Laminated Tabular AgBrI Grains with Gradually Varied Iodide Distribution

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Abstract

This paper reports on a precipitation of laminated type tabular crystals (or double-structure grains with bromide-iodide core covered with bromide shell) and describes some of their properties. This type of crystals has been created by means of physical ripening of fine grained emulsion. The fine grained emulsion has been precipitated by the process allowing to vary smoothly iodide content within each grain. A correlation between iodide concentration in the tabular grain's core as well as profiles of iodide concentration variation and some photographic features of the crystals are under discussion.

Introduction

Nowadays photographic science and technology of tabular grain based films deals with both study of formation and growth of these grains and improving upon tabular grains of the heterojunction type known also as "double structure". The latter are lateral, laminated and epitaxial crystals. Design of these species concerns with combination and location of halide phases with different halide content and concentration.

The presented work is dedicated to the tabular system of laminated type which apart of lateral type grains has no lateral zones but its bromideiodide core is completely covered with silver bromide shell. In the laminated crystal like in the lateral one the same separation of photo generated charge carriers tales place, causing formation of latent image on limited surface area. Alike the lateral crystal the laminated one has no iodide ion on its surface that gives certain advantages to the film on its base, especially during film development[1]. On the other hand abrupt variation of iodide concentration inside bromide/iodide shell can generate structural defects and phase boundaries which are recombination centers and therefore potentially are able to decrease effect of latent image formation. Some previous papers pertain to this subject with regard to regular double structure grains or tabular grains precipitated by means of controlled double-jet precipitation[2,3]. The work under consideration is an attempt to create laminated tabular grains with smooth variation of iodide in bromide/iodide phase and to study photographic characteristics of films based on these grains.

Experimental

Laminated tabular grain emulsions have been created during physical ripening of fine grained emulsions of double structure type. These fine grained emulsions comprised crystals with smooth varied iodide ion concentration from its maximum in the core and its null on the shell's surface. Precipitation of the fine grained emulsion has been carried out by means of slightly modified method of double-jet precipitation. To vary iodide ion concentration in sodium halide solution input we used additional buffering mixture vessel. The scheme of precipitation installation is shown on fig.l.

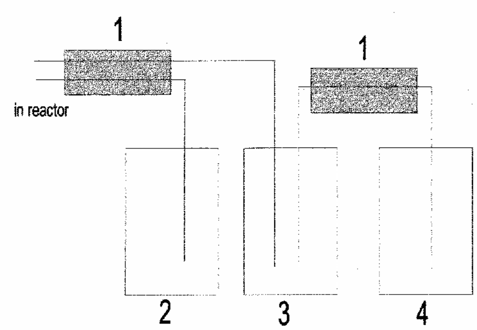

Fig.1. Scheme of solution flows in the precipitation installation. 1.Pomps; 2.silver nitrate solution volume; 3.buffer volume; 4.potassium bromide volume.

1M solutions were used for the precipitation. An iodide ion concentration range in an outset solution for different sets of emulsions was within 0 and 12 molar percent. By the end of the precipitation the iodide concentration in buffering volume and therefore in the reactor was 0 percent or close to this level. The rest of precipitation conditions has been chosen so that final size and habitus of fine grains was uniform for all sets of emulsion.

The physical ripening of the fine grained emulsion has been carried out at 60°C and pBr = 1.

Fine grained and tabular crystal size was controlled by means of electron microphotography of their carbon replicas. Chemical ripening has been carried out according to standard procedures with chlorogoldhydrogenic acid.

Results and discussion

Table 1 shows some characteristics of the photolayers A, B and C. These layers comprised tabular grains of same size and size distribution. Emulsion A based on AgBrI homogeneous grains with 12 molar percent of iodide. Emulsion B comprised laminated tabular grains with 12 molar percent iodide concentration in the core, the iodide percentage smoothly decreasing to null on the surface. Emulsion C comprised AgBr tabular grains. Table 1 reveals optimal level of D_{max}, fog density and gradient factor of chemically ripened emulsion layers. It is seen that the characteristics of layers C and B are close to each other and they evidently higher than those of the layer A.

Table 1. Photographic characteristics of photolayers of different tabular grain types.

