## Crystal Growth of Rod-Shaped $\beta$ -LiAlO<sub>2</sub>

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LiAlO<sub>2</sub> crystals are obtained conventionally in the form of powder. In a few publications, crystal growth of rod-shaped  $LiAlO_2$  has been described, but the fiber length was very short,  $<4 \ \mu m$ . In the present study, rod-shaped  $\beta$ -LiAlO<sub>2</sub> crystals 10 to 15  $\mu$ m long were grown using LiOH-Al<sub>2</sub>O<sub>3</sub>-NaOH as the raw material.

THE use of fuel cells is a highly effective method of generating electric power.<sup>1-3</sup> For this application, LiAlO<sub>2</sub> crystals, which are inert against alkali carbonate, are desirable as a reinforcement material. Alkali carbonates are used commonly as the electrolyte in the molten-carbonate fuel cell. Long rod-shaped or fibrous LiAlO2 crystals forming a fine porous structure are especially desirable as a reinforcement for the electrolyte. Although there are a few reports on the synthesis methods of LiAlO<sub>2</sub> crystals as powders,<sup>4-7</sup> spherical grains,<sup>8</sup> and very short rods <4  $\mu$ m long,<sup>9,10</sup> there are no reports on methods of making long crystallites or fibers.

Synthesis methods for rod-shaped LiAlO<sub>2</sub> crystals which use LiOH-Al<sub>2</sub>O<sub>3</sub>-alkali hydroxide<sup>11</sup> (length of synthesized rod-shaped LiAlO2 crystals is not clearly recorded) and LiOH-Al<sub>2</sub>O<sub>3</sub>-alkali chloride<sup>10</sup> (length of synthesized rodshaped LiAlO<sub>2</sub> crystals is 1 to 3  $\mu$ m) as raw materials have been published in provisional Japanese patent publications, but to the best of our knowledge, there are no research papers describing the use of LiOH-Al<sub>2</sub>O<sub>3</sub>-alkali hydroxide as a raw material except LiOH-Al<sub>2</sub>O<sub>3</sub>-KOH (length of synthesized rod-shaped LiAlO<sub>2</sub> crystals is 4  $\mu$ m).<sup>9</sup> In this paper we report on the synthesis of rod-shaped  $\beta$ -LiAlO<sub>2</sub> crystals 10 to 15  $\mu$ m long. To the best of our knowledge, there are no reports of such long LiAlO<sub>2</sub> crystals regardless of the processing method.

### SYNTHESIS OF LONG, ROD-SHAPED $\beta$ -LiAlO<sub>2</sub> Crystals

After LiOH·H<sub>2</sub>O,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and NaOH were mixed well (mole ratio  $LiOH \cdot H_2O: \gamma - Al_2O_3: NaOH = 4:1:4)$  and placed in a mold (25 mm in diameter and 10 mm deep), columnar test pieces were shaped under 9.8 MPa using a universal testing machine. The test pieces were placed in a muffle furnace (65 wt% Al<sub>2</sub>O<sub>3</sub>, 31 wt% SiO<sub>2</sub>, interior dimensions 180 by 80 by 80 mm) for calcination, heated to 600°C at 5°C/min, and held for 3 h (in preliminary experiments this heating condition was best for crystal growth). After EXPERIMENTAL RESULTS

disentangled.

The disentangled products were confirmed to be  $\beta$ -LiAlO<sub>2</sub> crystals by X-ray analysis; these rod-shaped  $\beta$ -LiAlO<sub>2</sub> crystals are shown in Fig. 1(A). Most of these rod-shaped crystals are 1.5  $\mu$ m in diameter and 10 to 15  $\mu$ m long. A scanning electron micrograph of the products made from KOH instead of NaOH and heated at 600°C for 3 h is shown in Fig. 1(B). Most of these rod-shaped crystals are 1  $\mu$ m in diameter and 4  $\mu$ m long.

the pieces were heated and cooled, they were dipped into water for 24 h and

Heating conditions and combination ratios of raw materials were varied extensively, but the length of  $\beta$ -LiAlO<sub>2</sub> crystals remained <4  $\mu$ m. From the facts described, it is evident that an NaOH flux shows the greatest effect on the growth of rod-shaped  $\beta$ -LiAlO<sub>2</sub> crystallites. A controlling factor for the growth of long rod-shaped  $\beta$ -LiAlO<sub>2</sub> crystals is generally considered to be the effect of vaporization of the alkali compound liquid, but in this case it does not explain the effect of NaOH on crystal growth, and the fact that it is more effective than KOH.

