

## AACH 를 이용한 고순도 알루미나 분말 제조

# Preparation of Ultra Fine Alumina Powder Via Ammonium Aluminium Carbonate Hydroxide

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### Abstract

The ultra fine gamma-alumina powder was prepared via ammonium aluminium carbonate hydroxide (AACH). The XRD, SEM, BET, thermal analysis were used to characterize the samples. The effects of various reaction parameters as concentration, of solution, anion on specific area, PH, aging time and thermal decomposition condition on the produced AACH and alumina were discussed.

Keywords :  $Al_2O_3$  powder, AACH, AHC

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### 1. Introduction

Surveying the patents, Shuzo Kato and Takeo Iga patented JP 51-140900 in Japan on December 4 1976, then in the United States as US 4,053,579 on October 11 1977 for the invention on the method for manufacture of sintered alumina from Ammonium Aluminium Carbonate Hydroxide ( AACH ). The synthesis method of the compound AACH was described by this patent for the first time, The claimed method was to add an aluminium containing solution to a solution of ammonium hydrogen carbonate

( AHC ) with the concentration from 140 g/L to 270 g/L, and the resulting addition being conducted at a temperature of from 30 to 35 °C and a pH of from 7.5 to 9.0. Anyway, the compound, AACH itself was not included in the claim. It is because that at that time only a preparation method instead of a new compound could be protected by a patent.

Afterwards, M. Pajot and L. Seigneurin patented a European Patent 7833 on June 2 1980 for a method to prepare alumina with a specific surface area as high as 600 m<sup>2</sup>/g by thermal decomposition of AACH at 325 to 375 °C, and the AACH was obtained by adding water to a mixture of benzene, aluminium isopropanol and dry ammonium hydrogen carbonate and stirring for five hours at 25 °C. H. Reisner and E. Raisner patented in East Germany for DD 234

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662 on September 4 1986. An aluminium sulfate solution was obtained by leaching aluminium containing raw materials then reacted with ammonium carbonate or ammonium bicarbonate to precipitate  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$ , AACH. Alumina was produced upon thermal decomposition of the AACH at 300 °C, and the purity of the alumina depended on the purity of the raw material. As foresaid, the compound AACH itself was not protected by the Japanese patent, therefore in the preparation methods or the preparation conditions were different. Two new patents JP 63-147820 and JP 63-147821 were published on June 20 1988 in Japan by two inventors Yoshio Murase and Takeo Iga. In these patents aluminium hydroxide or hydrate were reacted and aged in AHC solution at a temperature from 60 to 140°C for from 1h to 140h, then an acicular AACH was formed, from which an acicular alumina with a length of 1 to 2 micro meters and width of 0.01 micro meters was obtained. Recently, Yamaguchi Hideo and Okabayashi Masayerki and AHC mixed solution reacts with an aluminium hydroxide and AHC mixed solution reacts with an aluminium ammonium alum solution, spray during the formed precipitation and firing the material at 350°C to 1200°C, then a fine alumina is obtained. Obviously, the process is also via the precursor compound AACH.

The experiment in this study focused on the preparation of gamma-alumina with high specific surface area. The effects of different reaction parameters on the produced AACH and alumina are discussed.

## 2. Experiments

The basic experiment procedure was to mix a solution of AHC and a solution of aluminium at preset conditions. AACH is synthesised by mixing an aluminium solution with the solution of AHC at a constant flow rate of the two solutions in a continuous way and at a constant temperature, instead of adding aluminium solution to AHC solution and controlling the resulting temperature of from 30 to 35°C. Alumina was produced upon thermal decomposition of the AACH at 400 ~ 1050°C.

The impurity elements in AACH and alumina determined by ICP. The BET specific surface

area, XRD and SEM were also used for the characterization.

## 3. Results and discussion

The experience on the preparation of alumina via AACH in our laboratory concentrated on alpha-alumina with high purity, therefore the experiment focused on the preparation of gamma-alumina with high specific surface area. The basic experiment procedure was to mix a solution of AHC and a solution of aluminium at preset conditions. The effects of different reaction parameters on the produced AACH and alumina are discussed in this study.

Table 1 Effect of anions on the specific surface area(S. S. A.) of alumina prepared

Anions	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{NO}_3^-$
S.S.A. $^2$ /g	365.9	310.7	294.3

Synthesis conditions:  $[\text{AHC}]/[\text{AA}] = (10/1)$  concentration of AHC = 0.78M, temperature 45°C, aging time/1h.

