- Press, N.Y. (1975) p. 173-86.
- 8) K. Ando and Y. Oishi, *J. Chem. Phys.*, **61**, 625-29 (1974).
 - 9) R. Lindner and A. Akerstrom, *Z. Phys. Chem. NF.*, **18**, 303-10 (1958).
 - 10) R.J. Bratton, *J. Am. Ceram. Soc.*, **52**, 417-19 (1969).
 - 11) S.K. Rhee, *J. Am. Ceram. Soc.*, **55**, 300-03 (1972).
 - 12) Y. Oishi and W.D. Kingery, *J. Chem. Phys.*, **33**, 480-86 (1960).
 - 13) A.E. Paladino and W.D. Kingery, *J. Chem. Phys.*, **37**, 957-62 (1962).
 - 14) J.M. Blakely and C.Y. Li, *Acta Metall.*, **14**, 279-84 (1966).
 - 15) M. Yamashita, T. Maruyama and W. Komatsu, *Z. Phys. Chem. NF.*, **105**, 187-96 (1977).
 - 16) J.B. Wachtman, Jr. and L.H. Maxwell, *J. Am. Ceram. Soc.*, **40**, 377-85 (1957).
 - 17) R.L. Coble, *J. Appl. Phys.*, **32**, 793-99 (1961).
 - 18) K. Kitazawa, T. Kiriyaama, K. Fueki and T. Mukaibo, *J. Am. Ceram. Soc.*, **60**, 363-66 (1977).
 - 19) D.W. Ready and R.E. Jech, *J. Am. Ceram. Soc.*, **51**, 201-08 (1968).
 - 20) P.S. Maiya, W.K. Chen and N.L. Peterson, *Metal. Trans.*, **1**, 801-04 (1970).

論文・Paper

Analysis on Formation Process of Ultrafine Alumina Particle from NH_3 gas- AlCl_3 solution

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It was reported that the ultrafine particles of alumina was prepared by the reaction of NH_3 gas and AlCl_3 solution. A particle size decreased with decreasing NH_3 gas composition or AlCl_3 concentration. The particles of less than 50 Å in size were prepared.

The formation mechanism was discussed as follows. While a mass of AlCl_3 solution falls from the top to the bottom of a stream in a flask, NH_3 gas is absorbed from the surface of a mass. The generation zone on the surface of solution defined in preceding paper shifts toward the innerpart of mother liquid during the very short exposure time for NH_3 gas, so that the ultrafine particles and excess OH^- ions remain in the stocking zone behind the generation zone. The particles and OH^- ions are carried into the mother liquid by the stream in the flask and the excess OH^- ions make the relatively large particles by inhomogeneous reaction with Al^{3+} ions there. The particles exist in the mother liquid as a stable colloid for the very near equilibrium state of the mother liquid. [Received March 17, 1979]

NH_3 ガス- AlCl_3 溶液からのアルミナ超微粒子生成過程の解析

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NH_3 ガスと AlCl_3 水溶液との反応により、アルミナ超微粒子が生成されることを報告した。粒子径は、 NH_3 ガスや AlCl_3 溶液濃度の減少に従って減少した。その結果 50 Å 以下の粒子径を持つ微粒子が得られた。

生成機構は以下のように議論された。 AlCl_3 溶液がフラスコの流れの頂上から下まで流れ落ちる間に、アンモニアガスがその表面から吸収される。前報で定義された溶液表面の粒子の発生帯が、この NH_3 ガスを吸収している短い時間の間、母液内部へ移動する。その結果超微粒子と過剰の OH^- イオンが発生帯の後ろにある貯留帯に残される。この粒子と OH^- イオンはフラスコ内の流れに乗って母液に運ばれる。母液に運ばれた過剰の OH^- イオンは母液中の Al^{3+} イオンと不均一反応を起こし、比較的大きな粒子を作る。これらの粒子は母液が平衡状態にたいへん近いために安

定なコロイドとして存在する。

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Key-words : Alumina, Aluminum hydroxide, Colloids, Nucleation, Particles, Powders, Precipitation

1. Introduction

The relationship between the particle size of the precipitate and the concentrations of reactants has been known as Weimarn's precipitation law¹⁾. But it is considered that the Weimarn's law is the relationship after the growth of nuclei. Generally, a precipitation reaction was always accompanied by the growing or aggregate reaction of nuclei after the generative reaction of them. For example, aluminum hydroxide gel consists of aggregates of small particles²⁾.