#### CONCLUSION

In this study NaOH fluxes were used rather than the well-known KOH or alkali chloride fluxes, and heating conditions and combination ratios of raw materials were optimized. In this way, long, rod-shaped  $\beta$ -LiAlO<sub>2</sub> crystals 10 to 15  $\mu$ m long were obtained by using LiOH-Al<sub>2</sub>O<sub>3</sub>-NaOH as the raw material.

#### REFERENCES

<sup>1</sup>T. Shirogami, "Trends of Research and Devel-opment of Fuel Cells," Kagaku Kogyo, **37** [10] 693-95 (1984). <sup>2</sup>T. Ozawa, "New Electric Power Sources for the





Scanning electron micrograph of  $\beta$ -LiAlO<sub>2</sub> crystals: (A) LiOH·H<sub>2</sub>O:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: NaOH=4:1:4 (mole ratio) and (B) LiOH·H<sub>2</sub>O:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: KOH=4:1:4 (mole ratio).

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Future," Kagaku Kogyo, 37 [10] 679–83 (1984).
<sup>3</sup>K. Fueki, "Trends of Research and Development of Power Generation Technologies and Batteries," Kagaku Kogyo, 37 [10] 662–66 (1984).
<sup>4</sup>K. Kinoshita, J. W. Sim, and G. H. Kucera, "Synthesis of Fine Particle Size Lithium Aluminate for Application in Molten Carbonate Fuel Cells," Mater. Res. Bull., 14, 1357–68 (1979).
<sup>5</sup>M. Nakanishi, T. Sugiyama, S. Waraya, and Y. Hirose, "The Process of Lithium Aluminate Powder."

Hirose, "The Process of Lithium Aluminate Powder,"

provisional Jpn. Pat. Publ. No. 45113, 1983. <sup>6</sup>A. Muneuchi, K. Murata, and T. Shirogami, "The Process of Matrix Powder for the Molten-Carbonate Fuel Cell," provisional Jpn. Pat. Publ. No. 87772, 1983

7T. Sugiyama, T. Sawada, and T. Ichiyanagi, "The Process of Lithium Aluminate," provisional Jpn. Pat. Publ. No. 10057, 1986.

<sup>8</sup>L. Yan, R. R. Medico, and W. A. Bow, "The Process of Spherical Grain of Lithium Aluminate," pro-

visional Jpn. Pat. Publ. No. 176122, 1983. <sup>9</sup>K. Kinoshita, J. W. Sim, and J. P. Ackerman,

"Preparation and Characterization of Lithium Alumi-

<sup>10</sup>S. Oziwa and T. Sugiyama, "The Process of Lithium Aluminate Powder," provisional Jpn. Pat. Publ. No. 65719, 1985. <sup>11</sup>K. Kinoshita and J. P. Ackerman, "The Process

of the Electrolyte in the Fuel Cell," provisional Jpn. Pat. Publ. No. 136638, 1978.

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# Devitrification and Delayed Crazing of SiO<sub>2</sub> on Single-Crystal Silicon and Chemically Vapor-Deposited Silicon Nitride

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The linear growth rate of cristobalite was measured in thin  $SiO_2$  films on silicon and chemically vapor-deposited silicon nitride. The presence of trace impurities from alumina furnace tubes greatly increased the crystal growth rate. Under clean conditions, the growth rate was still 1 order of magnitude greater than that for internally nucleated crystals in bulk silica. Crystallized films cracked and lifted from the surface after exposure to atmospheric water vapor. The crystallization and subsequent crazing and lifting of protective SiO2 films on silicon nitride should be considered in long-term applications.

