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

Yoichi Hosoya and Shigeharu Urabe*

Ashigara Research Laboratories, Fuji Photo Film Co., Ltd., Kanagawa, Japan

On the mechanism of nucleation and growth of (111) tabular silver halide crystals, it is proposed that twinning (nucleation) occurs by stacking fault and that the anisotropic lateral growth is brought about by the ridge trough structure on tabular grain side faces. Although the "coalescence" model for nucleation and the "rough-smooth" side face structure for anisotopic growth were proposed recently, they have not yet been supported by direct experimental evidence. We analyzed the nucleation process by a combination of light scattering and X-ray diffraction and examined the coalescence of untwinned fine grains after decomposition of gelatin. These experimental results provided evidence to support the coalescence model for twinnning. We observed by TEM imaging of ultramicrotomed sections of side faces of tabular grains that have relatively thick spacings between parallel twin planes and confirmed that on the side faces of tabular grains, both rough-smooth and ridge-trough structures exist.

Journal of Imaging Science and Technology 42: 487–494 (1998)

Introduction

It is necessary to understand the mechanism of nucleation and growth of tabular grain since tabular silver halide crystals are now very important for highly sensitive photographic emulsion.

Berriman and Herz[1] found that most tabular silver bromide crystals were twinned on the (111) plane. They proposed that the twinning occurs as a result of a stacking fault during nucleation (or growth) and considered that the reentrant geometry in the "ridge-trough structure" resulting from multiple twinning was sufficient to account for tabular growth. Berry, Mriono, and Oster[2] have proposed that twinning occurs according to a "stacking fault" mechanism caused by deposition of complexes on the (111) grain surface at low pBr. They speculated that under the low pBr condition where the dominant complex is $AgBr_3^{2-}$, twinning results from the failure of this complex to occupy the normal site, owing to its larger Br^- to Br^- distance than occurs in the crystal and its strong polarizability. Although the mechanism of deposition of the $AgBr_3^{2-}$ complex at low pBr has not been verified, this mechanism has been widely accepted.

Saitou[3] suggested that pBr is not the only parameter that controls twinning and formation of tabular silver halide grains. The other parameters included gelatin concentration, degree of mixing, degree of supersaturation, temperature at nucleation, the concentration of solvent, ionic strength, and iodide concentration. Some doubts were cast on the validity of the low pBr deposition mechanism.

Mumaw and Haugh[4] proposed a "coalescence" mechanism for the formation of twin planes in silver halide crystals. Recently Antoniades and Wey[5] found strong correlation between degree of flocculation and the resulting fraction of tabular grains and concluded that coalescence preceded by flocculation, caused twinning in the nucleation stage of tabular grains. Although the relation between coalescence and twinning was demonstrated as clear evidence for the coalescence mechanism, it was not quantitative. That a high population of tabular silver bromide grains could be formed at various pBr values in the nucleation period was also demonstrated, thus raising a question on the validity of the idea that twinning occurred only at low pBr.

Hamilton and Brady[6] observed a ridge-trough structure on the side face of a large tabular grain by electron microscope. They proposed that the reentrant grooves in the ridge-trough structure on the side face was the cause of the lateral growth of tabular grains. Maskasky[7] demonstrated that the shape of tabular grain depended on whether the number of twin planes was odd or even by examining the orientation of silver chloride epitaxies formed on the main surface of the tabular grain. He has suggested that the acute lip structure of a ridge-trough side face structure plays an important role for the anisotropic lateral growth of tabular grains.

Jagannathan and co-workers[8] suggested on the basis of ball model simulation for the growth model that side faces of a tabular grain are not bounded solely by (111) but by both (111) and (100) planes, and they proposed that the anisotropic growth of tabular grains would take place with rough-smooth side face structure since the (100) surface is rough and the (111) surface is smooth at relatively low pBr. Mehta, Jagannathan, and Timmsons[9] also demonstrated that the shape of tabular grain (i.e., equilateral triangles, regular hexagon, or shapes intermediate between these two) did not depend on whether the number

Original manuscript received May 8, 1998

* IS&T Member

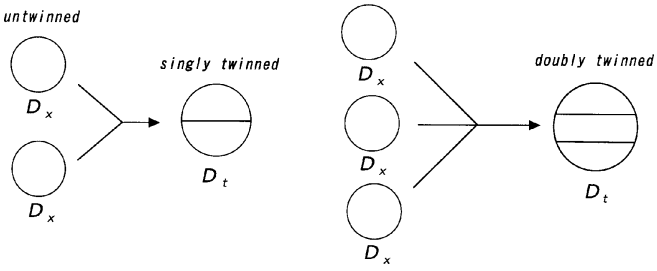

Figure 1. Formation of twinned and untwinned nuclei, where D_t and D_x are crystal size and crystallite size, respectively.

of twin planes is even or odd, but could be explained by cubooctahedral side face structure. Although the side face structure of tabular grains was demonstrated as evidence for this proposal, it was not necessarily unequivical, insofar as 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 a better understanding of the twinning mechanism and growth mechanism and also to obtain experimental evidence for the proposed model.

Experimental

Nucleation of Tabular Grains (Twinning). Silver bromide nuclei were prepared continuously in a mixing chamber (8-mL volume) into which 1-M silver nitrate aqueous solution and 0.143-M potassium bromide aqueous solutions containing various concentrations of low-molecular-weight gelatin (molecular weight ca 20,000) were added at room temperature. The flow rates of the reactants were 25-mL/min for silver nitrate solution and 185-mL/min for potassium bromide solution containing gelatin, and the pBr of the effluent of the mixing chamber was kept at 2.88.