The preparation method of ultrafine particle of less than 100 Å was reported³⁾ and the formation mechanism in liquid film was discussed in the preceding paper⁴⁾.

The particles of aluminum hydroxide with the reaction of aqueous ammonium hydroxide with aluminum chloride solution (L-L method) grow up to the large particle in any condition. Because, if the very dilute ammonium hydroxide and aluminum chloride solutions were employed to precipitate the aluminum hydroxide, the supersaturation ratio is very small so that the nucleation rate is very small. Consequently, the precipitation occurs on any activated points in the solution, that is, impurities, flaws of vessel, etc., and then the particle grows up to large one.

If the concentrated ammonium hydroxide and aluminum chloride solution were employed, the reaction takes place at the interface of both liquids and very small particles are produced at the reaction place because the high supersaturated state appears and nucleation rate rises up to the limit. However an aggregation of these small particles occurs because the reaction continues at the same place of the interface by flowing the both Al^{3+} and OH^- ions into the reaction place. Therefore, if the reaction place was forced to shift by any method, the aggregation would be avoided.

In this paper, the mechanism not to aggregate the small particle is discussed and the change in particle size with the concentration of AlCl_3 solution and the composition of NH_3 gas (G-L method) was examined.

2. Experimental and results

The present precipitation method, namely G-L method, was described in previous papers^{3), 4)}.

Time dependence of the pH value for the reaction with 0.1 mol/l AlCl_3 solution and 0.005 atm $\text{NH}_3\text{-N}_2$ gas mixture was shown in Fig. 1.

The effects for particle sizes with changes of Al^{3+} ion concentration such as 3.2 mol/l, 1.0 mol/l, 0.5 mol/l and 0.1 mol/l under pure NH_3 gas were examined, each precipitate under the above condition was washed 3 times by distilled water using a centrifugal separator, and it was dispersed again in distilled water. A drop of this suspension was put on the mesh for electron microscope which was treated previously with collodion and carbon, and then dried on a filter paper. After the mesh was heated up to 400°C in vacuum, it was subjected to observation by electron microscopy. The instrument for observation was a type H-700 of Hitachi Co., Ltd. whose voltage was 100 kV and resolving power was 6 Å. A decrease in the concentration made the smaller particles of alumina gel as shown in Fig. 2.

The effects for particle size with the change of gas composition such as 100%, 25%, 3.3% and 0.31% by volume of NH_3 mixed with N_2 under 0.1 mol/l AlCl_3 solution were also examined. Same observation method mentioned above was employed. Such a decrease in the gas composition also made the smaller

Fig. 1. Variation in the pH with the time in reaction of 0.1 mol/l AlCl_3 solution with $\text{NH}_3\text{-N}_2$ gas mixture ($p_{\text{NH}_3} = 0.005$ atm).

Fig. 2. Variation in particle size of alumina gel from the AlCl_3 solutions with various concentrations by absorbing the pure NH_3 gas. (a) : 3.2 mol/l, (b) : 1.0 mol/l, (c) : 0.5 mol/l, (d) : 0.1 mol/l.

Table 1. Variation in size ($\text{\AA}$) of the largest particle in Figs. 2 and 3 with solute concentrations or gas compositions.

$\frac{P_{\text{NH}_3} (\text{atm})}{C_{\text{AlCl}_3} (\text{mol/l})}$	1	0.25	0.033	0.0031
3.2	3000	—	—	—
1.0	300	—	—	—
0.5	250	—	—	—
0.1	180	130	110	50

particles as shown in **Fig. 3**.

The largest particle size in each figure in Figs. 2 and 3 was listed in **Table 1**.

