Preparation of Fine Alumina Powder

Soh Deawha*, Jeon Yongwoo**, Korobova N.***

Abstract

Powder synthesis using the alkoxy precursor technique exhibits processing flexibility not available in traditional high temperature solid-state reaction. With proper process control, impurities can be reduced to very low levels. The major distinction of the present work lies in the method of accomplishing the hydrolysis reaction. In the present case, water is not added to the system. Instead the metal alkoxide/alcohol solution is heated to a temperature at which water is formed through dehydration of the alcohol solvent, causing precipitation of the corresponding metal oxide (hydroxide). The present method provides a means of producing amorphous alumina.

Key Words : Powder synthesis, alkoxy, hydrolysis reaction, dehydration, amorphous alumina

1. Introduction

This work represents a limited study on the preparation of alumina from alcoholic solutions of aluminum sec-butoxide. Hydrolysis of metal alkoxides is usually accomplished by contact with liquid water [1-3]. This method is practiced in the sol-gel process. The major distinction of the present work lies in the method of accomplishing the hydrolysis reaction [4].

In the present case, water is not added to the system. Instead the metal alkoxide/alcohol solution is heated to a temperature at which water is formed through dehydration of the alcohol solvent, causing precipitation of the corresponding metal oxide (hydroxide). The solvent, sec-butyl alcohol, was found to be ideally suited for this purpose. It undergoes dehydration in a controllable manner, at convenient temperatures in the neighborhood of 250°C (Fig. 1).

Liberation of water from sec-butyl alcohol is accompanied by formation of isobutene and dibutyl ether. The work was undertaken in

* : Myongji University
(E-mail : dwhsoh@mju.ac.kr)
** : Sungduk College
*** : Combustion Problems Institute, Kazakstan

expectation that sudden precipitation would occur from a single crop of nuclei, resulting in fine particles and a narrow distribution.
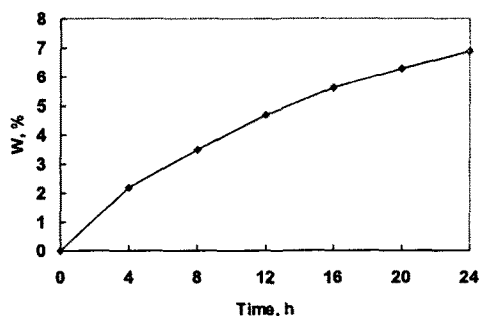

Fig. 1. Dehydration of sec-butyl alcohol at 250± 5°C

2. Experimental Procedure

Two autoclave reactors were used in the present study: a 300-cm³, nonstirred vessel and a 1-L vessel equipped with stirring capability. The following is a description of a typical run in the 300-cm reactor. Comparative results obtained from the two reactors are described in the text (see Table 1).

To 73.60 g of sec-butyl alcohol in a glass test tube, serving as autoclave liner, was added 31.57 g of aluminum sec-butoxide.

The liquid level was within 11.43 cm of the top of the glass liner. The autoclave was sealed and purged with nitrogen 3 times before heating. The heating profile of this run as follows: 3.5 h to reach 250 ± 5℃ and 6.5-h holding time at temperature, followed by an over night cool-down.

Table 1.

Reaction conditions				
Run No.	Autoclave volume (cm^3)	ASB* (wt%)	Stirred	Total run time (min)
1	300	10	No	360
2	300	10	No	240
3	300	30	No	600
4	1000	10	Yes	250
5	1000	10	Yes	360
6	1000	10	Yes	240
Product properties				
Run No.	Water content in filtrate (wt%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Carbon content (wt%)	X-ray**
1	1.17	205	1.33	2.23	Amorphous + γ/χ
2	0.17	851	1.49	8.93	Amorphous
3	3.93	187	0.965	2.67	Amorphous + γ/χ
4	0.49	532	1.70	5.08	Amorphous
5	2.64	180	1.11	1.47	Amorphous + γ/χ
6	11.89	50	1.72	0.32	Boehmite

It is likely that no precipitation took place in the reaction solution before attainment of the plateau temperature, 250℃. One control experiment revealed that dehydration of sec-butyl alcohol did not occur at a measurable rate during the heat-up period to 250 ℃. In addition, no solid was found in a reaction mixture that was examined after reaching a temperature of 160℃.

The weight of the wet cake after filtration of the product was 17.13 g. The cake was vacuum dried at 85℃ for 4.5 h. The dry cake weight was 6.69 g. Addition of water to the filtrate produced no preci- pitate, indicating that hydrolysis of the metal alkoxide was complete.

The properties of the aluminas produced in the individual runs are summarized in Table 1. The part- icular preparation described in the Experimental Sect- ion is listed as run 3. The reaction variables examin- ed include the following: holding time at temperature, stirring, pH, and concentration of aluminum sec- butoxide (10 vs 30 wt%). Reaction temperature was kept constant at 250 ± 5℃. This temperature is below the critical temperature of sec-butyl alcohol (263℃). Stirring had a major influence on the particle size and particle size distribution of the alumina powders produced. Finer and more narrowly distributed part- icles were produced when mild stirring of the reaction solution was used. Particles having a mean diameter of 1.35 μm with standard deviation of 0.38 were gene- rated in a typical, stirred, 1-L autoclave run. Graphi- cal representation of the particle size distribution for a stirred preparation, obtained by sedimentation anal- ysis, is shown in Fig. 2.
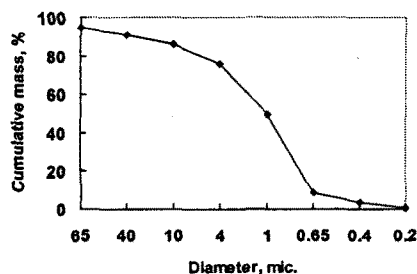

Fig. 2. Particle size distribution (μm) by sedimentati- on of the alumina produced in run 4.