Determination of the Crystal Size and Crystallite Size of the Nuclei. As shown in Fig. 1, twinned crystals consist of at least two crystallites (single twin, two crystallites, doubly twin, three crystallites), whereas untwinned crystal (regular crystal) consists of only one. The crystal size of nuclei was determined turbidmetrically by using the Rayleigh equation, as shown below:[10a,b]

$$D_t = (\tau_\lambda \rho_s / C_s)\lambda m^4 / 4\pi^4 \mu^2,$$

$$\mu = \left(m^2 - 1\right)/\left(m^2 + 1\right),\ m = n_p / n_m,$$

where D_t is crystal size; τ_λ is turbidity at wavelength λ; ρ_s and C_s are density of crystals and suspension of crystals, respectively; λ_m is wavelength in the medium; and n_p and n_m are refractive indices of crystal and medium, respectively. The turbidity was measured at 700 nm after quenching the reactor effluent by 2% aqueous solution of 4-hydroxy-6-methyl-1,3.3a,7-tetraazaindene(TAI).[10] Crystallite size of the nuclei was determined by x-ray diffraction with the Scherrer equation as shown below:[11]

$$D_x = 0.9\lambda / \beta \cos\theta,$$

where D_x is crystallite size for the direction perpendicular to (hkl); λ is wavelength of the x-ray beam, β is the half angular width of the diffraction beam; and θ is the Bragg angle. The x-ray source was CuK_β, and the plane of the diffraction employed was (200).

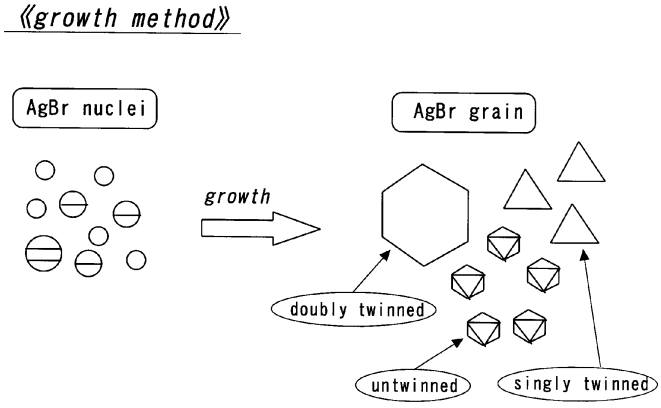

Figure 2. Method to determine the proportion of twinned nuclei by grain growth.

Determination of Proportion of Twinned Grains by Growing a Nuclei Emulsion. In order to determine the proportion of twinned grains in a population of nuclei, the nuclei were grown by a double-jet method in which aqueous solutions of $AgNO_3$ and KBr were simultaneously added under such a relatively high supersaturation condition that neither renucleation nor physical ripening would occur. In this growth process, pBr was kept at 2.41 and the emulsion was kept at 40°C. As illustrated in Fig. 2, untwinned nuclei, singly twinned nuclei, and doubly twinned nuclei are grown to small octahedral grains, small triangular grains, and large tabular grains, respectively. The morphology of the emulsion grains obtained was observed by scanning electron microscopy and the proportion of untwinned octahedral crystals, small triangles (singly twinned crystal), and tabular grains (doubly twinned crystal; mainly regular hexagons, with a few large equilateral triangles and shapes intermediate between these two) were determined.

Twinning Caused by Coalescence of Untwinned Nuclei Formed Beforehand. We developed a new technique to cause twinning by coalescence of untwinned nuclei formed beforehand. Although nothing occurred when an untwinned fine-grain emulsion was ripened at 40°C, twinning took place under the same condition after the gelatin in the untwinned fine-grain emulsion was decomposed by treatment with an enzyme. The experimental procedure was as follows. Three untwinned fine-grain emulsions (average grain size; 0.03, 0.04, and 0.06-μm) were made using low-molecular-weight gelatin as a protective colloid. After adjusting the silver potential of these emulsions to various values [-70 mV to 300 mV reference electrode versus saturated calomel electrode (SCE)], 0.1 g enzyme, which decomposed the gelatin, was added to 1 L emulsion, which was then ripened for 30-min at 40°C. After deionized ossein gelatin solution was added to the emulsion, the emulsion grains were grown in the same manner as that mentioned above. The resulting emulsion grains were analyzed by scanning electron microscopy.

Coalescence of Nuclei in the Absence of Gelatin. In order to estimate the relation between the coalescence of nuclei and silver potential in the absence of gelatin, after precipitation at 0 mV (reference versus SCE) in the absence of gelatin, the nuclei were ripened at three different silver potentials (200, 0, and –70 mV) at 40°C. The grain

