

## Synthesis and characterization of high purity aluminum sec-butoxide from aluminum dross

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**Abstract**—Aluminum sec-butoxide (ASB) was synthesized to a high purity grade from Al dross through dissolution reaction and vacuum distillation under the condition of 3 mol C<sub>4</sub>H<sub>9</sub>OH/mol Al as a stoichiometric reactant ratio and 10<sup>-3</sup> mol HgI<sub>2</sub>/mol Al as a catalyst. The dissolution reaction proceeded for 24 hours, then pure ASB was recovered by vacuum distillation from the Al solution obtained after the dissolution. The ASB thus synthesized was quantitatively analyzed by a complexometric method for purity. This reaction gave a 99.2% purity and 28% yield. Characteristics of the synthesized ASB were analyzed by FT-IR, <sup>27</sup>Al-NMR, and <sup>1</sup>H-NMR. The result of analysis revealed that the crystalline structure between the synthesized ASB and commercial ASB was identical. Especially, the yield synthesized through this experiment corresponded to the total amount of Al metal existing in Al dross.

Key words: Al Dross, Dissolution, Vacuum Distillation, High Purity, Aluminum Sec-butoxide

### INTRODUCTION

Aluminum dross is a byproduct formed by surface oxidation of Al metal in the process of Al can recycling. The Al dross with its slag-like appearance is formed by water and oxygen in air when Al metal is dissolved in the furnace. Although the Al dross contains considerable Al component in the inner, it is usually dealt with as a common solid waste and landfilled in soil because there is no method to recover the remaining Al component [1]. Al dross contains a considerable Al metal component and it especially includes many impurities such as Mg, Si, Ca, Mn, Cu, Pb, Na, Cr, Zn, Ti and O at the same time. Table 1 shows the typical composition of Al dross. As shown in Table 1, the Al component in Al dross has about 28% average, but most of the remaining component consists of Al<sub>2</sub>O<sub>3</sub>.

For the purpose of reducing the amount of solid waste and reusing the valuable metal components, we conducted a study on the synthesis of Al alkoxide from Al metal component existing in the Al dross as shown in Eq. (1).



In the previous studies of alkoxide compounds, we have examined the synthesis of AIP (Al iso-propoxide) or AE (Al ethoxide) from Al dross or Al Can [3-5] and its kinetics [6], but Al sec-butoxide has been also used widely as a starting material for the synthesis of high purity alumina. The Al sec-butoxide is one of the most representative raw materials for the preparation of high purity alumina. The representative Al alkoxides have three compounds according

to the type of alcohol groups bonded in the Al alkoxides, for example, AE, AIP and ASB. Among these Al alkoxide compounds, Al sec-butoxide especially has a stable liquid phase different from other alkoxide materials. When it is used in an industrial process, the Al sec-butoxide with a liquid phase has more convenient advantages than other alkoxides because there is no clogging in columns, nozzles, valves and pipes.

### MATERIALS AND METHODS

Fig. 1 shows the flowchart of the synthesis of ASB from Al dross. The dissolution reaction of Al dross proceeded for 24 hours at a reaction temperature of 100 °C and stirring velocity of 100 rpm based on the kinetic study of Al sec-butoxide [7], and then the vacuum distillation proceeded to obtain pure ASB under the condition of 3 mmHg and 200 °C. After the dissolution reaction between Al dross and SBA was completed, pure ASB was recovered and purified by vacuum distillation from the Al solution because the Al solution has many impurities.

If water or air penetrates into the reactor during vacuum distillation, side-products such as AlO(OH), Al(OH)<sub>3</sub> will be formed. Therefore, it is important to prevent water or air from penetrating into the reactor during vacuum distillation.

Table 2 shows this experimental condition. In the reaction, 3 mol SBA/mol Al (C<sub>4</sub>H<sub>9</sub>OH, Daejung, >99%) is added as a reactant and 10<sup>-3</sup> mol HgI<sub>2</sub>/mol Al as a catalyst (HgI<sub>2</sub>, Fluka, >99.0%) per 1 mol Al existing in Al dross.

