A Study on the Mechanism of Nucleation and Growth of Twin Tabular AgBr Crystals

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Abstract

On the mechanisms of nucleation and growth of (111) tabular silver halide crystal, it has been proposed that the twinning (nucleation) occurs by "Stacking-Fault" and the anisotropic lateral growth is brought by "Ridge-Trough" structure on the tabular side face.

Although "Coalescence" model for the nucleation, and "Rough-Smooth" edge structure for the anisotropic growth have been proposed recently, they have not yet been necessarily supported by direct experimental evidences.

We analyzed the nucleation process by a method in combination of light scattering with Xray diffraction and observed TEM images of ultramicrotomed sections of side faces of tabular grains which have relatively thick spacings between parallel twin planes .

Above-stated experimens provided evidences to support "Coalescence" model and"Rough -Smooth"model .

Introduction

Tabular silver halide crystals are now very important for highly sensitive photographic emulsions. The majority of these crystals are approximate equilateral triangles, regular hexagons, or shapes intermediate between these two. R.W.Berriman and R.H.Herz [1] found that most of these tabular silver bromide crystals were twinned on the (111) planes. They have proposed that the twinning occurs as a result of stacking fault during nucleation (or growth) and considered that the re-entrant geometry in "Ridge-Trough" structure resulting from multiple twinning was sufficient to account for tabular growth.

C.R.Berry et al have proposed that twinning occurs according to "Stacking Fault" mechanism caused by deposition of complexes on the (111) grain surface at low pBr. They have speculated that at low pBr condition where the dominant complex is $AgBr_3^{2-}$, twinning results from the failure of this complex to deposit in the normal orientation owing to its larger Br^--to-Br^- distance than occurs in the crystal and its strong polarizability. Although the low pBr complex deposition mechanism have not been verified, it has been widely accepted.

M.Saitou[3] has suggested in his patents that pBr is not the only parameter that controls the generation of twinning and formation of tabular silver halide grains. The parameters were the gelatin concentration, mixing condition, degree of supersaturation, temperature at nucleation, concentration of silver halide solvent, ionic strength, iodide concentration. Some doubts have been casted on the validity of the low pBr deposition mechanism.

C.T.Mumaw and H.F.Haugh[4] have proposed the "Coalescence" mechanism for the twinning in silver halide crystals. J.F.Hamilton and L.E.Brady[5] observed "Ridge - Trough" structure on the side face of large tabular grains by an electron microscope. J.E.Maskasky[6] demonstrated that the shape of tabular grains depended on whether the number of twin planes was odd or even by examining the orientation of silver chloride epitaxies formed on the main surfaces of the tabular grain. He has suggested that the acute lip structure of side faces of tabular grains plays an important role for anisotropic lateral growth of the tabular grain.

Recently M.G.Antoniades and J.S.Wey[7] found the strong correlation between the degree of flocculation and the resulting fraction of tabular grains and concluded that

"Coalescence" preceded by flocculation, caused the twinning in nucleation stage of tabular grains. Altough the relation between coalescence and the twinning was demonstrated as a clear evidence for the "Coalescence " mechanism, it was not quantitative. It is also demonstrated that high population of tabular silver bromide grains can be formed at various pBr value in the nucleation period , thus raising a question about that the twinning occurs only at low pBr.

R.Jagannathan et al[8] has suggested that side faces of a tabular grain, are not bounded solely by (111) but both (111) and (100) planes by ball model simulation for the growth model and proposed that the anisotropic growth of a tabular grain would takes place with "Rough-Smooth" side face structure. R.V.Metha et al[9] also demonstrated that the shape of tabular grain(i.e. equilateral triangle, regular hexagon, or shapes intermediate between these two), did not depend upon whether the number of its twin planes is even or odd, but could be explained by its cubo-octahedral side face structure. Although the side face structure of tabular grains was demonstrated as an evidence for their proposal ,it was not necessarily clear, since the spacing between parallel twin planes was too thin to determine the structure of the side faces clearly.

The goal of our study is to gain better understanding of the mechanisms of nucleation and growth of (111) tabular grains by obtaining direct experimental evidences for the proposed models.