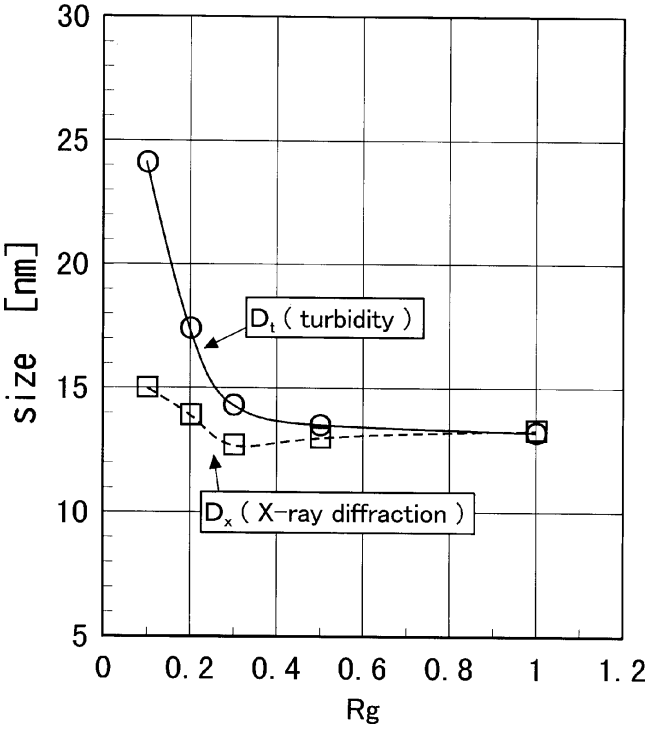

Figure 3. Influence of Rg (grain of gelatin/grain of $AgNO_3$) on sizes measured by turbidity (O,D_t) and x-ray diffraction (□,D_x).

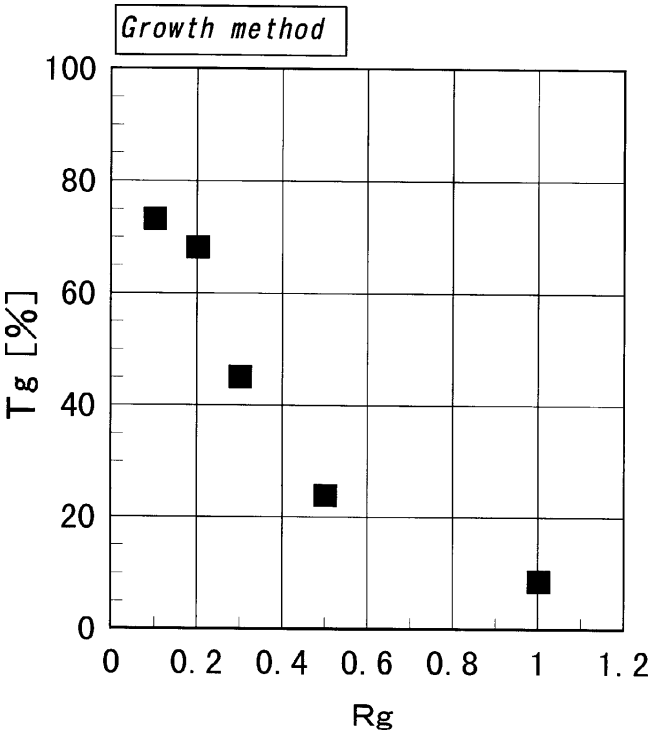

Figure 4. Relation between proportion of twinned grains [Tg (%)] among those grown from nuclei and Rg (grain of gelatin/grain of $AgNO_3$).

sizes of the resulting emulsion grains were determined turbidmetrically, as described above.

Observation of the Side Face Structure of Tabular Grains. By using the above technique, it was possible to make tabular grains having relatively thick spacing between parallel twin planes. After the twinning by ripening following the gelatin decomposition, the nuclei were grown to $AgBrI_{0.1}$ tabular grains by the double-jet method. The side face structure of $AgBrI_{0.1}$ was preserved well compared with AgBr tabular grains, since $AgBrI_{0.1}$ is less soluble than AgBr. We observed the side face structure of these tabular grains by transmission electron microscopy (TEM) images of the their ultramicrotomed sections.

Result and Discussion

Mechanism of Nucleation. The values of D_x (crystallite size) and D_t (crystal size) are shown as a function of added amount of gelatin, Rg (g/g of silver nitrate), in Fig. 3 and the proportion of twinned grains among the grains grown from the nuclei emulsion is shown in Fig. 4. The proportion of tabular grain (i.e., twinning probability) increased with a decreasing amount of gelatin. When twinning occurred, the value of D_t became larger than that of D_x, which was nearly independent of gelatin concentration. These facts support the idea that twinning occurs by coalescence, as shown in Fig. 1. Because gelatin layers adsorbed on the surface of silver bromide grains can prevent the coalescence, it is reasonable to consider that twinning probability increases with a decreasing amount of gelatin. By using the values of D_t and D_x, the proportion of twinned nuclei (the proportion of tabular grains) can be calculated as follows.

The probability of twinning is embodied in Eq. 1.[12]

$$p(r) = {}_8C_r t^r (1-t)^{8-r}, \tag{1}$$

where $p(r)$ is fraction of tabular grains having r parallel twin planes, and t is probability of twinning. As shown in Fig. 1, the singly twinned crystal size $D_t(1)$ is $\sqrt[3]{2}\,D_x$ and the size of doubly twinned crystal $D_t(2)$ is D_x. Therefore the average size of crystals D_t is expressed by D_x and $p(r)$ as follows:

$$D_t = \frac{D_x\left(p(0) + \sqrt[3]{2}p(1) + \sqrt[3]{3}p(2)\right)}{p(0) + p(1) + p(2)}. \tag{2}$$

From Eqs. 1 and 2, D_t/D_x is expressed as a function of t as follows:

$$D_t/D_x = \frac{\left(28\sqrt[3]{3} - 8\sqrt[3]{2} + 1\right)t^2 + 8\sqrt[3]{2}t + 1}{20t^2 + 7t + 1}. \tag{3}$$