### 3.1 Effect of Anion on the specific Surface Area of Alumina

Preparation in sulfate solution resulted in the highest rate of sedimentation of AACH and also an alumina with the highest specific surface area.

### 3.2 Effect of The Concentration of Aluminium

Fig.1 shows that the reciprocal S.S.A. of the produced alumina is almost proportional to the concentration of aluminium used for synthesis of AACH. This demonstrates that the higher concentration of aluminium resulted in a smaller crystal grain of AACH. It was also found to recycle the mother liquid, which was the solution after filtration of the AACH, also benefited the formation of the small grains.

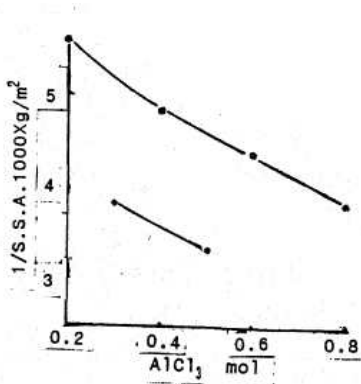


Fig. 1 Reciprocal of S. S. A. of alumina versus initial pH of AHC and aluminium solution

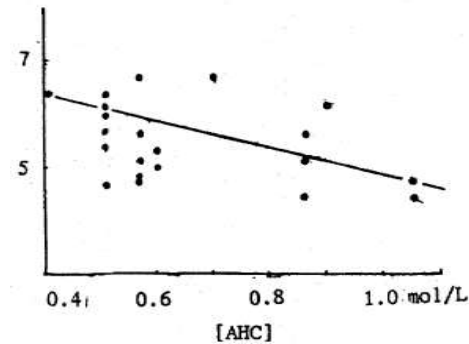


Fig. 2b Reciprocal S. S. A. of alumina versus initial AHC concentration

### 3.3 Effect of The Initial and End Concentration of AHC

The reciprocal S.S.A. of alumina has been put against initial  $[AHC]/[AA]$  and resulting  $[AHC]$  in Fig. 2a and Fig. 2b, respectively. A line has been drawn in each figure, above the lines the reaction temperature was 25 to 35°C and aging time was 1h, and it is shown statically that as the reaction temperature was higher than 45°C, alumina with high specific surface area could be obtained even at lower initial  $[AHC]/[AA]$  and end  $[AHC]$ .

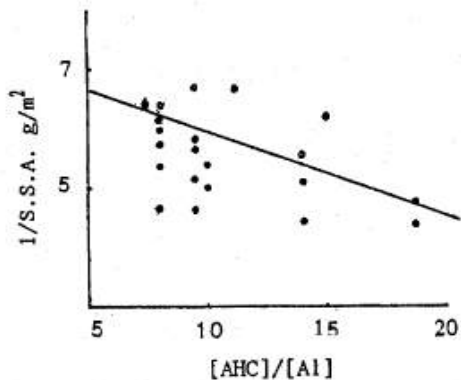


Fig. 2a Reciprocal S. S. A. of alumina versus initial ratio of  $[AHC]$  to  $[Al]$

### 3.4 Effect of pH

The data in Table 2 show that the initial pH value of aluminium has no obvious effect on the specific surface area of the produced alumina. The sedimentation rate of prepared AACH increased with the pH value. In other words, the high pH value benefited the formation of a grosser AACH crystal.

Changing the initial pH value of aluminium solution from 1.10 to 3.80 the resulting pH was always around  $8.86 \pm 0.08$ . It shows this reaction system was buffered by AHC, thereby the pH value of aluminium solution almost had no influence over the final pH value. The  $pH_{end}$  was lower than the  $pH_{mi}$  of AHC solution, because of the lower concentration of AHC in the end solution of the reaction. The initial pH value of the aluminium solution also had almost no effect on surface area of alumina, as shown in Fig. 3. Among the 56 experiments, the end pH value of 37 experiments fell into 8.6 to 9.1, only 12 resulting pH were higher than 9.2, and 7 of the 12 experiments produced alumina with a specific surface area less than  $150m^2/g$ . It demonstrates that a higher  $pH_{end}$  benefit producing alumina with higher special surface area.