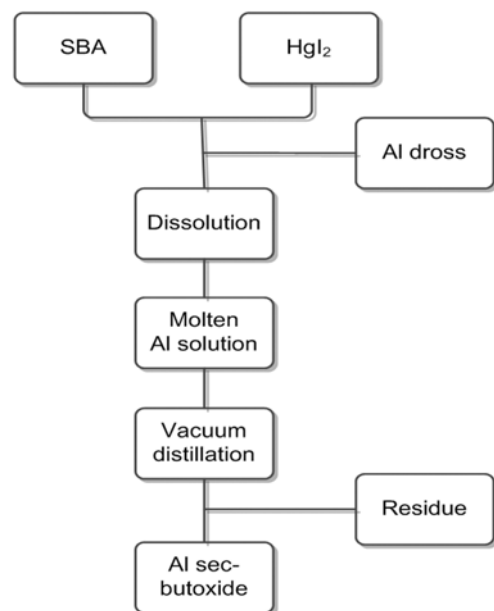
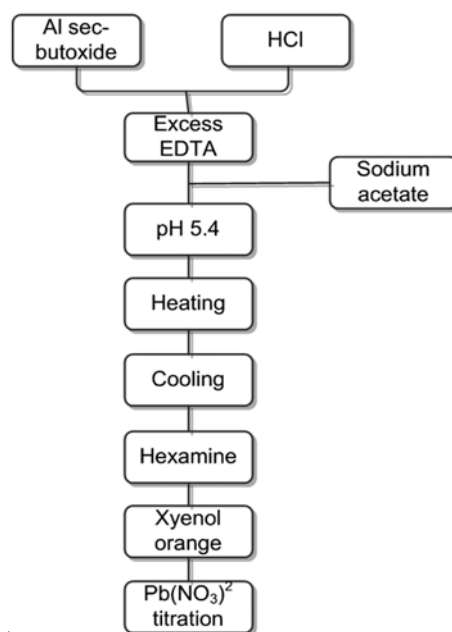
Characteristics of the synthesized ASB were analyzed by FT-IR (FTS-60, BIO-RAD), <sup>27</sup>Al solid state NMR (Static mode, 600 MHz (14. IT), Varian, US, INOVA), and <sup>1</sup>H-NMR. At this time, the amount of bonded groups of ASB was analyzed by Liquid FT-IR spectroscopy.

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**Table 1. Typical composition of Al dross [2]**

Element	Conc. (wt%)	Element	Conc. (wt%)	Element	Conc. (wt%)	Element	Conc. (wt%)
Al <sub>2</sub> O <sub>3</sub>	56.1	Cu	0.005-0.02	Co	0.02-0.08	Mg	0.1-0.6
Al	28	Ti	0.04-0.2	C	0.14	Zn	0.008-0.02
Na <sub>3</sub> AlF <sub>6</sub>	12.9	Fe	0.06-0.3	Si	0.1-0.4	Sn	0.008-0.02
Mn	0.03-0.2	Be	0.0004	Cr	0.02-0.07	B	0.08-0.4
Ni	0.01-0.07	Ca	0.2-0.08	V	0.4-1	W	0.06-0.25

**Fig. 1. Flowchart showing the ASB synthesis procedures.****Fig. 2. Flowchart for purity analysis.****Table 2. Experimental condition for synthesis of ASB**

Component	Al	SBA	HgI <sub>2</sub>
Mol ratio	1	3	10 <sup>-3</sup>

copy after the sample was dissolved in CCl<sub>4</sub> solvent.

Next, Al coordinate numbers were analyzed by <sup>27</sup>Al solid state NMR based on the standard of Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> as a reference standard under the condition of 600 MHz (14.1 T) and static mode. Moreover, the coordinate structure of protons existing around ASB was analyzed by <sup>1</sup>H-NMR as a reference standard of CDCl<sub>3</sub>.