By putting an experimentally obtained value of D_t/D_x into Eq. 3, the value t can be estimated and the value $p(r)$ is then calculated by putting the value of t in Eq. 1. The proportion of twinned nuclei (singly and doubly) Tc is expressed as follows:

$$\mathrm{Tc} = \frac{p(1) + p(2)}{p(0) + p(1) + p(2)} \times 100. \tag{4}$$

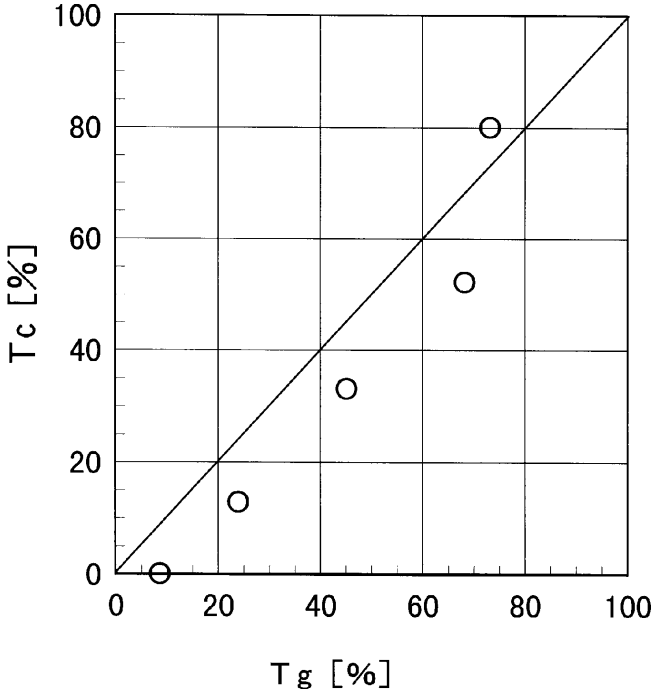

Figure 5. Comparison of the proportion of twinned nuclei [Tg (%)] as given by observing grains grown from the nuclei with that calculated on the basis of D_x and D_t.

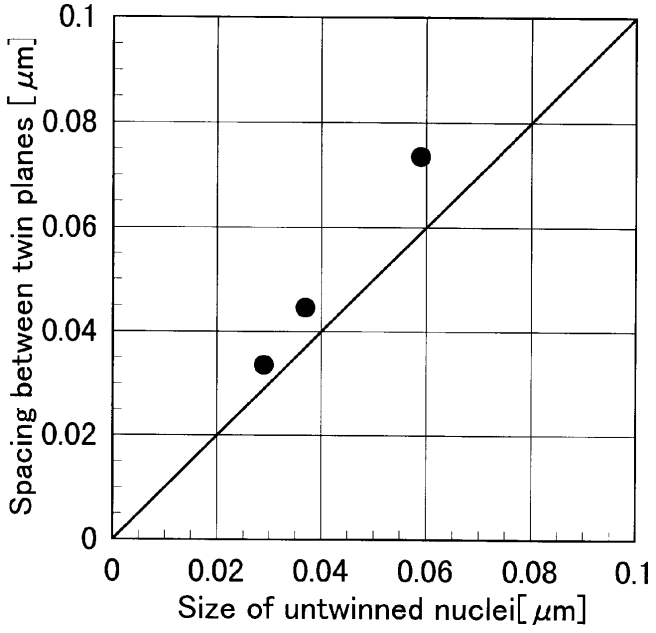

Figure 6. Comparison of spacing between parallel twin planes with untwinned nuclei size.

The value Tc now is calculated by putting the values obtained for $p(r)$ into Eq. 4. On the other hand, growth of nuclei gave experimentally the fraction of twinned tabular grains (singly and doubly twinned) Tg. As seen in Fig. 5, the calculated value fraction Tc almost coincided with the experimental value (Tg). This result supports the coalescence model.

Tabular grain emulsion was obtained when untwinned fine nuclei were ripened after decomposition of the gelatin and then were grown by the double-jet method. As shown

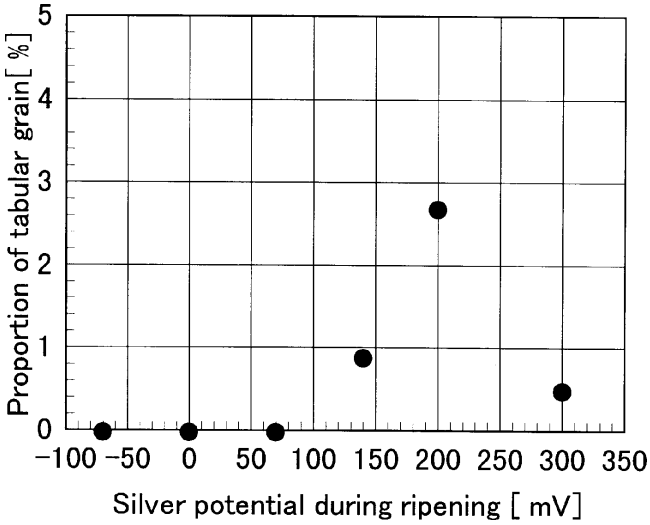

Figure 7. Dependence of the degree of coalescence (twinning) in terms of proportion of tabular grains on silver potentials during ripening.

in Fig. 6, the thickness of spacing between parallel twin plains almost coincided with the size of untwinned fine grains formed beforehand. This is another strong piece of evidence for the 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.