3. Discussion

3.1 Mechanism for formation of ultra-fine particle in liquid film

3.1.1 Movements of liquid in a flask

When a stirrer blade is rotating in a flask,

Fig. 3. Variation in particle size of alumina gel produced from the 0.1 mol/l AlCl_3 solutions by absorbing the NH_3 - N_2 gas mixtures with various compositions. (a) : 100%, (b) : 25%, (c) : 3.3%, (d) : 0.31%.

Fig. 4. Schematic figure of the movement of the liquid.

two types of movements of liquid must be present. One is PQRST as shown in **Fig. 4**. The other is rotating around the stirrer pole. The former movement of liquid bears an important role to carry the solute to the liquid film and the generated particles to the mother liquid.

As a mass of liquid at the point P in **Fig. 4** is pushed out from the stirrer blade, the mass is raised up to the top of the movement R along the wall of vessel, and then falls down to the bottom T along the surface of liquid with absorbing NH_3 gas. The distance between R and T was 7 cm, and the time to fall the distance might be 0.1 s.

3.1.2 Shift of generation zone

In this period, the following reaction must proceed in the liquid film.

And the solubility is

$$S_{\text{Al}^{3+}} = [\text{Al}^{3+}] = K/[\text{OH}^-]^3 \quad (2)$$

The solubility product constant K was

Fig. 5. Solubility change of $\text{Al}(\text{OH})_3$ with OH^- ion concentration calculated from the solubility product constant $K=9.9 \times 10^{-34}$ at 4°C .

chosen as 6.31×10^{-32} at 25°C for amorphous aluminum hydroxide⁵⁾ and corrected to the value of 9.9×10^{-34} at 4°C , and then plotted in **Fig. 5**.

The ion diffusion coefficient of Al^{3+} is considerably smaller than that of OH^- ion in the aqueous solution. Therefore, it was assumed that only the OH^- ion diffuses from the surface to the innerpart of the mother liquid and the Al^{3+} ion does not move.

The absorption of NH_3 gas starts at the point R in **Fig. 4** whose state is represented in **Fig. 6** (a). When NH_3 gas is still not absorbed, Al^{3+} and OH^- ion concentrations

Fig. 6. Schematic aspect of the shift of generation zone by absorbing the NH_3 gas in short time to fall the distance RT in **Fig. 4**. (a), (b) and (c) represent the place R, and (d) represents the place T. ⊕ and ⊗ represent the stocking zone and generation zone, respectively. ⊕ and ⊗ represent the gas film and liquid film, respectively.

($C_{Al^{3+}}$, C_{OH^-}) at the gas-liquid interface are equal to those ($C'_{Al^{3+}}$, C'_{OH^-}) of mother liquid, and the solubilities $S_{Al^{3+}}$ at the interface and $S'_{Al^{3+}}$ in the mother liquid can be derived from C_{OH^-} and C'_{OH^-} lines using Eq. (2). Immediately after the onset of absorption of gas, the partial pressure of NH_3 near the interface decreases as shown in Fig. 6 (b). The OH^- ion appears at the interface and a concentration gradient line FG for OH^- can be written because the concentrated OH^- ions at the interface diffuse to the mother liquid. $S_{Al^{3+}}$ curve AE can be written from C_{OH^-} line by Eq. (2). A highly supersaturated region ABCO is formed because $S_{Al^{3+}}$ curve increases steeply with decreasing the OH^- ion concentration as shown in Fig. 5. Therefore, the ultrafine particle can be exsolved in this zone which was defined as generation zone in the preceding paper⁴⁾, so the steeply increased DC for $C_{Al^{3+}}$ appears as shown in Fig. 6 (c).

As the $S_{Al^{3+}}$ curve shifts rapidly to the right hand according to the diffusion of OH^- ion toward the mother liquid, the $C_{Al^{3+}}$ curve follows the $S_{Al^{3+}}$ curve and the particles are present in a region OHIJ. The zone OH is defined as stocking zone. In this zone, the particles produced in the generation zone are stocked without dissolution.

