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Synthesis of beta-alumina powders by microwave heating from solution-derived precipitates

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Abstract

The synthesis of beta-alumina powder by microwave heating of the precipitate obtained through solution-precipitate techniques was described. A homogeneous mixture of $Al_2(SO_4)_3{\cdot}18H_2O$ and $Na_2SO_4{\cdot}10H_2O$ was precipitated by dropping the mixed solution of kaolin-derived aluminum sulfate and sodium hydroxide into ethanol with agitation by stirring. The precipitates were calcined at various temperatures for 1 h under conventional and microwave heating process for obtaining the beta-alumina powder with the structure consisting of β- and β″-alumina phases with a larger amount of β″-alumina phase. The amount of β″-alumina phase in the microwave-calcined samples was larger than that in the conventionally calcined samples.

Keywords: A. Microwave processing; A. Calcination; A. Powders; D. β-Al_2O_3; D. Al_2O_3; Synthesis

1. Introduction

Beta-alumina is well known as an efficient sodium ion conductor that can be used as the solid electrolyte of sodium-sulfur batteries [1]. Derivatives known as beta-alumina are generally found in materials of the type β-Al_2O_3 with the empirical formula of $Na_2O{\cdot}11Al_2O_3$, and in materials of the type β″-Al_2O_3 identified in the form $Na_2O{\cdot}5Al_2O_3$ [2]. The fabrication of beta-alumina can be separated three distinct stages [3]. The first stage is powder preparation, in which the chemical constituents are thoroughly mixed. Powder is then formed into the required shape and resultant green body is sintered to sufficient density to produce the required properties. One aspect of this processing that has received a significant amount of attention is powder preparation. Numerous methods of preparing beta-alumina powder have been performed by the solid-state reaction of mixed oxides, requiring high calcination temperature. Solution-precipitation processing is an alternative to conventional processing. This process has been aimed at attaining a more intimate mixing of reactants and high-purity composition that are difficult to make by the conventional processing [4].

Microwave technology as non-conventional energy source has attracted interest lately as an alternative to conventional thermal processing [5]. Microwave processing has been employed for chemical synthesis, drying, material decomposition and sintering with the following attractive characteristics; fast reaction rate, low reaction temperature, and superior structure and properties of product [6,7]. However, the application of microwave processing for the synthesis of beta-alumina powders through solution-precipitate method has received less attention. It was reported that larger amounts of β″-Al_2O_3 in the beta-alumina consisting of β- and β″-Al_2O_3 are desired to maximize the ionic conductivity of an electrolyte [3].

In this study, we reported the synthesis of beta-alumina powders by the microwave heating of solution-derived

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precipitate, and compared differences in the amount of β''-Al_2O_3 phase that resulted from the microwave and conventional heating.

2. Experimental procedure

Kaolin and reagent-grade sodium hydroxide were used as the starting materials for the preparation of beta-alumina powder. The chemical analysis of kaolin is given in Table 1. Kaolin powder was heat treated at 800 °C for 3 h in an electric muffle furnace to loosen alumina component and ground to below a size of about 74 μm in an agate mortar. Beta-alumina powders were synthesized by the reaction of kaolin-derived aluminum sulfate solution and sodium hydroxide. The kaolin-derived aluminum sulfate solution was prepared as follows: First, about 18 g of calcined kaolin was charged with 600 ml of 1.0 M H_2SO_4 solution in a Pyrex glass flask, fitted with a thermometer and a reflux condenser. The solution was continuously stirred with an electric stirrer, maintained at 80 °C for 3 h in a water bath, then cooled to room temperature. After reaction, leach residue was separated by filtering the solution to obtain aluminum sulfate solution, as described in detail elsewhere [8]. Next, 68.0 weight percent of Al_2O_3 in the kaolin sample was completely reacted to form an aluminum sulfate solution. NaOH pellets were then added to the aluminum sulfate solution to obtain a complex of desired composition for beta-alumina powders. In this process, the nominal mole ratio of N_2O/Al_2O_3 in the solution was adjusted to be 1.0/1.0. The mixed solution was stirred until it became translucent to obtain an ionic solution. Then, 200 ml of the mixed solution was dropped at a rate of 5.0 ml min^{-1} into 900 ml of ethanol with agitation by magnetic stirring; ethanol was used as a precipitation agent. Precipitation occurred immediately after addition of the mixed solution to the ethanol. Precipitates were dried at 80 °C for 24 h after washing, and then calcined at various temperatures for 1 h in an electric muffle furnace. Resultant powders were referred to as 'conventionally heated sample'. Microwave heated sample was prepared following the same procedure as for conventionally heated sample except that the precipitates were calcined by microwave heating in a microwave hybrid furnace.

