Creation of Subsuface Lattice Defects in AgBr(I) Tabular Microcrystals by Splash Iodide Addition Technique

L.V. Sotnikova, B.A. Sechkarev, M.A. Bezjazychnaja, J.N. Afonkina Kemerovo State University, Russia

Abstract

The influence of the methods of the addition of iodide solution with different concentrations, halide composition of substrate tabular crystals and dispersion characteristics of resulting heterophase AgBr(I) tabular crystals with subsurface lattice defects on photographic characteristics of these crystals have been investigated.

Introduction

To increase photographic speed of photographic layers with AgBr(I) tabular grains it is necessary to effectively use photoelectrons formed by the action of light on a grain. In order to concentrate the latent image on a minimum number of centers it is suggested [1, 2] that structural defects in subsurface areas of a grain be formed by incorporating the I⁻ ions when crystallizing the tabular grains.

Experiment

The core emulsion containing AgBr tabular grains with an average equivalent diameter d = 0.8 microns and the size variation factor Cv = 30 % was obtained by the method of two-jet crystallization using the mixing device [3] providing for intensive mixing at the point of pouring the reagent solutions. An electronic micro photo of the core emulsion is given in Fig. 1. The emulsions differed in the way of incorporating the Γ ions before the crystallization of the shell resulting in different distributions of Γ ions in the shell of grains.

Then three types of photo emulsions containing A, B and C grains were obtained (see Fig. 2).

In case A the 2 M KI solution was poured simultaneously with the solution of silver nitrate of the same concentration. The given way of the introduction of solutions of the reagents provided for a maximum narrowing of the zone of the introduction of I ions into grains and creating the areas with a high concentration of AgI. Type B was obtained by alternating one-jet crystallization of KI and AgNO₃ solutions. The rate of the introduction of reagents and their concentrations for A and B types were the same. The grains of A and B types at the end of the synthesis should not have the AgI impurity on the surface of grains. In grains of type C Γ ions were incorporated together with Br-ions during the crystallization of the shell. In this case the most uniform distribution of the Γ ion in the shell of grains was achieved. The quantities of AgBr/AgI for the three emulsion types were the same, the concentration of AgI - 3 mol %.



Figure. 1. The electronic micro photo of the core emulsion containing AgBr tabular grains. x 5400



Figure. 2. The scheme of the distribution of I ions in grains.

After that, photographic emulsions of all these types were subjected to sulfur-plus-gold chemical sensitization (CS) in the presence of the KSCN solution and used for preparing the photographic layers.

The photographic layers containing different grains were found to differently respond to the presence of KSCN. Photographic speed (PS) and optical density of a fog (D_0) of the sample depend both on the way of the incorporation of KI, and on the concentration of KSCN under the CS of the emulsion. Dependences of the D_0 level from the concentration of KSCN for different types of emulsion layers are given in Fig. 3.



Figure. 3. Dependence of optical density of the fog (D_0) from the concentration of KSCN for photographic layers containing grains of different types.



High D_0 on samples A and B is not due to the presence or the absence of I⁻ ions on the surface of grains since grains synthesized like A grains, but having uniform distribution of I⁻ ions in the shell like C grains (see Fig. 3 D), also fog in the presence of KSCN.

Thus, it is the presence of areas with a higher concentration of AgI in grains that results in an increased sensitivity of the system in the presence of the solvent – KSCN under CS. Sulfur-plus-gold CS of such systems does not require the presence of AuSCN.

Sensitometric characteristics meeting optimum conditions of sensitization of photographic emulsions of various types were obtained for all three types of emulsion layers. Optimum sensitometric characteristics and conditions for carrying out sensitization are given in Table 1.

Table 1.Optimum sensitometric characteristics and conditions for carrying out sensitization

emulsion	$S_{0,85}$	$S_{0,2}$	D_0	$\mathrm{D}_{\mathrm{max}}$	Na ₂ S ₂ O ₃]x10 ⁻⁵ mol/molAg	[KSCN]x10 ⁻³ mol/molAg	[HAuCl ₄]x10 ⁻⁵ mol/molAg
А	55	12	0,02	3,7	5,4	-	2,8
В	55	15	0,05	2,3	4	2,7	2,6
С	30	8	0,09	4,5	5,4	11	2,6
D	25	11	0,08	1,3	9,2	-	2,6
Е	85	22	0,07	1,9	7	-	2,8

The present authors investigated the dependence of sensitometric characteristics of emulsion layers containing A grains from the concentration of KI. The concentration of I⁻ ions varied in the 0 - 5 mol % range. The results of sensitometric tests of the resulting photographic layers are presented in Table 2.

As seen from the Table, the maximum increase in photographic speed is observed for the samples containing 3,2 mol % of Γ ions. A higher concentration of Γ ions results in the decrease of maximum optical density (D_{max}) of the developed image and decrease in photographic speed (S). D_{max} decrease with the increase of the concentration of Γ ions in grains, is due to the change of the habit of developed silver [4].

Figure. 3. The scheme of the distribution of I ions in grains.