Figure 7 shows the dependence of the coalescence (twinning) on the silver potential of the nuclei after gelatin was decomposed by enzyme. It was clear that coalescence occurred at high silver potential (200 mV), which was almost the same as the isoionic point of silver bromide. This phenomenon is completely contrary to twinning at low pBr, where silver potential is negative, for example, –40 mV, as Berry et al. emphasized. We conclude that the probability of twinning caused by coalescence increases with decreasing gelatin concentration, and coalescence takes place with maximum frequency at high silver potential (high pBr), which is nearly the isoionic point of silver bromide when gelatin concentration is fairly low. It is reasonable to suppose that at the isoionic point, the electric charge of each grain determined by adsorbed Br^- ions would be minimum and that the coalescence would take place easily because the electrostatic repulsion force among grains was likewise minimum.

Figure 8 shows the grain size of the emulsion nuclei precipitated without gelatin, and ripened also in the absence of gelatin at three different silver potentials. At 200 mV, the rapid grain size increase with ripening time was observed, whereas at 0 mV, the size of the grains hardly changed. We infer that at high silver potential, corresponding to the isoionic point of silver bromide, the electric charge of each grain would become so small that "rapid coagulation" takes place. On the other hand, at 0 mV, the coagulation would not occur owing to electrostatic repulsion caused by Br^- adsorption on the grain surface. At –70 mV, relatively slow increase in grain size compared with that at 200 mV was observed. We considered that this "slow coagulation" took place owing to the decrease in electrostatic repulsion force caused by high ionic strength due to the high concentration of KBr in the reaction solution, and that, at –70 mV, "Ostwald ripening" might take place easily since the solubility of silver bromide is larger at –70 mV than that at 0 mV.

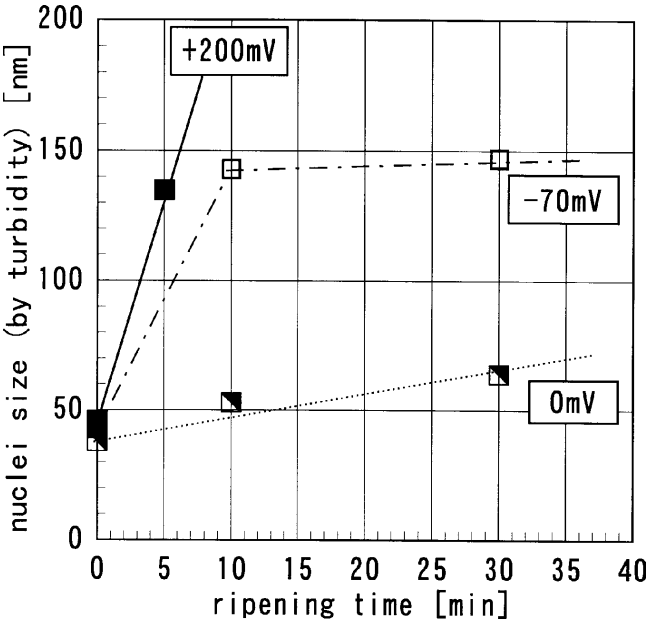

Figure 8. Dependence of the degree of coalescence in terms of nuclei size on potential ripening time in the absence of gelatin.

In the precipitation system in which solutions of Ag^+ and Br^- ion are introduced simultaneously into a reaction vessel where an emulsion is stirred vigorously, the high-silver-potential region will be produced in the vicinity of the exit of the pipe for introduction of Ag^+ aqueous solution. Furthermore, in this region, the concentration of gelatin is fairly low compared to the bulk of the reaction vessel in spite of vigorous stirring. We infer that the twinning takes place by a rapid coagulation process in this high-silver-potential region where the gelatin concentration is fairly low.

Mechanism of Tabular Grain Growth.

Structure of the Side Face of the Tabular Grains. We could control the thickness of the spacing between two parallel twin planes of tabular grains, as noted above. It was difficult to observe the structure of the side face of ordinary tabular grains, because spacing between two parallel twin planes was as thin as 0.015 μm. Now we could clearly observe the structure of the side face of tabular grains in which spacings between parallel twin planes was ca 0.04 to 0.05 μm.

We considered all the cases of side face structure based on the assumption that both (100) and (111) exist on the side face of the doubly twinned tabular grain. There are five side face structures, that are A–E as shown in Fig. 9. Among these types, E is the ridge-trough type in which the side faces are bound only by (111) or (100) surfaces. We observed the TEM images of ultramicrotomed section of tabular grains. Figure 10 shows a TEM image of the ultramicrotomed sections of tabular grains. The side face structure of some tabular grains were not necessarily clear, because they were microtomed at various angles as seen in Fig. 10. However, we could choose images of the tabular grains that were cut almost perpendicular to both their main surface and edges. Figure 11 shows the chosen TEM images of the ultramicrotomed section. The structures of Types A, B, C, and E were observed, whereas that of Type D was not observed at all. These results are the clear evidence for the rough-smooth side face structure. However, in Type E, ridge-trough side face structure bounded by