Experimental

1.Nucleation of tabular grain (twinning)

The silver bromide nuclei were prepared continuously in the mixing chamber into which an aqueous solution of silver nitrate and an aqueous solution of potassium bromide containing various concentration of gelatin were added. As shown in Fig.1, a twinned crystals consists of at least two crystallites,(single twin;2 crystallites, doubly twin; 3 crystallites)whereas untwinned crystal(regular crystal) consists of only one. The crystal size of the nuclei was determined turbidmetrically by using the Rayleigh equation as shown below.[10]

$$Dt=(\tau_\lambda \rho_s/C_s)\lambda_m{}^4/4\pi^4\mu^2$$

Dt;crystal size, τ_λ ;turbidity at wavelength λ, ρ_s;density of the crystal, C_s;suspension density of the crystal, λ_m;wavelength in the medium, μ;$(m^2-1)/(m^2+1)$, $m=n_p/n_m$, n_p;refractive index of the crystal, n_m;refractive index of the medium

The crystallite size of the nuclei was determined by X-ray diffraction with the Scherer equation as shown below[11].

$$Dx=0.9\lambda/\beta\cos\theta$$

Dx;crystallite size for perpendicular direction to (*hkl*), λ;wave length of X-ray, β;half angular width of the diffracted beam, θ;Bragg angle

In order to determine the proportion of twinned grains in the nuclei emulsion, the nuclei emulsion was grown by double jet method such relatively high supersaturation condition in that the re-nucleation and physical ripening would not occur.

2.Obsevation of the side face structur of tabular grains

We developed a new technique to cause twinning by coalescence of untwinned nuclei formed beforehand. Although nothing occured when an untwinned fine grain emulsion was ripened at 40℃, twinning took place under the same condition after gelatin in the emulsion was decomposed by treatment with the enzyme. The silver potential(reference; saturated calomel electrode) during ripening (coalescenc) was varied and the grain size of untwinned nuclei formed beforehand were also varied. By using this technique it was possible to make tabular grains having relatively thick spacing between parallel twin planes. After the twinning,the twinned nuclei were grown to AgBrI$_{0.1}$ tabular grains. The side face structure of AgBrI$_{0.1}$tabular grain is preserved well compared with AgBr tabular grain since AgbrI$_{0.1}$ is less soluble than AgBr.We could observe the side face structure of these tabular grains by TEM image of the ultramicrotomed sections.

Result and Discussion

The relation between Dx (crystallite size)and Dt(crystal size) as a function of the amount of added gelatin (Rg;gelatin/silver nitrate),is shown in Fig.2. and the proportion of twinned grains grown from the nuclei emulsion is shown in Fig.3. The proportion the tabular grains(twinning probability) increased with decreasing the amount of added gelatin (Rg), and when twinning occurred, the value of Dt became larger than that of Dx, which hardly changed with decreasing gelatin concentration. These facts support the idea that twinning occurs by coalescence as shown in Fig. 1. Because the gelatin layer adsorbed on the surface of the silver bromide grain can prevent the coalescence , it is reasonable that the twinning probability increases with decreasing of the amount of gelatin.

Using the values of Dt and Dx, the proportion of twinned nuclei (the proportion of tabular grains) can be calculated as follows.

The probability of twinning are expressed as equation (1).[12]

$$p(r)=8Ct^{r}(1-t)^{8-r}\cdots\cdots\cdots\quad(1)$$

p(r);fraction of r times twinned crystal, t;probability of twinning.

The crystal size Dt is expressed by p(r) as follows.

$$Dt=Dx(p(0)+\sqrt[3]{2}\,p(1))+\sqrt[3]{2}\,p(2))/\ p(0)+\ p(1))+\ p(2)\cdots(2)$$

The substitution of Dt and Dx by measured values in equation(2) gave the proportion of twinned nuclei (singly and doubly),Tc. On the other hand the growth of nuclei gave the proportion of twinned tabular grains,Tg experimentaly.As seen in Fig.4, the calculated value Tc almost coincided with the experimental value Tg. This result indicates that "coalescence" model is valid. Furthermore the spacing between twin planes almost coincided the size of untwinned fine grains formed beforehand as shown in Fig.5. This is another strong evidence for "coalescence " model since the distance between parallel twin planes never changes during the growth stage and should be the same as the size of the untwinned nuclei formed beforehand.