When stirring was not used, the mean particle diameter was 5 μm with standard deviation of

0.6. It is assumed that in the absence of stirring, temper- ature gradients within the reactor resulting in a non- uniform production of water in the solution and a nonuniform precipitation of metal oxide.

Electron microscopy (Fig. 3 and 4) reveals that the solid produced is composed of micrometer-size agglo- merates that consist, in turn, of extremely small part- icles in the range of 0.02 μm. The crystallite size for this alumina is among the smallest available [4-5].

Fig. 3. Transmission electron photomicrograph of the alumina produced in run 3.
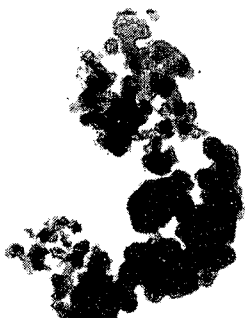

Fig. 4. Scanning electron photomicrograph of the alu- mina produced in run 3.

Aside from the effect of stirring on particle size distribution, the amount of water formed was the single most important factor studies with respect to physical properties of the product. Crystallinity, sur- face area, and carbon content were sensitive to the quantity of water produced in the reactor (see Table 1). High

surface area and high carbon content are favored at short reaction times when the amount of water produced is small. Absence of crystalline products occurred only when the water content was not explored.

The present method provides a means of producing amorphous alumina. According to the data in Table 1, limitation of the amount of water formed (short reaction times) is the required condition (runs 2 and 4). At longer reaction times, amorphous alumina was invariably accompanied by crystalline, dehydrated for- ms, χ and γ in the present series of runs. The X-ray pattern obtained for run 1 is reproduced in Fig. 5. It is consistent with the assignment of amorphous and crystalline χ and γ phases. Boehmite was observed only in run 6, in which considerably more water was generated as a result of the acid (H_2SO_4) catalyzed sec-butyl alcohol dehydration conditions employed.
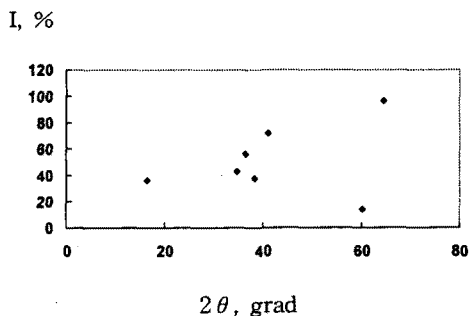
I, %

2θ, grad

Fig. 5. X-ray pattern of dried and uncalcined alumi- na from run 1.

The amorphous alumina produced consists of a hydrated form as judget from weight-loss measure- ments at elevated temperature. Following drying at 110℃ an amorphous alumina sample lost 19.5 wt% during calcination at 75 0℃. From the organic content in the precalcined sample (3.85 wt%), the overall stoichiometry of the alumina is $Al_2O_3 \cdot 1.1H_2O$. Under the same conditions, a mixed amorphous/crystalline sample

lost only 5.9 wt% (1.73 wt% organic), indicating a composition of $Al_2O_3 \cdot 0.25 H_2O$.

Since amorphous alumina is produced at short reaction times, the results indicate that a hydrated form of alumina is first formed which subsequently converts, with water loss, to dehydrate crystalline forms even though additional water is being gene- rated from the solvent at the reaction conditions.

The conversion of an alumina hydrate to a less hydrated form in the presence of water appears to be a general phenomenon in alumina chemistry. The hydrothermal conversion of $Al_2O_3 \cdot 3H_2O$ to $Al_2O_3 \cdot H_2O$ is well known. The reaction occurs at the 200℃ under autogenous pressure. The rate has been found to be dependent on particle size [5]. Although the particular species involved in the present case are different, it is interesting that the general transformation and reaction conditions are quite similar.

3. Conclusion

The practical performance of a ceramic component, the microstructure of the ceramic, and powder beha- vior during processing are strongly dependent on the physical and chemical characteristics of starting powders. The choice of starting powder character- istics depends on the intended microsructure and application of the final ceramics. In this work we noted the advantages another kind of metal alkoxide hydrolysis. Since amorphous alumina is produced at short reaction times, the results indicate that a hydrated form of alumina is first formed which sub- sequently converts, with water loss, to dehydrate crystalline forms even though additional water is being generated from the solvent at the reaction conditions.

References

[1] Mah T., Hermes E.E., Mazdiyasni K.S., "Multicomponent ceramic powders", in Chemical process- ing of ceramics. Ed. by B. I. Lee, E. J.A. Pope, p. 75, 1994.

[2] Bradley D.C., "Metal alkoxides as precursors for electronic and ceramic materials", Chem Rev., vol. 89, p.1317, 1989.

[3] Malghan S.G., Dragoo A.L., "Characterization of ceramic powders", in Engineered Materials Hand- book Ceramic and Glasses, ASM International, , p.65, 1991.

[4] Korobova N., Ph.D. thesis: "Sols and Electro- phoretic Films on the Base of Aluminum - tri-iso-Propoxide", Leningrad Russia, p. 135, 1988.

[5] Korobova N., "The metal alkoxides as source ma- terials in the sol-gel technique. Book 1. Alum- inum silicate sol-gel materials: ceramics and thin films", Almaty, p. 110, 1997.