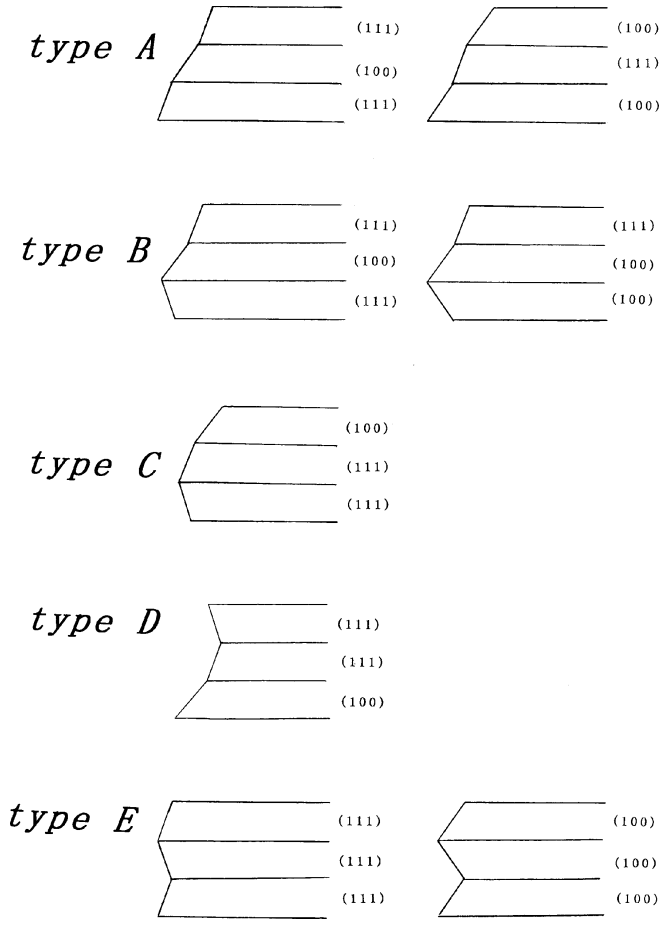

Figure 9. Probable side face structures of doubly twinned tabular grains.

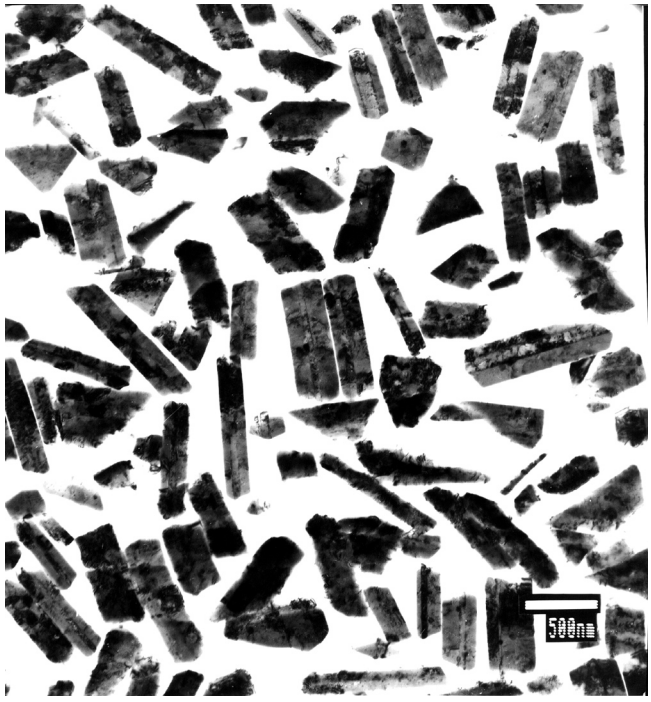

Figure 10. A TEM image of ultramicrotomed sections of tabular grains; the length of the bar in this figure is 500-nm.

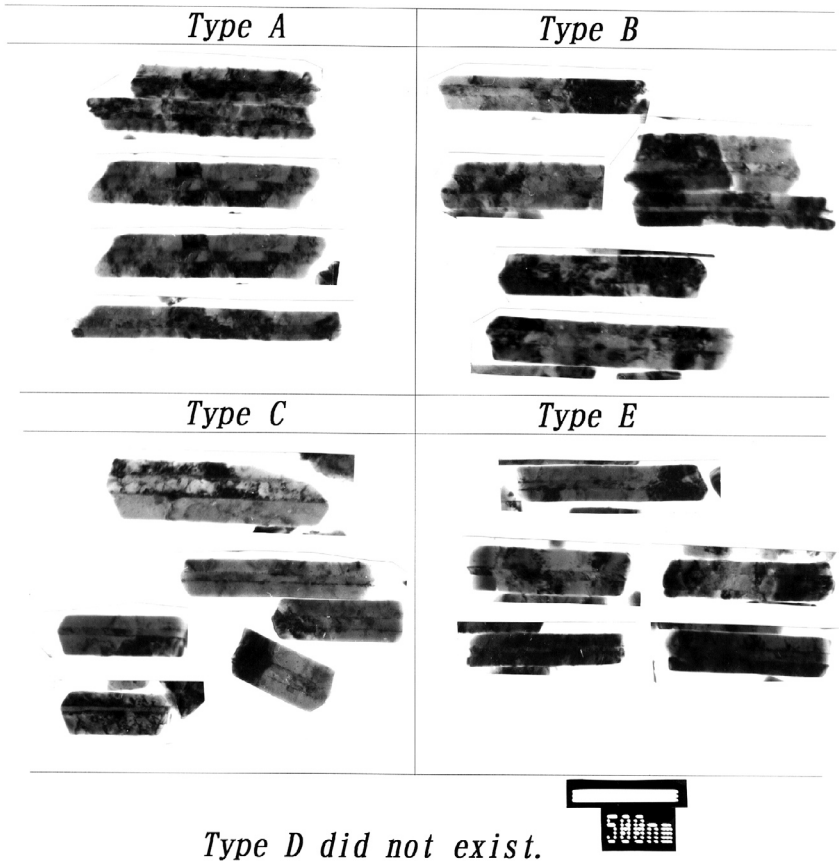

Figure 11. All the side face structures of tabular grains observed by TEM images of ultramicrotomed sections of tabular grains.

only (111) surface was also observed. Consequently we conclude that not only rough-smooth but also ridge-trough side face structures exist in the side faces of tabular grains.