On the other hand, the purity of synthesized ASB was analyzed by a complexometric method using a Xylenol orange as shown in Fig. 2. First, an excess (10 ml) of EDTA (2Na) solution (Ethylenediaminetetraacetic acid disodium salt solution ([CH<sub>2</sub>N(CH<sub>2</sub>CO<sub>2</sub>Na)CH<sub>2</sub>CO<sub>2</sub>H]<sub>2</sub>, 0.0501 M in water, volumetric standard, Aldrich) was added to 5 ml sample solution containing about 0.250 g ASB per 50 ml acidic solution, and the pH was adjusted to 5.4 with buffers (acid-sodium acetate(Reagent grade, Aldrich)). The sample solution was heated by mantle for a few minutes, cooled, and 1 g of hexamine (Hexamethylenetetraamine, >99.5%, Riedel-deHaën) and 1 ml of 0.03% Xylenol orange indicator (GR. Daejung Chemicals & Metals Co.) were added. The back-titration with lead nitrate solution (Pb(NO<sub>3</sub>)<sub>2</sub>, 0.0500 M in water, 99.99%, Aldrich) was begun. The end-point was recognizable by a very sharp color change from

a light orange to pink [8].

## RESULTS AND DISCUSSION

Using Al dross and SBA for reactants, the dissolution reaction was carried out 24 hours for complete reaction. Although the role of catalyst has not been understood completely to date, it is known that Al metal is amalgamated by the catalyst and then the amalgamated Al readily reacts with SBA [2,9-13].

After the dissolution, the molten Al solution is in a black-colored solution state containing many impurities of Al dross. Therefore, vacuum distillation must be carried out to separate only the pure ASB from the molten Al solution. The vacuum distillation was controlled to the range of 200 °C, 3 mmHg. The vacuum distillation apparatus must be designed to maintain a perfect vacuum condition because it forms side-products like Al(OH)<sub>3</sub>, AlO(OH), and Al<sub>2</sub>O<sub>3</sub> if water or air penetrates into the vacuum distillation apparatus.

Fig. 3 shows Liquid FT-infrared (FTS-60, BIO-RAD) spectra of the synthesized ASB and the commercial ASB. The type and the amount of bonding groups existing in the ASB were analyzed in the range of 400 to 4,000 cm<sup>-1</sup>. In general, the characteristic absorption peak of Al-O-C bond existing in the ASB appears at 1,058 cm<sup>-1</sup>, the vibration peaks by the Al-OAl co-ordinate bond occur in the vicinity of 990 cm<sup>-1</sup>, and the stretching vibration peak by Al-OAl

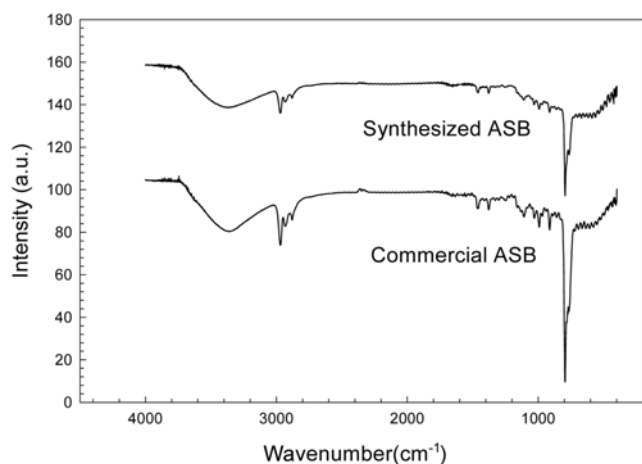


Fig. 3. FT-IR curves of synthesized ASB and commercial ASB.