Table 2. Optimum sensitometric characteristics and conditions for carrying out CS of photographic emulsions with a different content of Γ ions.

№ emulsion	%lom,'I	$\mathrm{S}_{0,85}$	${ m S}_{0,2}$	D_0	$\mathrm{D}_{\mathrm{max}}$	[Na ₂ S ₂ O ₃]x10 ⁻⁵ mol/molAg	[HAuCl4]x10 ⁻⁵ mol/molAg
1	-	25	6	0,05	4,5	5,4	2,8
2	1,6	40	10	0,07	3,7	5,4	2,8
3	3,2	55	21	0,01	3,3	5,4	2,8
4	4,8	20	13	0,25	1,5	5,4	2,8

Modeling experiments

Photographic grains under study do not exceed d = 2 microns, therefore it is very difficult to determine the distribution of AgI in an isolated crystal or the population of crystals. However, this problem is of great interest, as the dependence of photographic properties of grains from the way of incorporating the I⁻ions into the structure of grains is found out.

To understand the processes occurring during the incorporation of Γ ions into the structure of grains, model crystals having, mainly, a hexagonal habit (d = 5 - 10 microns) were synthesized and recrystallized together with an AgI fine-grain emulsion.

Optical micro photos of initial crystals and the crystals recrystallized together with AgI fine-grained crystals, (AgBr/AgI - 2:1) are given in Fig. 4. As seen from the figure, AgBr crystals after recrystallization with AgI fine-grained crystals have hills at the corners (c), or along the perimeter of the crystal (d) (see Fig. 4b).

The concentration increase in AgI in the mixte up to 1:1, causes recrystallization followed by the dissolution of AgBr tabular crystals and the formation of small size grains (see Fig. 5.).

Thus, it is found out that the topography of AgI hills on AgBr grains and the condition of the surface of AgBr grains depend on the concentration of AgI in the system. It means that the location and the extent of structural defects in the core-shell grains, and, hence, the location and the amount of CS centers and latent image centers depend on the concentration of AgI in the system.

The results obtained allowed us to explain the presence of the optimum concentration of Γ ions (see Table. 2) providing for higher photographic speed. The concentration of Γ ions -3,2 mol %, which is optimum for the investigated system, does not result in the dissolution of AgBr tabular grains and creates the structure with better concentrating of the latent image.



Figure. 4. Optical micro photos of model AgBr crystals (a), and AgBr crystals after the recrystallization together with AgI finegrained crystals (b) (AgBr/AgI - 2:1). x 400



Figure. 5. Optical micro photos of AgBr model crystals after the recrystallization together with AgI fine-grained crystals (AgBr/AgI - 1:1). x 400

Conclusion

The dependence of photographic properties of AgBr(I) grains, revealed in our experiments, from the technique of the inclusion of I ions into the structure of a grain can be explained by the approach used to study the types of de-

fects formed in grains for a particular case. Depending on the way of the inclusion of I^- ions into structure of AgBr grains, resulting AgBr(I) grains include the following different types of defects:

during the two-jet crystallization of a halide mix bromide and iodide, with the concentration of Γ ions in bromide = 40 %, grains with uniform distribution of Γ ions in AgBr crystal lattice are formed. These grains do not contain the dislocations, and the increased defect formation is caused by the presence of point defects as an replacement impurity (type C);

during one-jet crystallization of a halide mix, AgBr(I) grains containing dislocations are formed. The dislocations are due to a non-uniform inclusion of impurity ions into the structure of a grain during one-jet crystallization (type B);

two-jet crystallization of AgI under normal conditions results in the mix of grains with two types of crystal lattices. At excess concentration of silver ions, the mix of grains where an AgI microcrystal with a cubic lattice of the ZnO type prevails is formed. Crystallization with an excess of I ions or with equal concentrations of silver and iodide ions results in the formation of AgI having mainly hexagonal habit [4]. As seen from our model experiments, AgI hills in our system are formed along the periphery of AgBr grains and have a crystal lattice different from the AgBr lattice. The further build-up of the AgBr crystal mass makes the grain surface more smooth, but in the grain structure on the boundary of different crystal lattices there remains a deeper defect than the one in the above described cases. Probably, this defect as to its nature is likely to be close to the block boundary whose formation results in fogging the grains [4], especially, in the presence of solvent (type A).

Dislocations depending on the conditions of synthesis can have a different charge and, consequently, they concentrate either interstitial ions or anion vacancies in their neighborhood. Grains of type A are very sensitive to external effects, therefore, the research of the influence of various additives on the system of a similar type is most promising.

References

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Biography

Larisa V. Sotnikova was born in Kemerovo (Russia) on October 26, 1966. In 1989 graduated from the State University of Kemerovo, Chemical Department. Since 1989 she works on Kemerovo State University's Inorganic Chemistry Chair as a Scientific Researcher. Doctor of Science since 1998. Field of research is the silver halide photographic emulsion crystallization and chemical sensitization processes, the author of more than 50 scientific publications.