The Shape of Tabular Grains. Mehta and co-workers[13] demonstrated the basis of the rough-smooth model where a (100) surface is self-generated on a side face owing to difficulty in spreading the growth layer across the 218.90 ridge in the ridge-trough side face structure. On the other hand, they also proposed the cubooctahedral model based on the nature of twinning crystallites that are likely to be present under high supersaturation conditions that are known to exist in the reactor. They considered that although (100) surfaces are not stable in a high-bromide excess growth environment, the twinning geometry is expected to stabilize the coexistence of (111) and non-(111) surfaces. We considered all types of combinations of two side face structures that neighbor each other in the case of the parallel doubly twinned tabular grains, based on the assumption that both (100) and (111) surfaces exist on the side faces of the tabular grain. Because a hexagonal tabular grain is in triple rotational symmetry, there are only two kinds of side face structures in the tabular grain. It is therefore sufficient to consider the two neighboring side faces of each tabular grain. By model simulation of the tabular grain, the following conditions were confirmed between neighboring side faces:

1. The combination of neighboring surfaces (111)/(111) and (111)/(100) are possible, as proposed in the ridge-trough and the rough-smooth models.
2. The combination of neighboring surfaces (100)/(100) is not likely to exist because nuclei (twinning crystallite) bounded by solely (100) surfaces could not be twinned in the nucleation stage since the twinning takes place only on the (111) surface.

In Fig. 12, the combinations of side surfaces (111) and (100), Types A–C and E are shown on the left and, in each case, possible neighboring side surfaces are shown in the middle according to considerations based on conditions 1 and 2 mentioned above. Type D was not examined because its absence was confirmed experimentally. At low pBr, (100) surfaces would grow faster than (111) surfaces, because the (100) surface is rough and (111) surface is smooth. On the assumption that the lateral growth rate of a side face of a tabular grain depends on the number of (100) surfaces, as proposed by Mehta et al.,[9] we could predict the shape of the tabular grains after their growth. For example, if the two neighboring side faces of the tabular grain have the same number of (100) surfaces, this tabular grain will grow to regular hexagonal shape because each side face has the same growth rate. On the other hand, if the two neighboring side faces of the tabular grain have different numbers of (100) surfaces, this tabular grain will grow to an equilateral triangle or shapes intermediate between hexagonal and triangular, because the side faces that have more (100) surfaces will grow faster than other side faces. Without (100) surfaces in the neighboring side faces, that is, if the side face is bounded only by (111) faces, the hexagonal morphology will be obtained, but in this case, because of low rate of lateral growth of (111) surfaces, the tabular grain will grow to only small size. The shapes of the tabular grains resulting from all combinations of side faces