The surface of the liquid mass begins the gas absorption at R and terminates it at T in Fig. 4 in a very short time of 0.1 s. If the surface of the mass continues the gas absorption in an adequate long time, namely the distance between R and T is very long, the shifts of the $S_{Al^{3+}}$ line and the generation zone toward the mother liquid stop and the

liquid film having a constant thickness is formed at the surface. Therefore, the OH^- ions and the Al^{3+} ions diffuse into the quiet generation zone where the precipitate is accumulated there, so that the aggregation is taken place. In such a case, the above assumption that only OH^- ion diffuses toward the mother liquid can not be taken.

3.2 Maintenance mechanism of ultrafine particles in the mother liquid

The pH change with time in Fig. 1 was translated to the change of OH^- ion concentration as shown in Fig. 7 by use of the ion

Fig. 7. Variation in OH^- ion concentration in mother liquid with time calculated from Fig. 1.

Fig. 8. Schematic figures of various concentration changes in mother liquid with time. (a) : Reaction onset. (b) : Nearly equilibrium about M in Fig. 7. (c) : The order of change of concentrations in mother liquid; $C'_{Al^{3+}}$ decreases $\rightarrow$ C'_{OH^-} increases $\rightarrow$ $S'_{Al^{3+}}$ decreases.

product constant K_w of water 1.1×10^{-15} corrected at 4°C from 25°C. The process in this curve is composed of two kinds of reactions. One is between the reaction onset L and M. The other is whole process MN after M. **Fig. 8** explains these two stages at S in **Fig. 4**.

3.2.1 Soluble phenomena of particles during LM

The ultrafine particles of $\text{Al}(\text{OH})_3$ generated in the liquid film are carried from the liquid film into the innerpart of the mother liquid in **Fig. 4** by the violent stream. The particles in the mother liquid dissolve again because the solubility is much larger than Al^{3+} ion concentration, that is, $S'_{\text{Al}^{3+}} \gg C'_{\text{Al}^{3+}}$ as shown in **Fig. 8 (a)**. The dissolved particles form again both OH^- ions and Al^{3+} ions. These OH^- ions raise C'_{OH^-} in the mother liquid so that the solubility line in **Fig. 8 (a)** falls down rapidly by Eq. (2) and approaches to the line of $C'_{\text{Al}^{3+}}$. In this stage, for example, OH^- ion concentration increases from 0.5×10^{-11} mol/l (L) to 2.1×10^{-11} mol/l (M) in **Fig. 7**. Corresponding to the above values, the solubility in **Fig. 5** decreases to 0.1 mol/l in which the precipitate should occur. The deviation from the idealized curve LM was actually observed in **Fig. 7**. About this point M in a real reaction, the particles in the mother liquid can not be dissolved completely because the reaction rate for dissolution of the particle is not so fast for retaining the equilibrium.

3.2.2 Insoluble phenomena of particles during MN

With the rise of the OH^- ion concentration in the mother liquid $C'_{\text{Al}^{3+}}$, the solubility line $S'_{\text{Al}^{3+}}$ abruptly falls down in **Fig. 8 (a)** and approaches to the Al^{3+} ion concentration line $C'_{\text{Al}^{3+}}$, and then the particles begin not to dissolve because nearly saturated state appears as shown in **Fig. 8 (b)**.

During this reaction stage, Al^{3+} ions which were carried into the liquid film from the mother liquid precipitate by binding with the OH^- ions from the absorbing NH_3 gas, so that the Al^{3+} ion concentration $C'_{\text{Al}^{3+}}$ in the mother liquid decreases as shown in **Fig. 8(c)**. The small decrease of the $C'_{\text{Al}^{3+}}$ makes a difference between $C'_{\text{Al}^{3+}}$ and $S'_{\text{Al}^{3+}}$ lines, and then the more unsaturated state appears. Therefore, the surface of the particles of $\text{Al}(\text{OH})_3$

decomposes slightly. This decomposition at the particle surface renders the two kinds of effect for this system. One is the small increase of OH^- ion concentration C'_{OH^-} in the mother liquid in **Fig. 8 (c)** and the other is that of the plus charge of each particle. The small increase of C'_{OH^-} in the former effect makes the $S'_{\text{Al}^{3+}}$ fall down. In this manner, the unsaturated state which is very near for the equilibrium is continued through the following reaction. The increase in the plus charge on the particle surface in the latter effect makes the each particle be possible to exist as colloid in the mother liquid. In this manner the particles is maintained as stable colloid in the mother liquid without aggregation.

