

A Role Of The Electrostatic Charge In Tabular Crystals Coalescent Growth

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Introduction

Tabular grains can be formed during fine AgBr ripening by the coalescent mechanism. A coalescence is an isotropic process and in case of tabular grain growth there must be an anisotropic moving force. The anisotropic coalescence mechanism was proposed for the first time by Breslav¹ who suggests that only octahedral grains can form non-rectangular tabular grains. On the contrary, practice persuades that typical tabular triangles and hexagons can be obtained by ripening cubic fine AgBr. This contradiction as well as non-explicit anisotropic moving force in the Breslav's mechanism prompted us to propose another one model of the anisotropic coalescent growth.² We have proposed in our model that parallel twinned grains act as a nuclei of the anisotropic coalescence. In this case moving force of the process is electrostatic interaction between a side face of the parallel twinned grain and the regular grain. However, until now this model is not confirmed by required quantitative estimation and is not proved experimentally. The presented work is aimed at quantitative development of the model and its experimental proof.

Experimental

Tabular AgBr grains have been obtained by ripening fine AgBr grains. Dispersity and tabularity of emulsions have been studied by means of electron and optic microscopy. The number density of parallel twinned grain in fine emulsions has been estimated by following procedure: a certain volume of the fine AgBr emulsion was sampled immediately after the completion of precipitation and added to gelatin solution of the same pBr level. Then AgBr shell has been precipitated on these seeds, precipitation rate not allowing new phase formation. The final grain size after the second precipitation was about 0,5 mcm and parallel twinned grains were undoubtedly distinguished among regular grains by their morphology.

Ripening of fine emulsion has been carried out as it is reported in [2].

Results and Discussion

According to our model parallel twinned fine grains are centres of coalescent growth of tabular grains. Fig.1 shows this model schematically.

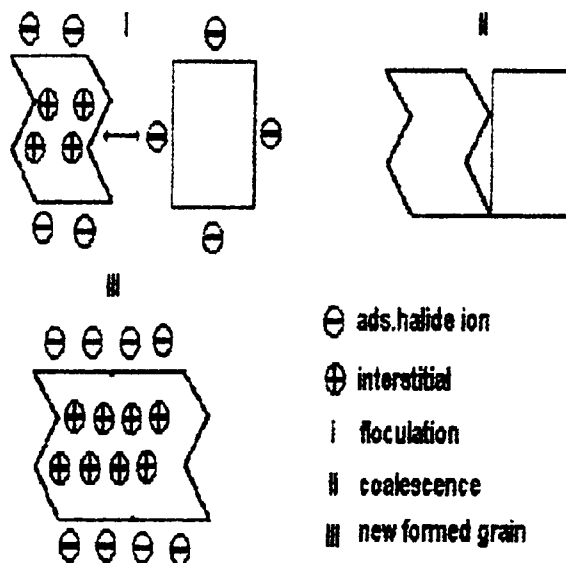


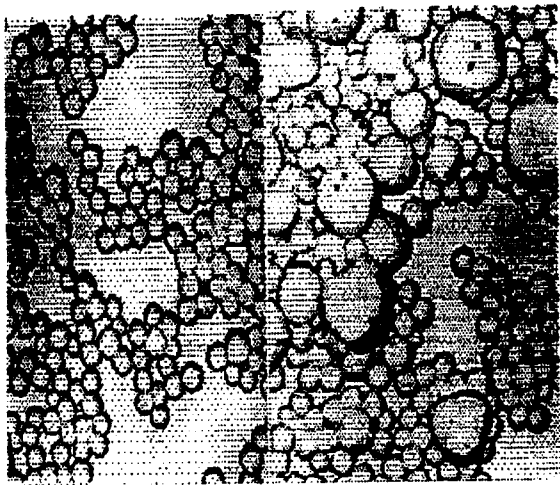
Figure 1. A scheme of tabular grain growth during fine AgBr ripening.

It follows from this supposition that number density of the parallel fine grains and final tabular grain average size must correlate, subject to equal volume concentration of all fine grains in ripening emulsions. It is known³ that pBr volume of precipitation effects rate of the twinning process. We have precipitated three fine emulsions which differed in pBr level of precipitation setout (1,0; 2,0 and 3,0). After some short time enough to complete a stage of nucleation, pBr level of precipitation of all emulsions has been slowly changed to the similar level (3,0). The rate of precipitation in each case was a bit different to compensate an influence of pBr level on grain size. Data on fine emulsions are enlisted in table 1.

Fig 2 shows microphotographs of the fine emulsion F13 before and after the second precipitation.

Table 1 Data on fine AgBr emulsions

Emulsion	Starting pBr	Final pBr	Average size, mcm	Parallel twins, %
F13	1,0	3,0	0,07	15
F23	2,0	3,0	0,07	9
F33	3,0	3,0	0,07	1



1 (X57000) 2 (X12000)
 Figure 2 Emulsion F13 before (1) and after (2) the second precipitation

Data on tabular grains obtained by fine AgBr ripening are listed in table 2.