Table 1
Chemical content of kaolin

Component	Content (wt.%)
SiO_2	51.53
Al_2O_3	45.00
K_2O	0.80
Na_2O	0.46
Fe_2O_3	0.77
MgO	0.32
CaO	0.53
Ignition loss	0.59

A commercial microwave oven operating at 2.45 GHz with powder of 700 W was modified for microwave heat treatment. Its modification includes the attachment of a PID temperature controller to maintain consistent temperature and the attachment of a mode stirrer to uniform microwave field. The insulation cavity was composed of alumina fiberboard and a SiC sheet was used as microwave coupling material [6].

The chemical contents of starting material were analyzed via atomic absorption spectroscopy (AAS; Perkin Elmer AA800, USA). The thermal decomposition characteristics of precipitates were determined by differential thermal analysis (DTA; Macscience TG-DAT 2000, Japan) at a heating rate of 10 °C min^{-1} in air. The powder morphology of calcined precipitates was examined by scanning electron microscope (SEM; Jeol JSM-5400, Japan). The phase composition of the calcined precipitates was examined by X-ray diffractometry (XRD; Rigaku RINT 2000, Japan) using nickel-filtered Cu kα radiation.

3. Results and discussion

3.1. Properties of as-synthesized precipitate

Fig. 1 shows X-ray diffraction patterns of the precipitate prepared from aluminum sulfate and sodium hydroxide solution. Two phases, $Al_2(SO_4)_3{\cdot}18H_2O$ and $Na_2SO_4{\cdot}10H_2O$, $10H_2O$, are insoluble in ethanol, whereas most of the Fe salts, including $Fe(SO_4)_3{\cdot}9H_2O$, are soluble [9]. It reflects the fact that the precipitate from ethanol does not contain Fe ions. Chemical analysis by atomic absorption spectroscopy revealed that the precipitate contained about 1.0 ppm Ca and trace amounts of other impurities. However, further studies on fundamental precipitation mechanism in ethanol are needed, although it is certain that ethanol as a precipitation agent drastically reduces impurities in this process. Differential thermal analysis was performed to confirm the X-ray

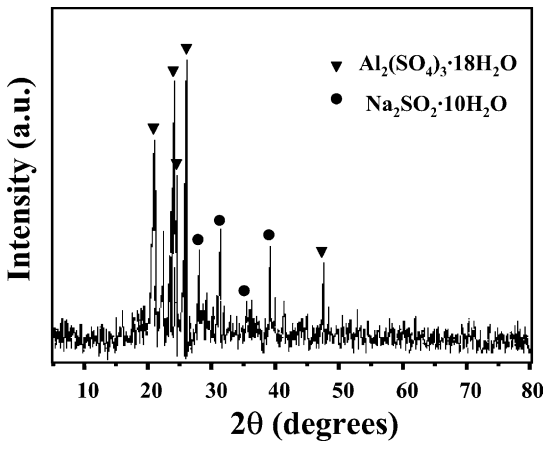

Fig. 1. XRD pattern of the precipitate prepared from aluminum sulfate and sodium hydroxide solution.

results on the precipitate. A large endothermic peak at about 140 °C was due to the loss of hydrated water. The endothermic peak at about 800 °C indicated the decomposition of dehydrated precipitate to oxides, mainly due to $Al_2(SO_4)_3$ decomposition.

3.2. Properties of beta-alumina with and without microwaves

The characteristics of samples were mainly investigated with respect to the phase change and the relative amount of β- and β″-Al_2O_3. The samples were obtained by calcining precipitates at various temperatures for 1 h under the microwave and conventional heating. Fig. 2 shows X-ray diffraction patterns of the precipitate calcined at 1000 °C for 1 h in the conditions of conventional and microwave heating. The diffraction patterns of conventionally heated sample indicate there phases, β-Al_2O_3, γ-Al_2O_3 and Na_2SO_4, whereas those of microwave heated sample show β-Al_2O_3, β″-Al_2O_3 and Na_2SO_4. It is noted that β″-Al_2O_3 phase appears in the microwave heated sample, whereas no β″-Al_2O_3 phase is detected in the conventional heated sample. With increasing temperature, both the microwave heated sample and conventionally heated sample were transformed to the beta-alumina phase consisting of β- and β″-Al_2O_3 with different amounts of phases. Fig. 3 shows that SEM pictures of the precipitates calcined at 1000 °C for 1 h in the conditions of conventional and microwave heating. Beta-alumina powders consisted of mostly plated-like fragmentary structures and melted-like agglomerated particles in the condition of conventional and microwave heating, respectively. It is assumed that melted-like particles will be obtained in the microwave-heated sample by localized heating or selective heating of microwaves [10].

