – molar volume, υ – microcrystal volume.

Chemical potentials for all intermediate forms can be estimated by calculation of S_{hkl} square. The simplest way to do it for spherical MC:

$$G = 4\pi r^2 \gamma, \quad V = \frac{4}{3}\pi r^3,$$

$$\mu_{сф} = V_m 8\pi r \gamma \bigg/ 4\pi r^2 = V_m \frac{2\gamma}{r}.$$

In common case, if facets $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$ exist in equilibrium with solution, then $\mu(h_1 k_1 l_1) = \mu(h_2 k_2 l_2)$. These forms of MC are referred to as balanced ones.

For tetradecahedrons of type (1) and (2) in work [3] chemical potentials were calculated for AgBr (111) MC and AgBr (100) MC. As a result it was shown that at $\gamma_{111}/\gamma_{100} \leq 0,57$, $\mu_{111} > \mu_{100}$; if $\gamma_{111}/\gamma_{100} \leq 1,73$, then $\mu_{100} > \mu_{111}$.

In this case $?_p^h \mu_p^{hkl} = \mu_{hkl} + \mu_0$, and for facets (100) and (111) we obtain: $\mu_p^{100} = \mu_{100} + \mu_\infty$, $\mu_p^{111} = \mu_{111} + \mu_\infty$, where μ_∞ – chemical potential for a particle of unlimited size, μ_p^{hkl} – chemical potential of solution in equilibrium with hkl MC facet. Taking into consideration the relations $\mu_p^{hkl} = \mu^0 + RT \ln \Pi^{hkl}$ and $\mu_\infty = \mu^0 + RT \ln \Pi^\infty$ (μ^0 – standard chemical potential, Π^{hkl}, Π^∞ – products of particle solubilities with hkl facet and infinite crystal, correspondingly, R – universal gas constant), we obtain the connection between the product of facet (hkl) solubility and chemical potential μ_{hkl}

$$\Pi^{100} = \Pi^\infty \cdot \exp(\mu_{100}/RT),$$

$$\Pi^{111} = \Pi^\infty \cdot \exp(\mu_{111}/RT).$$

It is seen from the relations that at $\mu_{111} > \mu_{100}$ for $\gamma_{111}/\gamma_{100} \leq 0,57$ crystals acquire octahedral facet independently on the initial one. At $\mu_{100} > \mu_{111}$ for $_{11}/\gamma_{100} \leq 1,73$ crystals are modified sequentially to spheric and cubic form.

In fact, owing to different solubility facet growth velocity if different that results in formation of octahedral or cubic microcrystals.

Thus, formation of sensitivity centres in AgBr (111) MC at maturing without addition of sulphur-containing additives takes place in the process of recrystallization of octahedral microcrystals. Change of microcrystal form depends on their sizes and conditions of keeping. With the increase of AgBr (111) MC sizes Gibbs-Woolf's condition becomes less stringent and their modification takes place only by means of facet (111) reconstruction without notable change of form. The last statement is true for the sizes of $d>1,2$ mkm. One can point out that for large sizes of MC Gibbs-Woolf's condition is not fulfilled. Nevertheless, the mechanism of surface and form modification of AgBr (111) MC is not same in all cases and the difference of chemical potentials and, hence, their solubility underlies them. MC solution results in oversaturation of the MC surface layer in solution of the thickness comparable with coefficient of Ag⁺ and Br⁻ ion diffusion. In this case growth of solution oversaturation makes similar the next process of natural maturing with reduction sensitizing, but without addition of

reducing agent to reactor. As it is evident from the results obtained in the experiment, on MC surface stable silver sensitivity centres are formed.

Presumably, the scheme of sensitivity centre formation includes the stage of MC solution with increase of relation r_{111}/r_{100}:

$$AgBr \rightarrow Ag^+_{sol} + Br^-_{sol} \qquad (1)$$
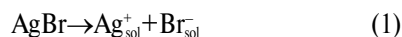
Further scheme of sensitivity centre formation can be written down as a complex of electron and ion stages on MC surface:

$$e^- + Ag^+_{sol} + Ag^+S \rightarrow Ag_2^+S \equiv SC \qquad (2)$$

$$e^- + Ag^+_{sol} + Ag_2^+S \rightarrow ... \qquad (2')$$
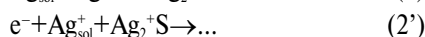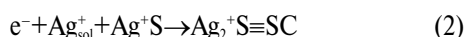
$...\rightarrow Ag_n^+S$ etc, with formation of fog centres,

where Ag^+S − silver ion on MC surface defect (for example, «a ledge of step»). The schemes with formation of Ag_n^0S are possible, for which a large number of electrons is necessary. Electrons (e^-) participating in formation of sensitivity centres can be captured from solution or from AgBr crystal as a result of dark thermal transition. It is remarkable that the fog level for all emulsion investigated, as a rule, is not more than the value $D_0=0,1...0,2$ in the process of maturing. Total or partial absence of reactions 1, 2 at maturing AgBr (100) MC accounts for the difference of these MC from microcrystals of octahedral habitus. Relatively less growth of photosensitivity at maturing of flat microcrystals obtained by CDC method can also be explained by less velocity of T-MC surface modification. The absence of sensibility increase effect in the process of flat microcrystal maturing obtained by coalescence method can be explained by polycrystal structure of microcrystals. Therefore, even in the case of sensitivity centre formation at T-MC maturing the possibility of latent image formation is negligible due to excess density of interstitial silver ions [4]. Thus, it is shown that the mechanism of sensitivity centre formation in AgBr (111) MC in thew conditions of natural maturing is connected with difference of chemical potentials of (111) and (100) facets of AgBr MC. The stated data permit to draw the following conclusion:

The effect of silver sensitivity centres in AgBr (111) microcrystals without introduction of sulphur containing additives (natural maturing) was found. The formation of silver sensitivity centres occurs in the process of microcrystal habitus modification at system oversaturation due to the difference of MC facet chemical potential $\mu_{111} - \mu_{100}$. Introduction of fine-grain emulsion in the process of maturing results in decrease of spontaneous sensibilization effect.

Literature

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