Synthesis of LiAlO₂ Powder by Hydrolysis of Metal Alkoxides

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Crystalline fine powders of LiAlO₂ can be prepared by hydrolysis of metal alkoxides for application to the breeder blanket in nuclear fusion. The precipitates were fine crystalline particles of β -LiAlO₂ of ≈ 0.1 - μ m size under controlled conditions. The transformation from β - to γ -phase was confirmed at temperatures between 700° and 750°C. The microstructure of a sintered body at 1000°C consisted of homogeneous fine particles and pores suitable for the blanket material. A fully dense sintered body could be prepared at 1400°C.

I. Introduction

ITHIUM-BASED oxide ceramics are likely candidates as solid Atritium breeder materials for fusion reactors. A number of investigations have been done on physical properties, thermal conductivity, specific heat, thermal expansion, stability, and tritium release. The dominant nuclear reaction occurs by 'Li neutron capture as follows:

$${}^{6}Li + {}^{1}n \rightarrow {}^{4}He + {}^{3}T$$
 (1)

Li₂O ceramics have been extensively studied for their high breeding ratio. However, these ceramics are markedly hygroscopic and react easily with CO₂, serious problems which must be solved for effective preparation and use. Grain growth and swelling in Li₂O sintered pellets must also be considered in the design of blanket materials.

In the Li₂O-Al₂O₃ system, LiAlO₂,¹ LiAl₅O₈, and Li₅AlO₄,^{2,3} are known; LiAlO₂ is especially anticipated to be a suitable tritium breeder for its thermal and chemical stability. Three polymorphs of LiAlO₂ are known, α -, β -, and γ -LiAlO₂ with hexagonal, monoclinic, and tetragonal structures, respectively. The α -phase was reported to transform to γ , the high-temperature form, at 900°C.^{4,5} The β metastable phase is assumed to transform to γ at $\approx 900^{\circ}$ C.⁶ These oxides have previously been prepared by various solid-state reactions of alumina with lithium carbonate or lithium hydroxide.⁷ Because of the evaporation of lithium at higher temperature, it is difficult to synthesize the pure LiAlO₂ with controlled particle size.

In this study, the preparation of crystalline fine powders by hydrolysis of metal alkoxides was investigated in order to prepare crystalline fine powders, sinterable at low temperature, giving highly pure and well-controlled grains in sintered bodies.

II. Experimental Procedure

(1) Preparation of LiAlO₂

Lithium ethoxide* (LiOC₂H₅, purity >99.9%) and aluminum ethoxide* (Al(OC₂H₅)₃), purity >99.9%) were used as starting materials; all handling was in a glovebox filled with dry nitrogen gas. The alkoxides were weighed in stoichiometric amounts and dissolved in ethanol by sufficient refluxing in a flow of dry nitrogen gas. The optimum concentration in ethanol was 0.1 mol/L for each alkoxide. Four times the amount of distilled and decarbonated water theoretically required for the hydrolysis was then added to the solution. After the hydrolysis reaction was completed, the precipitates were aged for 24 h under reflux. They were cooled to room temperature and ultrafiltered under nitrogen gas pressure of 500 kPa (5 bar), and dried carefully with a microwave range for 30 min.

(2) Calcination and Sintering

As-prepared precipitates were fired at 600°, 750°, and 1000°C in O_2 gas flow. In order to examine the effect of heating treatment time on structural changes in detail, the precipitates were also fired at 700° or 750°C for various times. Tablets, 10 mm in diameter, were prepared by uniaxially pressing in a die or cold isostatic pressing y-LiAlO₂ powder calcined at 750°C for 4 h and sintered at various temperatures between 1000° and 1450° C in O₂ gas flow. The open porosity and the pore distribution were measured by mercury porosimetry. The relative density of dense sintered bodies was measured by Archimedes' method with ethanol.