The relative amounts of β- and β″-Al_2O_3 phase of the samples calcined at various temperatures for 1 h were estimated. Single phase β- and β″-Al_2O_3 are unavailable

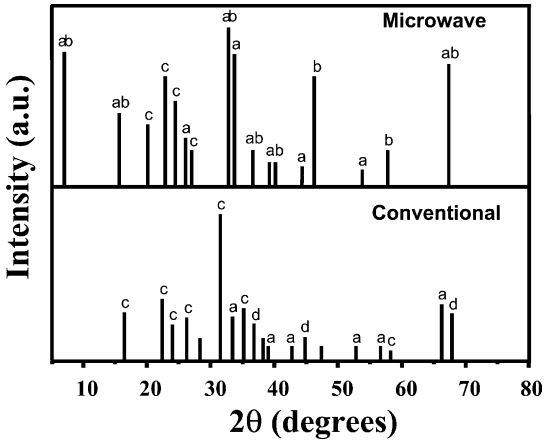

Fig. 2. XRD patterns of the precipitates calcined at 1000 °C for 1 h by microwave heating and conventional heating: a = β-Al_2O_3; b = β″-Al_2O_3; c = Na_2SO_4; and d = γ-Al_2O_3.

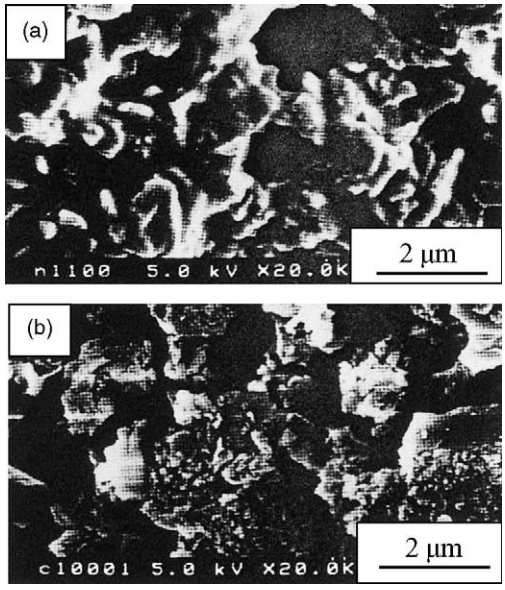

Fig. 3. SEM pictures of the precipitates calcined at 1000 °C for 1 h by (a) microwave heating and (b) conventional heating.

for preparing X-ray standards because β- and β″-Al_2O_3 have a similar hexagonal crystal structure and also because they are non-stoichiometric compounds. However, the relative amounts of phase present can be estimated from X-ray diffraction patterns of sample by measuring the intensities of major X-ray peak for β-Al_2O_3 and β″-Al_2O_3 phases, respectively [11]. The percentages of β″-Al_2O_3 phase were calculated using the X-ray peak intensity method. The data in Table 2 summarize the relative amount of β″-Al_2O_3 phase of the microwave heated and conventionally heated samples. It indicates that the relative amounts of β″-Al_2O_3 are increased with increasing calcining temperature in both heating conditions. The percentages of β″-Al_2O_3 obtained by conventional and microwave heating at same temperatures range from 0 to 40% and from 31 to 64%, respectively. It is interesting to note that the relative amounts of β″-Al_2O_3 of microwave heated samples are large than those of conventionally heated samples although both samples were obtained by heating same precipitate at the same temperature except for heating conditions, as given in Table 2. It is

Table 2
The relative amounts of β″-Al_2O_3 phases in the precipitates calcined at various temperatures for 1 h under microwave heating and conventional heating

Temperature (°C)	Relative amount of β″-Al_2O_3 (%)	
	Microwave heated sample	Conventional heated sample
1000	31	0
1100	42	13
1200	56	32
1300	60	35
1400	64	40

assumed that microwave affects strongly to the mobility of reaction species through selective and internal heating [12,13]. The microwave effect will be associated with reaction enhancement due to low activation energy of reaction and improved transport properties of ions through the reaction of a mixture of aluminum sulfate and sodium sulfate, resulting in β''-Al_2O_3 rich phase. However, further studies are necessary to explain the exact reaction mechanism that occurs by applying microwave heating.

4. Conclusions

The microwave heating process that has been described in the present paper has proven to be quite effective, in comparison to conventional heating, for the synthesis of beta-alumina with larger amount of β''-Al_2O_3 from the solution derived precipitates. Microwave processing probably facilitates formation of β''-Al_2O_3, because of its internal heating, leading to a reaction enhancement between Na_2O and Al_2O_3.

Acknowledgements

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