Emulsion	D_{max}	Gradient	D_0
A	1.7	1,2	0.1
B	3.5	2.5	0.1
C	4,5	3,0	0,1

The data from table 1 prove that physical ripening of fine grained emulsion doesn't involve significant recrystallisation and iodide ion doesn't migrate from grain bulk to its surface.

The following set of fine grained emulsions with different iodide concentration in core has been prepared. Table 2 contains some information about their size characteristics along with calculated values of surface iodide concentration. The calculation was carried out for iodide ion concentration in buffer volume at the end of precipitation. An equilibrium iodide ion concentration was assumed as its surface concentration.

Table 2. Crystallographic characteristics of the used fine grained emulsions.

№ emulsion	the start content. I^-, mol %	the concentration. I^- on the surface crystals, mol %	crystallographic characteristics of fine grained emulsions	
			d, mcm	Cv, %
1	0	0	0,10	14
2	2	0,04	0,12	15
3	4	0,08	0,12	18
4	6	0,012	0,13	18
5	8	0,016	0,13	16
6	12	0,02	0,13	18

The fine grained emulsions listed in table 2 were ripened. Table 3 contains data on resulted tabular grains.

Table 3. Crystallographic characteristics of the laminated tabular crystals.

№ emulsion	the start content. I^-, mol %	crystallographic characteristics of tabular grained emulsions		
		d, mcm	Cv, %	S_t, %
1	0	2,17	50	95
2	2	1,89	58	89
3	4	1,66	62	87
4	6	1,61	60	87
5	8	1,58	54	86
6	12	1,55	56	82

It is seen that the average size of the tabular crystals decreases with the increase of iodide content in the crystal's core. This correlation is quite reasonable since higher iodide concentration in a crystallization reactor during fine grain nucleation stage causes formation of higher portion of parallel twinned grains. It was recently shown that the latter played a role of tabular grain growth centres during physical ripening of the fine grained emulsion.[4]

Emulsions have been chemically digested. Table 4 contains optimum photographic characteristics of coatings prepared of these emulsions.

Table 4. Speed ($S_{0.85}$), maximal optical density (D_{max}), fog density (D_0) and gradient (γ) of the photolayers comprising laminated tabular grains digested under optimal conditions.

the start content. I^-, mol %	$S_{0,85}$	D_0	D_{max}	γ
0	40	0,10	4,5	3,0
2	100	0,12	4,0	3,0
4	150	0,11	3,8	3,0
6	200	0,10	3.8	3,0
8	210	0,11	3.3	2,4
12	195	0,10	3,1	2,5

It is seen that the increase of iodide concentration in the core leads to the drop of maximal optical density and gradient. This trend becomes acute with iodide concentration higher than 6% molar. The calculated surface iodide concentration at this point is 0.012% molar. That's low enough to provoke undesirable effects during development stage. So the loss of qualities can be caused either by high surface iodide concentration (higher than assumed from calculation) or by the decrease of tabularity factor. This factor decrease with the increase of iodide concentration is also related to an increase of twinning probability because along with growth of the parallel twinned nuclei portion the non parallel multiple twinned nuclei portion grows as well.

However the loss of the quality can be more possibly caused by the combination of the factors mentioned above. The level of sensitivity can be improved by chemical digestion in the presence of thiocianate ion. This component significantly improves sensitivity of lateral type tabular emulsion. In case of laminated type tabular emulsions under consideration the addition of the thiocianate ion during chemical digestion increases layers sensitivity about by two times.

Conclusions

1.lt is possible to obtain tabular grains with smoothly decreased iodide concentration from bulk to surface by means of physical ripening of fine grained emulsion with the same iodide distribution;

2.This type of crystal acts as the double structure;

3.The optimal conditions of precipitation of fine grained emulsion allows to obtain tabular laminated type crystal layers with characteristics close to those of AgBr tabular grain layer but with much higher speed. However it is difficult to avoid iodide pollution of crystals surface. On the other hand this system is nearly free from an inhibiting iodide affect during development stage.

References

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Biography

Shaihullina Svetlana graduated from Kemerovo State University in 1989 and got PhD degree in 1998. Since 1989 she works for chemistry dept. of the university. Her area of interest is the photographic chemistry and specifically problems of crystallization and chemical sensitization of silver halide emulsions.