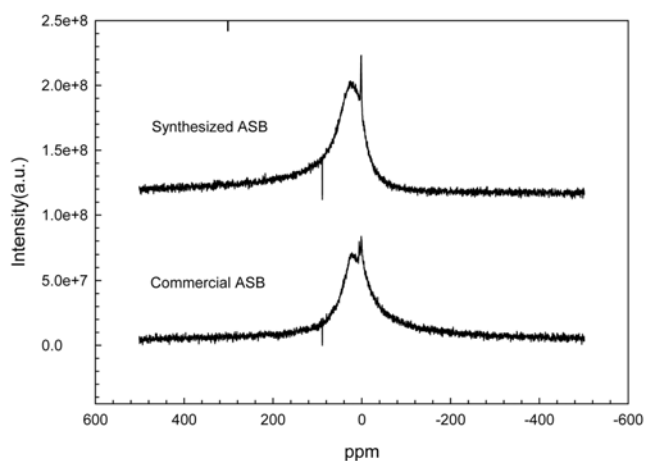


Fig. 4.  $^{27}\text{Al}$ -NMR spectra of ASB.

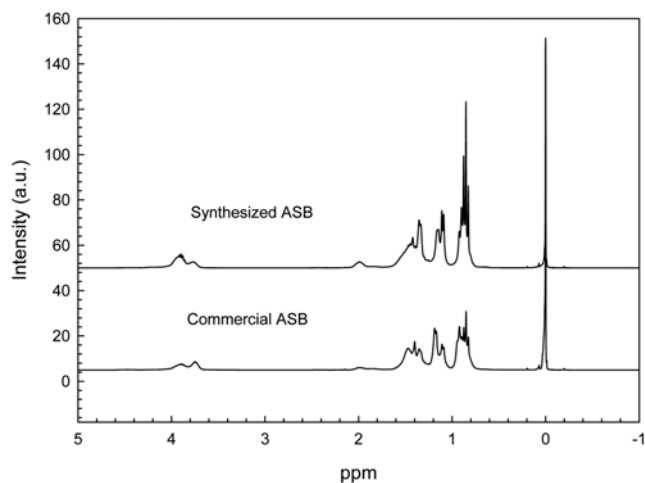


Fig. 5.  $^1\text{H}$ -NMR spectra of ASB.

appears at  $935\text{ cm}^{-1}$  [14]. On the other hand, the sharp peak of  $800\text{ cm}^{-1}$  indicates the characteristic peaks of  $\text{CCl}_4$  used as a solvent [15].

Fig. 4 shows the  $^{27}\text{Al}$ -NMR data of the synthesized ASB and commercial ASB. As has been reported in previous studies [6,15], the

spectra of aluminum alkoxides have already been investigated: hexa-coordinated Al atoms present peaks in the range of 3 to 7 ppm, while the chemical shifts of tetra-coordinated Al atoms are found in a wider region from 35.4 to 66.5 ppm. As for penta-coordinated Al atoms in aluminum alkoxide, the chemical shifts seem to range from 29 to 44 ppm. When our peaks are compared with the result of previous studies, ours totally shift within 5 ppm. The spectra of the synthesized ASB present two resonance peaks around 25 ppm and 2 ppm, both assigned to the five- and six-coordinated Al atoms, respectively. A comparison of these two peaks reveals that the two samples have the same coordinated structure of Al atoms.

Fig. 5 shows the result of  $^1\text{H}$ -NMR analysis. We can understand the structure of ASB through the existence of protons in ASB like  $\text{Al-O-CH}_2$ ,  $\text{CH}_2$ , and  $\text{CH}_3$ . The sharp peak at 0 ppm is caused by TMS (Tetramethylsilane) used as reference, the two peaks at 3 to 4 ppm are caused by  $\text{Al-O-CH}_2$ , the peak at 2 ppm is caused by  $\text{CH}_2$ , the peaks at 1.4 ppm are caused by  $\text{CH}_2$ , and finally the peaks at 0.8 to 1.2 ppm are caused by  $\text{CH}_3$ . When the coordinated bonds of protons by  $^1\text{H}$ -NMR are combined with the result of  $^{27}\text{Al}$ -NMR, the synthesized ASB is the same as a trimeric structure proposed by ASB Kriz et al. [16]. They have proposed that the spectrum of ASB presents three resonance peaks at 60 ppm, 30 ppm, and 2 ppm assigned to the four-, five- and six-coordinated Al atoms, respectively, according to the acid/alkoxide molar ratio in the case of pure ASB. The synthesized ASB also has the same structure as that of the commercial ASB.