Table 2 Relationship between the initial pH of aluminium solution and the specific surface area

$pH_{ini}$	1.10	1.74	2.01	2.97	3.80
$pH_{fin}$	8.87	8.98	8.81	8.74	8.74
S.S.A. $m^2/g$	340.5	360.0	339.0	326.7	357.7

\*  $pH_{ini}$ : initial pH of the aluminium solution,  $pH_{fin}$ : final pH of the reaction system.  $[AHC]/[AA]=10/1$ ,  $[AHC]=0.66M$ , reaction at  $50^\circ C$ , aging for 1h.

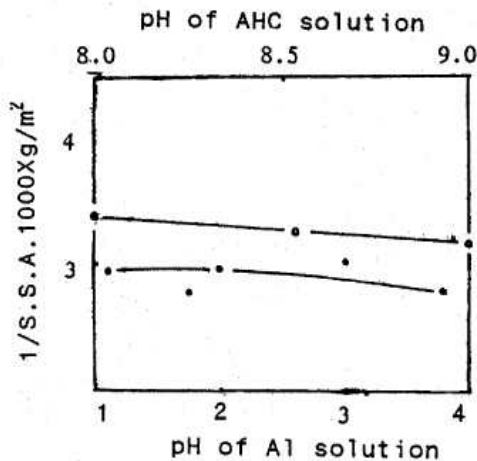


Fig. 3 The relationship between reciprocal S. S. A. and initial pH of AHC and aluminium solution

### 3.5 Effect of Aging Time

In order to optimise the aging time, investigation on the relationship between the aging time and the sedimentation rate of AACH and the specific surface area of the produced alumina has been carried out. Reaction at  $60^\circ C$  and aging for 15min resulted in a quite fast sedimentation rate(S.R.). Reaction at  $50^\circ C$  and aging for 30min S.R. was also fast enough, but it was not as fast as the former one. If reaction carried at a relative low temperature, 30 to  $40^\circ C$ , and aging at  $60^\circ C$  the aging time has no obvious influence upon the S.R., and all experiments resulted in a slow S.R. In this case, no matter how long the aging time was, the S.S.A. of produced alumina was always high, extending the aging time did not decrease the

S.S.A., and even increased it a little, as shown in Fig.4 and Table 3. It may be concluded that the aging process did not increase the dimensions of the forming AACH crystals. In order to produce an AACH with high S.R. and also an alumina with high S.S.A the reaction and aging should be undertaken at a higher temperature, say, higher than  $40^\circ C$ .

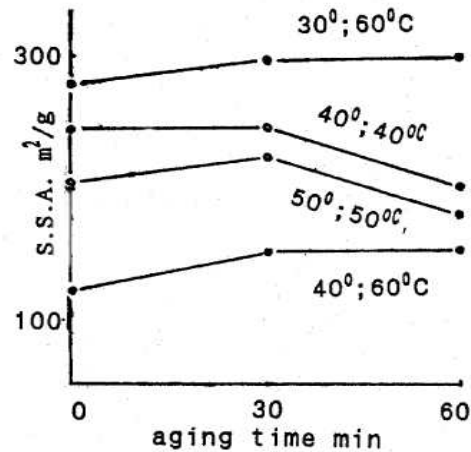


Fig. 4 The relationship between reciprocal S. S. A. of alumina and aging time

Table 3 Relationship between aging time and specific surface area of produced alumina

time(min)	0	30	60
S.S.A. $m^2/g$	122.9	153.2	154.0
	248.4	247.7	205.3
	206.7	227.5	182.0
	263.7	299.7	304.4

$[AHC]/[AA]=2.8/1$ ,  $[AHC]=0.65M$

### 3.6 XRD and TGA of AACH

The XRD pattern and TGA of AACH prepared which are the same as that reported in the literatures. The TGA shows decomposition temperature of AACH was at  $180^\circ C$  to  $205^\circ C$  with a weight loss of 57.1% to 62.2%, and that reported in the literature that were  $230^\circ C$  and 52.5%, respectively. AACH sample which was produced in large scale showed the same results as shown in Fig. 5. (SEM-photograph), Fig. 6.

(thermal analysis) and Fig. 7. (XRD pattern).