Fig.6 shows the dependence of the coalescence (twinning)upon the silver potential after the gelatin decomposition by enzyme.It was clear that coalescence occured at high silver potential(high pBr). This phenomenon was completely contrary to the twinning at low pBr as Berry et al emphasized. We concluded that the probability of twinning caused by coalescence, increased with decreasing the gelatin concentration and the coalescence took place only at high silver potential (high pBr), which is nearly the isoionic point of silver bromide when the gelatin concentration is fairly low. It is reasonabl to consider that at the isoionic point, the erlectric charge of grains by adsorbed Br^- ions, would be minimum and that the coalescence would take place easily because the repulsion force by electric charge among grains was minimum.

We could control the thickness of the spacing between two parallel twin planes of the tabular grains as mentioned above. Now we could observe clearly the structure of the side face of tabular grains in which spacings between parallel twin planes were ca. 0.04～0.05 μm, whereas those of ordinary tabular grains are less than 0.015 μm. Fig.7 shows TEM images ultramicrotomed sections of those tabular grains. The side face structure were considered in the case of the parallel doubly twinned tabular grain based on that both (100) and (111) exist on the side face of the tabular grain. We observed three typcal structures named A, B and C type as shown in Fig.7. The side face structures of some tabular grains were not necessarily clear, since they were microtomed with various angle. However we could choose the tabular grains, which were cut in perpendicular to both the main surface and the sides of the taular grains.As Metha et al proposed, it was observed that the side face structure of the tabular grain consisted with (111) and (100) surfaces. This was the clear evidence for "Rough-Smooth" model.

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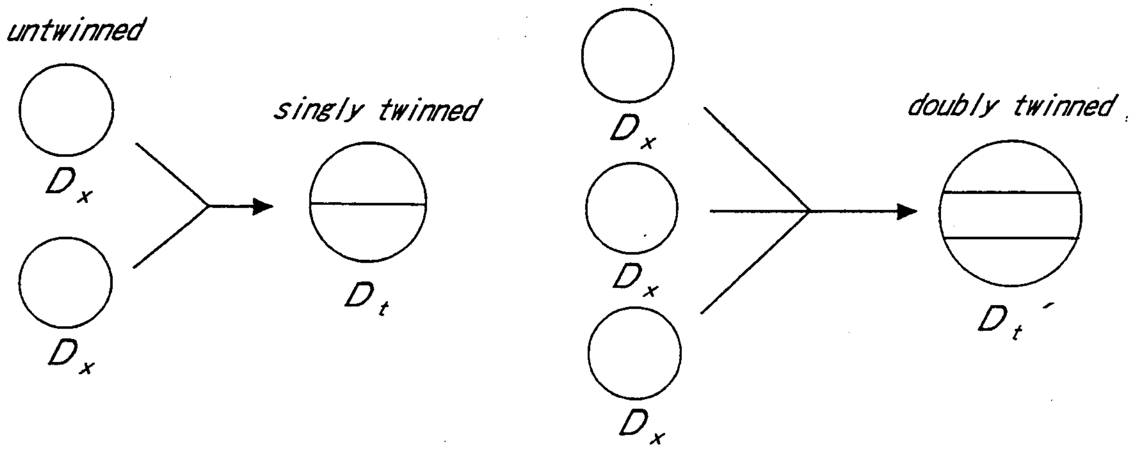

Fig.1 Twinned and untwinned nuclei (crystal Dt and crystallite Dx)

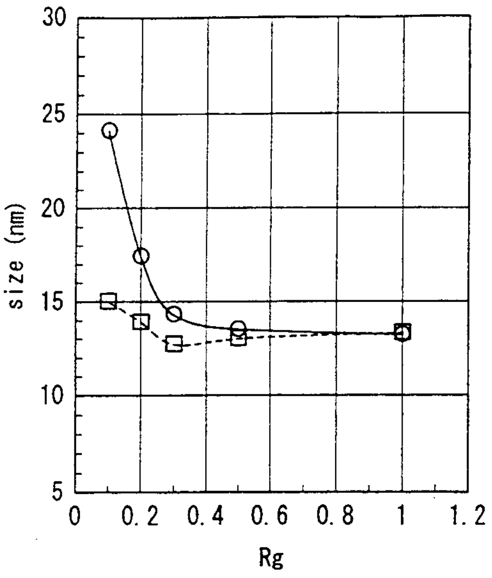

Fig. 2 Influence of Rg(amount of added gelatin /amount of added $AgNO_3$) on sizes measured by tubidity(○) and X-ray diffraction(□)