3.3 Effects of excess OH^- ions in stocking zone

3.3.1 The change in the size of large particle by the change of liquid concentration

The changes in particle size by the change of concentration of AlCl_3 solution are shown in **Fig. 2**. Two types of the particles can be observed typically in **Fig. 2 (c)**. Namely, one is very large particle of 100~250 Å and the other is very small particle of less than 30 Å. The large particles have the different shapes one another. The formation mechanism of the small particle has been explained in **Fig. 6**, but that of the large particles has still not. It is considerable that a mechanism for the large particle formation is not by a homogeneous nucleation reaction but due to the aggregation of each particle or an abnormal particle growth because the shapes and sizes of the large particles in this figure are considerably different one another.

The excess OH^- ions must be present in the stocking zone at the states S and T in **Fig. 4**. Because, Al^{3+} ions transforms almost to ultrafine particles of $\text{Al}(\text{OH})_3$ in the stocking zone OH in **Fig. 6(d)**, and then the OH^- ions in the stocking zone diffusing from the surface toward the generation zone can not react with Al^{3+} ions and stay there. As the unreacted OH^- ions in the stocking zone are carried into the mother liquid by the stream in the flask and are mixed with the mother liquid, the OH^- ions react with Al^{3+} ions there. This type of reaction is the same one

as the L-L method and only large particles are produced in this method mentioned above. Therefore two kinds of particles should be observed by means of electron microscope, namely, large particle and small particle be inhomogeneous and homogeneous reaction, respectively. This agrees with the results in Fig. 2.

The more concentrated solution of Al^{3+} ion is employed, the larger particle of $\text{Al}(\text{OH})_3$ is precipitated, when the liquid with same OH^- ion concentration is employed for the reaction. This agrees with the results in Fig. 2 and Table 1.

3.3.2 The change in the size of large particle with the change of gas composition

In the same manner, the change in particle size with the gas composition is explained as follows. The mean OH^- ion concentration in the stocking zone OH in Fig. 6 (d) decreases with decreasing the composition of NH_3 in the gas phase. When the very dilute OH^- ion solution in this zone is reacted with the AlCl_3 solution coexisting with the great number of ultrafine particle in the mother liquid, the slightly supersaturated state appears, and the excess Al^{3+} ion exsolves homogeneously on the each ultrafine particle without the generation of nuclei corresponding to (d) in Fig. 3. While, when the concentrated solution of OH^- ion is mixed with the AlCl_3 solution, the both reactants react at the interface and grow up to the large particle or pile up the other ultrafine particle, corresponding to (a) ~ (c) in Fig. 3. These are given also in Table 1.

4. Conclusion

The generation zone on the surface of solution shifts into the mother liquid in the very short exposure time with NH_3 gas, so that the ultrafine particles and excess OH^- ions remain in a zone defined as stocking zone behind the generation zone. The particles and the excess OH^- ions in the stocking zone go into the mother liquid by a violent stream and the excess OH^- ions make the relatively large particles by inhomogeneous reaction with Al^{3+} ions there. The particles exist in the mother liquid as a stable colloid for the very near equilibrium state of the mother liquid.

A particle size decreased with decreasing NH_3 gas composition or AlCl_3 concentration. The large particle produced by inhomogeneous reaction reflects the change in gas composition or solute concentration. The particles of less than $50 \text{ \AA}$ in size were prepared under very dilute NH_3 gas and dilute AlCl_3 concentration.

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References

- 1) P.P. Weimarn, *Chem. Revs.*, **2**, 217 (1926).
- 2) P.W. Schmidt and W.O. Milligan, *Electronmicroscopy*, **10**, 238 (1961).
- 3) M. Takase and T. Sata, *Yogyo-Kyokai-Shi*, **86**, 506 (1978).
- 4) M. Takase and T. Sata, *ibid.* **87**, 495-500 (1979).
- 5) W. Feitknecht and P. Schindler, *Pure Appl. Chem.*, **6**, 130 (1963).