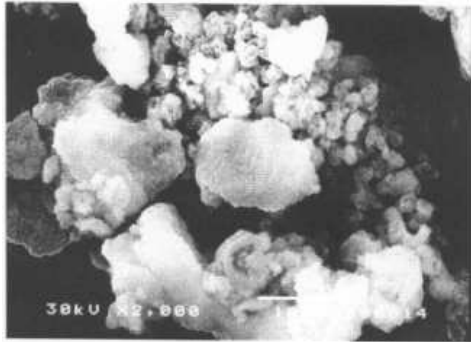


Fig. 5 SEM photographs of as-prepared AACH sample

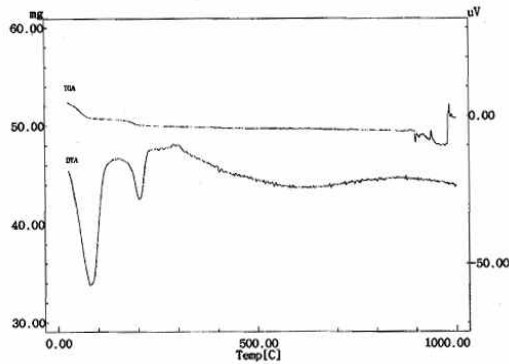


Fig. 6 Thermal analysis of as-prepared AACH sample

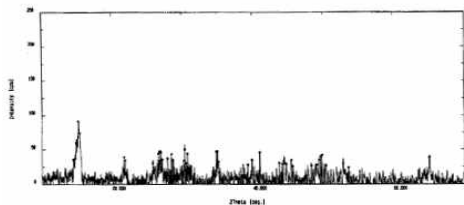


Fig. 7 X-ray diffraction pattern of as-prepared AACH sample

### 3.7 Effect of Thermal Decomposition Time And Temperature

Data in Table 4 and 5 and Fig. 8 show that S.S.A. decrease with the increase of the thermal decomposition time and temperature. Fig. 9 is the XRD pattern of products at different thermal decomposition temperature. It shows that amorphous alumina produced at 400 to 500°C,

gamma-alumina at 700°C, delta- at 800°C to 1000°C and alpha- when it higher than 1050°C. Because of the small size of the primary particle of products in this process, transferring gamma-alumina to alpha- proceed at lower temperature.

Table. 4 Relationship between thermal decomposition time and special surface area (S.S.A.)

time h	1	2	3	4
S.S.A. m <sup>2</sup> /g	286.4	270.8	252.2	196.0
Thermal decomposition temperature, / 700°C				

Table. 5 Relationship between thermal decomposition temperature and special surface area (S.S.A.)

temp. °C	400	500	600	700	800	900	1000	1050	1100
S.S.A. m <sup>2</sup> /g	164.9	357.9	147.8	270.8	119.4	100.9	70.1*	52.9	18.4

\*For 1h, other for 2h.

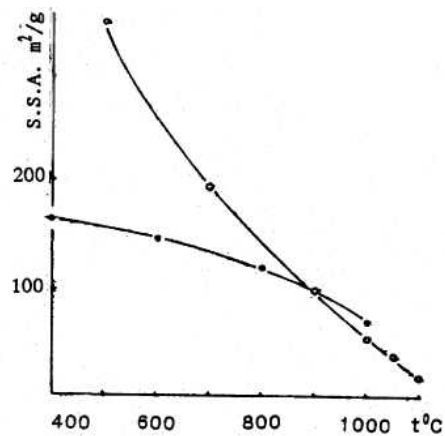


Fig. 8 Specific surface area of alumina versus thermal decomposition temperature

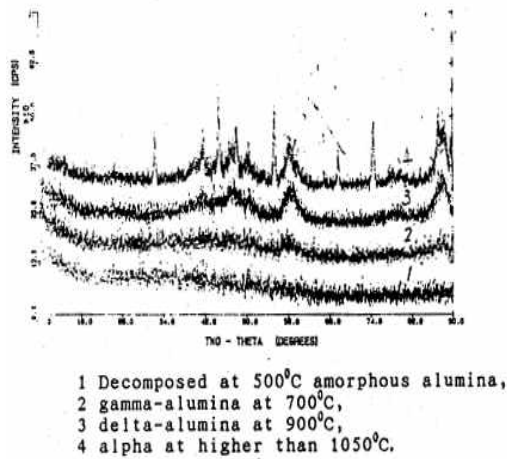


Fig. 9 X-ray diffraction pattern of alumina thermal decomposed at different temperature

### 3.8 XRD of as-prepared Alumina

Fig. 10 shows the comparison of XRD pattern of gamma-alumina produced in large scale and that of a Sumitomo Chemical's sample.