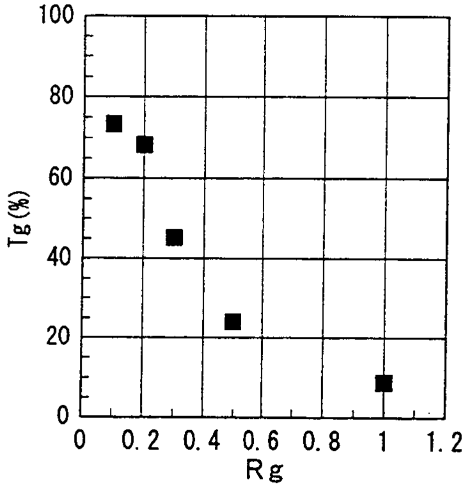

Fig. 3 Relation between proportion of twinned grains(Tg(%))grown from nuclei and Rg (amount of added gelatin /amount of added $AgNO_3$)

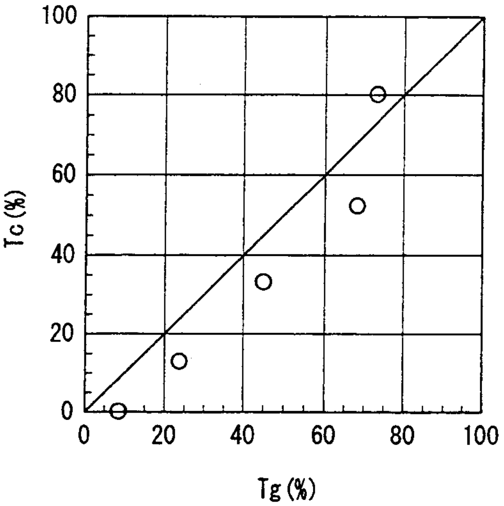

Fig. 4 Comparison of a proportion of twinned nuclei (Tg(%)) observed after growing nuclei with that caluculated with D_x and D_t.

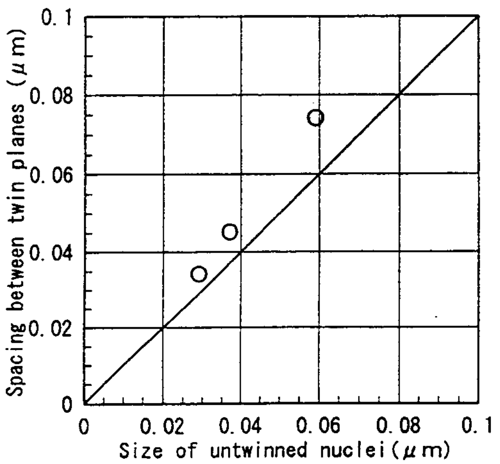

Fig. 5 Comparison of spacing between parallel twin planes with untwinned nuclei grain saize.