Our study focused on the synthesis of ASB with a high yield and purity in particular. Pure ASB was obtained finally through vacuum distillation under the condition of  $200^\circ\text{C}$  and 3 mmHg. After the vacuum distillation, it gave a 28% yield except the ASB adhered to the inner surface of the reactor or reflux columns. This yield corresponds to the total amount of Al component existing in the Al dross. Accordingly, we found that all Al metal existing in the Al

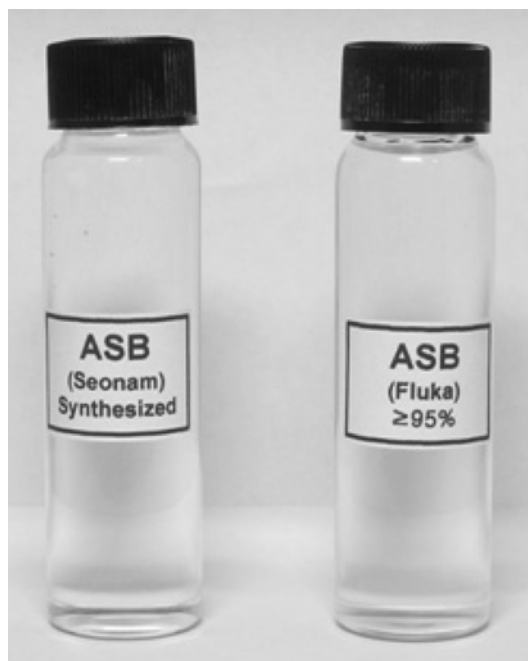


Fig. 6. Photograph of synthesized ASB and commercial ASB.

dross was recovered through the experimental apparatus.

The experiment must be given particular attention because the production of  $H_2$  gas and the reaction heat emitted in the dissolution reaction have a risk of explosion.

The result of purity analysis revealed that the synthesized ASB has a 99.2% purity, whereas the commercial ASB (Fluka, 95% purity) had a 98.1% purity.

Fig. 6 shows a photograph of synthesized ASB and commercial ASB. In appearance, the synthesized ASB is more transparent and colorless than the commercial ASB. On the other hand, the commercial ASB has a little yellowish color, which is caused by the existence of Iodine component used as a catalyst. That is, we found that the synthesized ASB has a higher grade than the commercial ASB does.

As mentioned in the introduction, Al dross includes many impurities except Al component. Among these impurities, the content of 0.1 wt% Na acts on the criterion for high purity  $Al_2O_3$  [17]. The Na content in the synthesized ASB was analyzed quantitatively by ICP (Inductively coupled plasma, GBC (Australia, Integra XL dual Mono). The result indicated that the Na content has a 0.007 wt% in the synthesized ASB. Thus we learned that the synthesized ASB is adequate as a starting material for high purity  $Al_2O_3$ .

## CONCLUSIONS

High purity ASB was synthesized from Al dross through dissolution reaction and vacuum distillation.

The results of FT-IR,  $^{27}Al$ -NMR, and  $^1H$ -NMR analysis revealed that the synthesized ASB has a trimeric structure and it is the same structure as that of the commercial ASB.

The synthesized ASB has a 99.2% purity and a 28% yield after the dissolution reaction of 24 hours. This yield corresponds to the total amount of Al component existing in the Al dross. No impurity was found in the synthesized ASB. These findings led us to conclude that the ASB synthesized through this experiment may be used as a starting material for the high purity  $Al_2O_3$ .

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