Identification, Chemical Analysis, and Observation by Scanning Electron Microscopy

The thermal behavior and structural changes on heating asprepared LiAlO₂ powders were examined by DTA-TG, XRD, and the infrared spectroscopic method. Infrared absorption spectra were analyzed by the KBr disk technique and the assignment was done on the basis of Gessner's interpretation.⁸ The elemental composition of Li, Al, and impurities in the y-LiAlO2 powders calcined at 750°C was determined by atomic absorption analysis, emission spectrochemical analysis, and X-ray fluorescence analysis. As-prepared and heat-treated powders were ultrasonically dispersed in ethanol, and the morphology of prepared particles and the microstructures of sintered compacts were observed by SEM.

III. Results and Discussion

(1) Thermal Behavior of As-Precipitated LiAlO₂

X-ray diffraction patterns of as-prepared and calcined specimens are shown in Fig. 1. As-precipitated powders were crystalline β -LiAlO₂, synthesized directly by the controlled hydrolysis of refluxed alcoholic solution of lithium ethoxide and aluminum ethoxide at 80°C (Fig. 1(a)). By heat treatment at 600°C, the crystallinity of β -LiAlO₂ increased (Fig. 1(b)). The expected conversion to γ -phase was commenced at 750°C with complete transformation to highly crystalline y-LiAlO₂ at 1000°C after 2 h. as shown in Figs. 1(c) and (d). Further detailed experiments revealed that the transformation to γ -LiAlO₂ is complete at 700°C after 24 h and becomes obvious at 750°C after 4 h. Transformation was found to be lower by $\approx 200^{\circ}$ C than that at which α -LiAlO₂ transformed to γ -LiAlO₂.

By DTA-TG (Fig. 2), an endothermic peak due to the evaporation of water and adsorbed solvent was observed below 200°C. A weak exothermic peak was observed between 250° and 450°C, which was attributable to the combustion of adsorbed ethanol. This exothermic peak was lowered by employing ultrafiltration instead of centrifugation. In this experiment, the endothermic peak from the phase transition in the range 700° to 800°C could not be detected.

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Fig. 1. X-ray diffraction pattern of as-prepared and calcined LiAlO₂: (a) as-prepared, (b) 600°C for 5 h, (c) 750°C for 4 h, (d) 1000°C for 2 h; (\bigcirc) β -LiAlO₂, (\bigcirc) γ -LiAlO₂.



Fig. 2. DTA and TG curves of as-prepared powders.



Fig. 3. Infrared spectra of LiAlO₂: (a) as-prepared, (b) heat-treated at 600°C for 5 h, (c) heat-treated at 1000°C for 2 h.







Fig. 4. Scanning electron micrographs of as-prepared and heat-treated powders: (A) as-prepared, (B) heat-treated at 600° C, (C) heat-treated at 750° C.



Fig. 5. Scanning electron micrographs of fracture surfaces of sintered bodies: (A) 1000°C for 4 h, (B) 1200°C for 4 h.

Table I. Total Pore Volume and Relative Density of Tablets Sintered under Various Conditions

Specimen	Press forming (kg/cm ²)	Cold isostatic pressing (kg/cm ²)	Sintering condition	Total pore volume* (cm ³ /g)	Relative density [*] (%)
LA-0510 LA-0511 LA-0512 LA-3C10 LA-3C14	500 500 500 500 500 500	3000 3000	1000°C, 4 h 1100°C, 4 h 1200°C, 4 h 1000°C, 4 h 1400°C, 4 h	0.3 0.09 0.03 0.015	77.2 90.5 96.6 92.0 ≈100

*Pore volume by mercury porosimetry. 'Bulk density by Archimedes' method in ethanol. Theoretical density of γ -LiAlO₂: 2.6154 g/cm³.

Table II.	Pore Distribution of Tablets
Sintered	under Various Conditions*

Pore	 Pore volume (cm ³ /g)					
(nm)	LA-0510	LA-0511	LA-0512	LA-3C10		
200.0 145.0 105.0 75.0 53.0 37.5 27.5 20.0 14.5 10.5 7.5 5.3	0.01 0.18 0.05 0.04 0.02	$\begin{array}{c} 0.004\\ 0.004\\ 0.012\\ 0.024\\ 0.024\\ 0.008\\ 0.008\\ 0.008\\ \end{array}$	0.01 0.01 0.01	0.015		

*Numbers of tablets are the same as shown in Table I. On LA-3C14 tablet, pores were not detected.