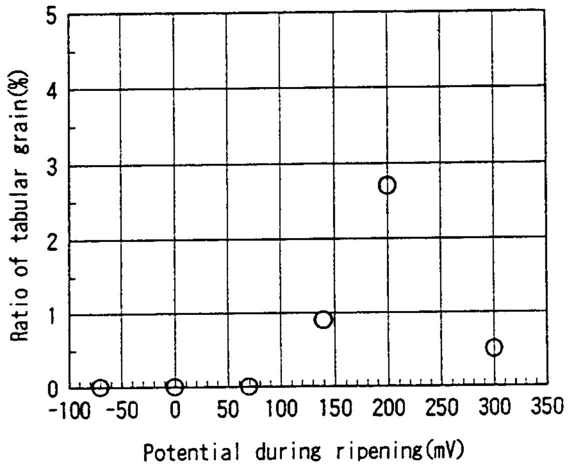

Fig. 6 Dependence of coalescence (twinning) upon potential durig ripening

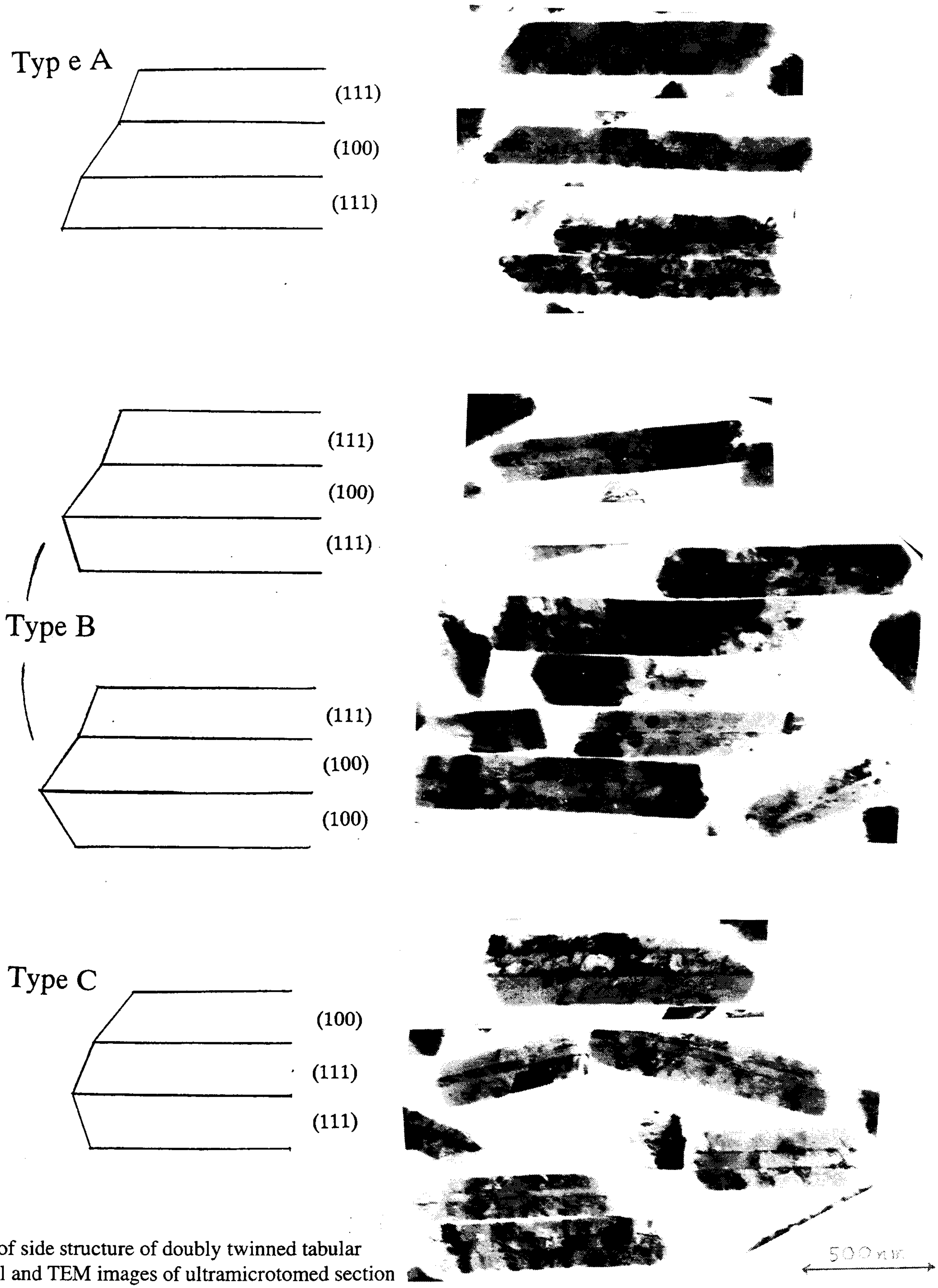

Fig. 7 Types of side structure of doubly twinned tabular crystal and TEM images of ultramicrotomed section