The peaks of both samples at  $2\theta$  near  $88^\circ$  are the same in this work but at  $47^\circ$  and  $58.5^\circ$  the peaks are sharper than that of Sumitomo's. It shows the transfer of alumina to the gamma form of the sample is more complete to a certain extent.

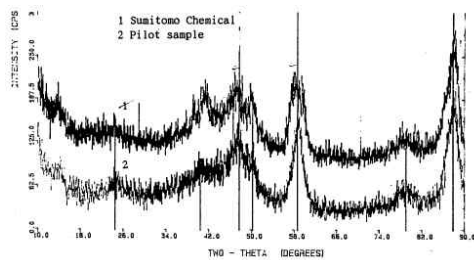


Fig. 10 X-ray diffraction pattern of alumina of Sumitomo Chemical and the produced sample

### 3.9 Impurities

The impurities determined with ICP shows that the purity of the produced alumina is stably higher than 99.99%. The results are shown in

Table 6 and 7.

Table 6 Main impurities in AACH

Sample No.	Si	Mg	Fe	Cu	Na	Ti
	ppm					
29	<5	1.6	<5	1	<5	1
30	<5	1.0	<5	1	<5	0.5
31	<5	1.0	<5	1	<5	1
32	<5	3.0	<5	1	<5	4.8

Table 7 Main impurities in gamma-alumina

Sample No.	Si	Mg	Fe	Cu	Na	Ti
	ppm					
25	<5	1	<5	3	<5	2
26	<5	39	<5		<5	2

## 4. Conclusions

The Ultra fine gamma-alumina was prepared via Ammonium Aluminium Carbonate hydroxide. Through this method, the resulted alumina powder showed same physical and chemical properties and even a better quality than that of commercial ones. The continuous process of this method has also the advantages of high efficiency, easy operation and quality control.

## Acknowledgements

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## Reference

- [1] S. Kato, T. Iga, S. Hatano, Y. Isawa. "Synthesis of AACH", Yogyo-kyokai-shi, vol. 84, pp. 215-220, 1976
- [2] Von E. erdos, H. Altrorfer. "Werkstoffe and korrosion", vol. 27, pp. 611-618, 1976
- [3] Yoshi Murase, Tmado Iga, "Formation and

- thermal decomposition of  $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$  acicular microcrystals", *Yogyo-Kyokai-Shi*, vol. 95, No. 5, pp. 55-68, 1987
- [4] Koichi Hayashi et al, *Journal of the Ceramic Society of Japan*, NT. Edition, vol. 98, pp. 457, 1990
- [5] P. Micheal and L. Sergneurn Eur pat C 01 F 7/30 C 01 F 7/56 0,007,833
- [6] Baozheng Dong, Wenjun Sheng, Henglin Yang, Zhijie Zhang, *J. Appl. Cry.*, vol. 30, pp. 877, 1997
- [7] H. G. Krauthaeuser, *Physica A*, vol. 211, pp. 317, 1994
- [8] Ma Chicheng. "Studies on the preparation and thermal decomposition of AACH with differing morphology", Thesis of Master Degree The Institution of Chemical Metallurgy of Chinese Academic of Sciences, 1997, Beijing
- [9] 日本セラミクス協會, セラミクス工業ハンドブック、技報堂出版, p. 2298, 1997
- [10] ファインケル事典編集委員會、ファインケル事典、ツエムシ, p. 630, 1982
- [11] 이종근, 무기재료 원료공학, 반도 출판사, p. 90, 1995
- [12] 元山 孝, ファインラミクス移用技術集片,サイエンスオーラム, p. 34, 1983
- [13] 日本金屬學會·結晶成長, vol. 17, pp. 147, 1975
- [14] D. L. Catone and E. Matijevic, *J. Dolloid Interface Sci.*, vol. 48, No. 2, pp. 2291, 1974
- [15] 人工元料のニコセラミクスへのアプローチ (實業協會東海支部, 1982)
- [16] 石橋渡, 荒木徹世, 岸本勝利, 久野春夫. Vol. 6, No. 6, pp. 461, 1971
- [17] 加藤修三, 伊賀武雄, 幡野昭五, 伊澤雄一, 實業協會誌, vol. 84, pp. 255, 1976
- [18] 山田興一, セラミクス, vol. 17, pp. 810, 1982