As it was expected the number density of parallel twinned grain correlates with both tabular grain growth rate and their average size. The growth rate increases with the increase of parallel twinned grain number density. At the same time average size of grown tabular grains becomes smaller. Such correlations are possible only in case parallel twinned grain is the centre of tabular grain growth. Increase of the growth centres number results in the growth acceleration. On the other hand a mass of regular fine grains per one growth center becomes smaller thus the average size of tabular grains decreases.

These correlation can be considered as qualitative proof of the proposed model. Then, if the moving force of the process is the coulombs attraction between positively charged side face of the parallel twinned grain and negatively charged surface of regular fine grain, it is reasonable to make a quantitative estimation of the model in terms of electrostatics.

Table 2 Data on tabular AgBr emulsions

Emulsion	Growth rate, min ⁻¹	Average size, mcm	Cv, %
T13	0,013	1,7	56
T23	0,007	8,5	50
T33	0,006	12,0	41

Let's consider interacting parallel twinned grain a flat two-dimensional surface, and charged face of regular fine grain a point charge. Fig.3 shows a scheme of interacting "macrocharges".

It is seen that the charge -Q of the system B is repulsed from the system A by forces F1, F2 and is attracted by forces F3, F4, simultaneously. It is explicit that systems drawing together will prevail if a net force of attraction overwhelms a net force of repulsion i.e. when:

$$F_1 + F_2 < F_3 + F_4 \quad (1)$$

From the Coulomb's law with regard to the geometry it follows:

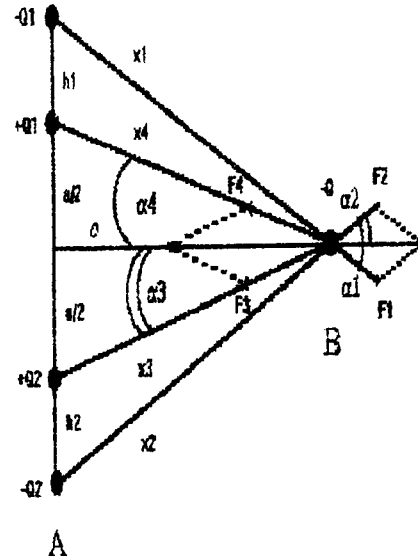


Figure 3. A model of interaction of the "macrocharges" A (Q1 and Q2) with the macrocharge B (-Q)

$$F_1 = k \frac{QQ_1}{x_1^2}, F_2 = k \frac{QQ_2}{x_2^2},$$

$$F_3 = k \frac{QQ_2}{x_3^2}, F_4 = -k \frac{QQ_1}{x_4^2}, \quad (2)$$

$$\sin \alpha_1 = \frac{h_1 + a/2}{x_1}, \sin \alpha_2 = \frac{h_2 + a/2}{x_2}$$

$$\sin \alpha_3 = \frac{a/2}{x_3}, \sin \alpha_4 = \frac{a/2}{x_4}, \quad (3)$$

$$\cos \alpha_1 = \frac{\sigma}{x_1}, \cos \alpha_2 = \frac{\sigma}{x_2}, \cos \alpha_3 = \frac{\sigma}{x_3},$$

$$\cos \alpha_4 = \frac{\sigma}{x_4}, \quad (4)$$

$$x_1^2 = \sigma^2 + (h_1 + a/2)^2,$$

$$x_2^2 = \sigma^2 + (h_2 + a/2)^2,$$

$$x_3^2 = \sigma^2 + \frac{a^2}{4} = x_4^2. \quad (5)$$

$$\frac{F_1}{F_2} = \frac{Q_1 x_2^2}{Q_2 x_1^2}, \quad \frac{F_3}{F_4} = \frac{Q_2}{Q_1}. \quad (6)$$

It follows from (1) that

$$F_1 \cos \alpha_1 + F_2 \cos \alpha_2 < F_3 \cos \alpha_3 + F_4 \cos \alpha_4 \quad (7)$$

Substituting (2) and (4) in (7) gives the following expression in case when $Q_1 \neq Q_2$ (consequently $h_1 \neq h_2$):

$$\frac{Q_1}{[\sigma^2 + (h_1 + a/2)^2]^{3/2}} +$$

$$\frac{Q_2}{[\sigma^2 + (h_2 + a/2)^2]^{3/2}} < \frac{Q_1 + Q_2}{[\sigma^2 + (a/2)^2]^{3/2}}$$

If $Q_1 = Q_2$, one can derive a geometric condition of attraction : $h > a$. It means that in case of nearly equal charge magnitude of Q_1 and Q_2 attraction overwhelms, if $h > a$. Regarding the interaction distance σ it is obvious that the attraction force becomes greater with shortening of the distance as: $1/\sigma^2$.

At a short distance of interaction a profile of the system A, ie. side face of growing tabular grain becomes an important factor which influences the magnitude of the attraction force. It is known that potential gradient is higher at a sharp verge of a conductor i.e. at a place where the curvature radii is smaller. Surface field intensity is proportional to surface charge density which in its turn is

proportional to the relation between total charge and square radii. It means that some amount of charge in conductor tends to occupy its sharp outstanding parts. Like in the common case, elements of the re-entrant structure of the growing tabular grain can amplify the electrostatic field strength. Existence of protruding areas on the side faces of the tabular grains with two and three parallel twin planes was proved recently by Mehta et al⁴.

References

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