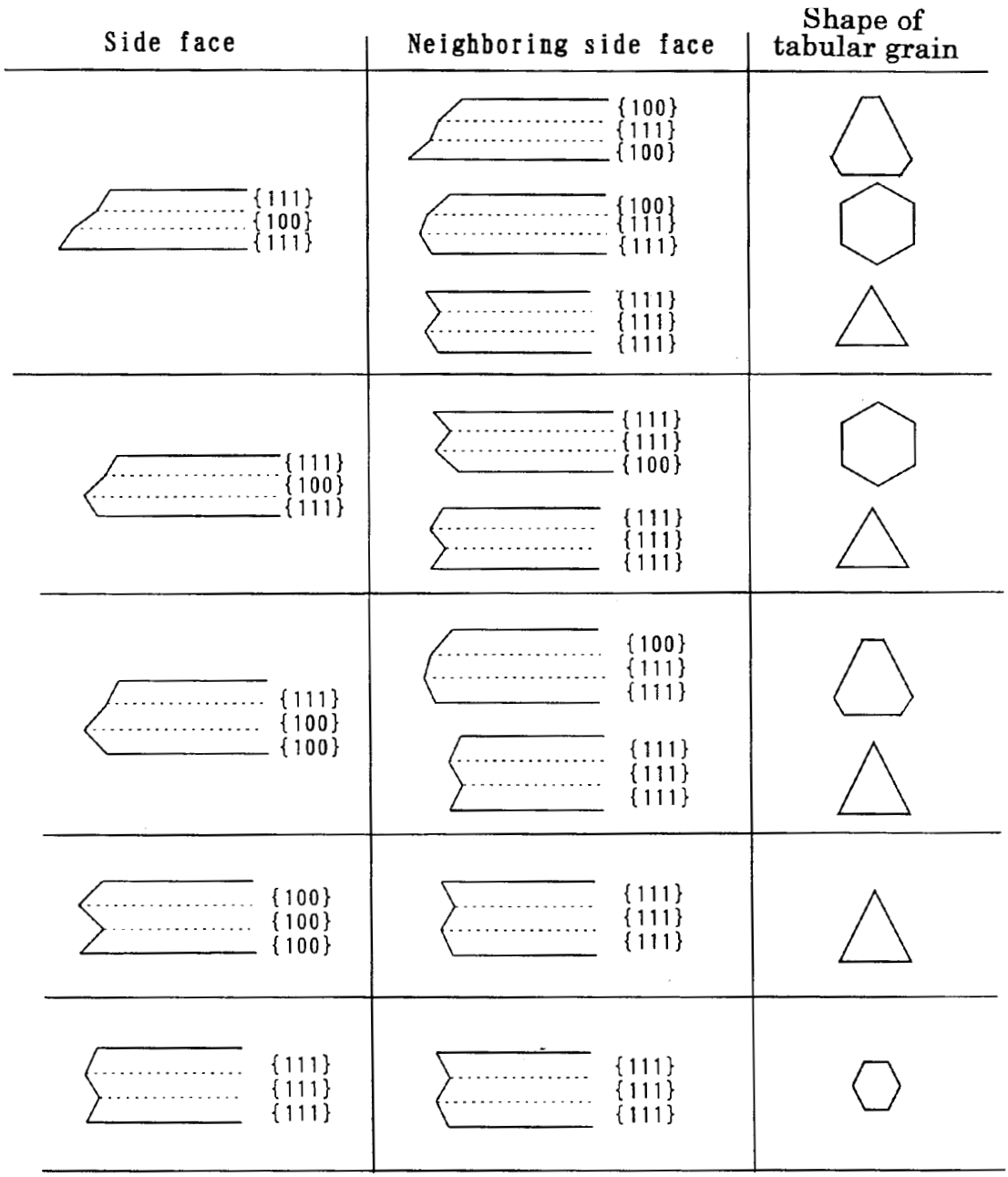

Figure 12. Probable combinations of neighboring side faces and shapes of the tabular grains.

would then be expected in the manner indicated in the right column in Fig. 12. As shown in this figure, tabular grains are classified, not by the number of twin planes, but by side face structures, and many kinds of tabular grains exist, for example, in the case of doubly twinned tabular grains. If the cases of single and triple twinning are taken into consideration, the number of kinds of tabular grains will be even more. These numerous kinds of grains will have different lateral growth rates corresponding to each side face structure. At low pBr, because the (100) surface is rough, the characteristics of each grain will generate the various tabular grain shapes, resulting in the fact that the shapes of tabular grains vary continuously between regular hexagon and equilateral triangles as demonstrated by Maskasky,[14] and the size distribution becomes wide.

Conclusion

We conclude that in the nucleation of twin tabular AgBr grains, twinning occurs by the coalescence model supported by the following three experimental observations.

1. When the twinning occurred, the crystal size became larger than that of crystallite size, which hardly changed with decrease in gelatin concentration.
2. The calculated twinning probability, estimated on the basis of the assumption that twinning occurred by coalescence, almost coincided with the experimental value.
3. When the twinning takes place by coalescence of untwinned nuclei after decomposition of gelatin, the spacing between parallel twin planes almost coincided with the size of the untwinned fine grains.

Twinning caused by coalescence takes place most frequently at high silver potential, that corresponded to the isoionic point of silver bromide, and at low gelatin concentration. In the precipitation system for silver halide emulsions, the high silver potential is produced in the vicinity of the pipe for introduction of an Ag^+ aqueous solution, where the concentration of gelatin is fairly low, and twinned nuclei will be generated in this region of the reactor.

With respect to the side faces of tabular grains, not only rough-smooth, but also ridge-trough structure exist.

It is reasonable that many kinds of tabular grains exist with respect to side face structure, and growth rate, as well as the shape of the tabular grains after growth, will depend on the modes of combination of adjacent side face structures. ▲

References

1. R. W. Berriman and R. H. Herz, *Nature* **18,** 293 (1957).
2. C. R. Berry, S. T. Mriono, and C. F. Oster Jr., *Photogr. Sci. Eng.* **5,** 332 (1961).
3. M. Saitou, US Patent 4,945,037 (1990).
4. C. T. Mumaw and E. F. Haugh, *J. Imaging Sci.* **30,** 198 (1987).
5. M. G. Antoniades and J. S. Wey, *J. Imaging Sci.* **39,** 323 (1995).
6. J. F. Hamilton and L. E. Brady, *J. Appl. Phys.* **35,** 414 (1964).
7. J. E. Maskasky, *J. Imag. Sci.* **31,** 15 (1987).
8. R. Jagannathan, R. V. Metha, W. K. Lam, D. L. Black, and J. A. Timmons, *J. Imaging Sci.* **39,** 67 (1995).
9. R. V. Mehta, R. Jagannathan and J. A. Timmsons, *J. Imaging Sci.* **37,** 107 (1993).
10. M. G. Antoniades and J. S. Wey, *(a) J. Imaging Sci.* **36,** 517 (1992); *(b) J. Imaging Sci.* **37,** 272 (1993).
11. K. Miyake, T. Tani and O. Nittono, presented at the 67th Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, April, 1994.
12. R. Jagannathan and V. V. Gokhale, *J. Imaging Sci.* **35,** 113 (1991).
13. R. V. Mehta, R. Jagannathan, W. K. Lam, D. L. Black, and J. A. Timmsons, *J. Imaging Sci.* **39,** 67 (1995).
14. J. E. Maskasky, *J. Imaging Sci.* **40,** 79 (1996).