 $S_{\rm dynamically}^{\rm ILICON}$  and silicon nitride are thermodynamically unstable under oxidizing conditions, and at high temperatures a protective SiO<sub>2</sub> layer is formed on the surface. Under clean conditions and at short heating times, the SiO<sub>2</sub> film is amorphous. At temperatures greater than 1000°C and at longer times, cristobalite crystals nucleate and grow in the amorphous film. The rate of nucleation and growth depends strongly on the temperature, the impurity content of the glass, and the ambient atmosphere.

Ainslie *et al.*<sup>1</sup> reported that the growth rates of cristobalite crystals on fused silica in oxidizing atmospheres (i.e., O2 and H<sub>2</sub>O) were  $\sim 10$  times greater than those under an inert atmosphere (i.e., Ar) and varied as  $t^{1/2}$ , suggesting that oxidant diffusion was rate controlling. Wagstaff et al.<sup>2</sup> found that the crystal growth rate on vitreous silica in O<sub>2</sub> and H<sub>2</sub>O atmospheres showed two different time dependencies: (i) for reduced vitreous silica  $(SiO_{2-x})$  the growth rate was proportional to  $t^{1/2}$ ; (ii) for stoichiometric vitreous silica, it was proportional to t. In later work, Wagstaff<sup>3,4</sup> reported that the crystal growth rate of cristobalite internally nucleated and grown in vitreous silica followed linear growth kinetics with time and could be represented by the equation

$$U = A \Delta T / \eta \tag{1}$$

where U is the crystal growth rate at temperature T, A is a constant,  $\Delta T$  is the degree of undercooling below the melting point of cristobalite, and  $\eta$  is the viscosity of vitreous silica at T.

Bihuniak et al.5 investigated the dependence of the viscosity of vitreous silica in the transformation range on low-level impurities,  $Al_2O_3$  (25 to 350 molar ppm) and  $R_2O$  (1.0 to 75 molar ppm). They found that both viscosity and activation energy increased with the molar ratio  $Al_2O_3/R_2O$  up to ~8 and were constant at higher ratios. In a subsequent study, Bihuniak reported that the crystal growth rate in vitreous silica varied inversely with the molar ratio  $Al_2O_3/R_2O$ . This was explained as a direct consequence of the effect of these trace impurities on viscosity. Wagstaff<sup>3</sup> reported that sodium contamination of the furnace atmosphere by impure ceramic tubes can also increase cristobalite crystal growth rate.

Hetherington et al.<sup>6</sup> reported that the activation energy for viscous flow decreases with increasing hydroxyl concentration or other impurities effective in breaking Si-O-Si bonds. They measured viscosity in the range 900° to 1400°C for different types of vitreous silica with addition, in some cases, of specific impurity elements.

Davidge<sup>7.8</sup> reported that the main oxidation product formed on reaction-sintered silicon nitride (RSSN) at 1000° and 1400°C was cristobalite. Cristobalite has a very large contraction on cooling due to the  $\beta$ - $\alpha$ phase change at 200°C and the large thermal expansion coefficient (TEC) of the  $\alpha$ form. However, thin oxide layers formed at 1000°C did not crack or craze on cooling while thicker cristobalite layers formed at 1400°C crazed. Many other investigators have reported devitrification and crazing of oxide layers on silicon nitride.9-1

The purpose of the present work was to measure the growth rate of cristobalite in thin films of SiO<sub>2</sub> grown on silicon and chemically vapor-deposited silicon nitride (CVDSN) under carefully controlled conditions and to compare these results with previous observations on growth rates in bulk SiO<sub>2</sub>. A second goal of the work was to observe the onset of crazing and relate this to the effectiveness of crystallized SiO<sub>2</sub> films to act as protective layers against long-term oxidation of silicon nitride structural ceramics.

#### EXPERIMENTAL PROCEDURE

The materials used for this study were (111) semiconductor-grade single-crystal silicon and chemically vapor-deposited silicon nitride (CVDSN).<sup>†</sup> The latter material

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