Figure 3 shows infrared absorption spectra of as-prepared and heat-treated samples at 600° and 1000°C. Gessner and Müller⁸ reported that both β - and γ -LiAlO₂ have aluminum ions only tetrahedrally coordinated; therefore, they are expected to have similar spectra, though the absorption frequency is slightly different, and in the range from 520 to 900 cm⁻¹ correspond to the Al-O stretching vibration. The spectra of heat-treated powders at 600° and 1000°C were identical with those reported by Gessner *et al.* as β - and γ -LiAlO₂, respectively.⁸ These results agree with the XRD.

Scanning electron micrographs of as-prepared and heat-treated

powders at 600° and 750°C are shown in Fig. 4. The former was β -LiAlO₂ agglomerates consisting of $\approx 0.1 - \mu m$ particles and this remained unchanged up to 600°C. The size increased to 0.3 μm or larger hy heating at 750°C with conversion to γ -phase.

The results of chemical analysis showed that the Li/Al molar ratio of the calcined γ -LiAlO₂ powder was 0.96, which was essentially the same as that of the original composition, i.e., Li/Al = 1.00.

Although lithium hydroxide and oxide are known to have a high solubility in water and ethanol, their dissolution into water and ethanol hardly occurred on the hydrolysis of a mixture of lithium alkoxide and aluminum alkoxides. This may reflect that the lithium ethoxide existed as the state of double metal alkoxides similar to those reported by Scholder *et al.*⁹

The γ -LiAlO₂ powder contained trace amounts of impurities such as Ca, Sr, Fe, and Zn.

(2) Characterization of Sintered Body

Tablets were sintered at temperatures from 1000° to 1450°C. The tablet of β -LiAlO₂ uncalcined powder cracked during sintering because of the volume change associated with the phase transformation to γ -phase. Calcination of the as-prepared β -LiAlO₂ powder must be carried out before being sintered to avoid this. The calcination of β -LiAlO₂ to γ -phase is more favorable than that of α -phase as grain growth and hard aggregation are suppressed by lowering the calcination temperature.

Figure 5 shows a SEM of the fracture surface of bodies sintered at 1000° and 1200°C. At 1000°C, the sintered body has a homogeneous texture with fine particles and pores; much greater grain growth occurred in bodies sintered above 1200°C.

Table I shows the pore volume and relative density of tablets sintered under various conditions. The pore distribution of each tablet is shown in Table II. The relative density of tablets sintered at 1000°C, after cold isostatic pressing, was >90%, consisting of homogeneous micropores with pore radius from 7.5 to 10.5 nm. For the tablet sintered at 1400°C, after the cold isostatic pressing, open pores were not detected, and the relative density was nearly 100%. The sintering of γ -LiAlO₂ tablets was considerable at temperatures above 1200°C. Porous bodies sintered at 1000°C, however, are suitable for blanket material, since it is composed of a proper amount of fine pores favorable for the diffusion path of He gas release. Physical measurements on sintered bodies with neutron irradiation are in progress.

IV. Conclusion

Crystalline powders of LiAlO₂ were successfully prepared by hydrolysis of metal alkoxides. The precipitated powders were found to be metastable β -LiAlO₂, with fine agglomerated particles as large as $\approx 0.1 \,\mu\text{m}$. Transformation of β -LiAlO₂ to γ -phase occurs between 700° and 750°C, lower by about 200°C than that of $\alpha\text{-LiAlO}_2.$ In order to prepare a sintered $\gamma\text{-LiAlO}_2$ body with controlled texture, β -LiAlO₂ is superior to α -LiAlO₂. γ -LiAlO₂, which is the high-temperature phase, is suitable for the blanket material, and the conversion to γ -phase is monotropic. The fracture surface of bodies sintered at 1000°C consisted of homogeneous texture with fine particles and many micropores which are favorable for the diffusion path of He gas release. These results will aid the development of useful blanket materials.

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