Mechanical and Electrical Properties of Preferentially Oriented Na β -Alumina Ceramics

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配向性 Na β -アルミナセラミックスの作製と力学特性及び電気特性評価

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Na β -alumina is a two-dimensional ionic conductor in which conducting planes of Na⁺ ion are separated by insulating spinel block layers. For practical use, Na β -alumina needs not only high ionic conductivity but also mechanical reliability. Therefore, we prepared preferentially oriented Na β -alumina ceramics by hot pressing and evaluated the ionic conductivity and mechanical strength. The ionic conductivity perpendicular to the *c*-axis-oriented plane was five times higher than that parallel to *c*-axis. From the preferentially oriented Na β -alumina ceramics three types of test pieces were cut for a three-point bending test. In one type of test piece, the longest side was parallel to the hot-pressing direction, while the longest sides were perpendicular to that direction in the other types of test pieces. The latter test pieces showed mechanical strength 1.5 times that of the former.

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1. Introduction

Sodium β -alumina ceramics are the most probable candidate for solid electrolytes for electrochemical energy devices using sodium ion such as the sodium-sulfur battery (Na-S battery)¹⁾ and the alkali metal thermo-electric converter cell (AMTEC). However, the reliability of these ceramics' mechanical strength has not been sufficient for practical use to date. The crystal structure of Na β -alumina is characterized by NaO layers separated by insulating aluminum spinel block layers. Accordingly, Na⁺ ion can be conducted only through the NaO layers, producing two-dimensional sodium ionic conduction. In addition, the Na⁺ ion conducting plane is a cleavage plane, thus cracks propagate easily along this plane.²⁾

Generally speaking, solid electrolyte needs high ionic conductivity and high mechanical strength because it acts simultaneously as both separator and ionic conductor. We have previously reported that alumina-dispersed 8 mol% yttria stabilized zirconia (8YSZ) ceramics exhibited large mechanical strength almost twice that of monolithic 8YSZ ceramics while its ionic conductivity remained constant. By using such a material, the thickness of the separation wall can be thinned by half while maintaining the structural reliability. Therefore, the resistance through the electrolyte can be lowered, reducing the ohm loss at the electrolyte.³⁾⁻⁵⁾ Nevertheless, a contradiction arises between the development of high strength and high ionic conductivity because the ion conducting plane corresponds to the cleavage plane in Na β -alumina ceramics.⁶⁾ In such a case, a preferential-crystal-orientation-dependent mechanical and ionic conductivity change would be interesting. In this work, we prepared Na β -alumina of different orientations, and examined its conductivity and mechanical strength to evaluate its practical utility as a solid electrolyte.

2. Experimental

Commercially available α -alumina powder (Sumitomo Chemical Co., Ltd., AKP-30) or a mixture of α -alumina powder and Al(OH)₃ (Sumitomo Chemical Co., Ltd., CL-310) with plate-like morphology was used as the aluminum source. Sodium carbonate powder (RARE METALLIC

Co., Ltd., purity 99.9%) as a sodium source was mixed into the aluminum source powder or powder mixture with the atomic ratio (Al:Na) of 11:1.7. Each mixture of aluminum and sodium sources was wet blended with a planetary mill for 1 h using zirconia balls and ethanol. After drying, the resultant powder mixture was uniaxially pressed under 100 MPa. The powder compacts enclosed in a graphite mold were placed into a hot press (Futeck Furnace PF-1627) and initially heated at 850°C for 3 h to form Na β -alumina, followed by sintering at 1700°C for 30 min. After the ambient temperature reached 1000°C, uniaxial pressure of 30 MPa was continuously applied to the pellets until the sintering was completed under an argon stream. The relative densities of the sintered bodies were higher than 99%.

After surface polishing, hot pressed bodies derived from the two different aluminum sources were subjected to XRD measurement on a flat surface. The degree of orientation of the crystallographic *c*-plane to the hot pressing direction was evaluated by Lotgering's method.

Electrical conductivity was measured by the two-probe a.c. impedance method using an impedance analyzer (Solartron 1260). Platinum paste was attached as electrodes and electrical measurements were conducted both parallel and perpendicular to the hot pressing direction.

Mechanical strength was measured on three types of test pieces cut from the hot-pressed bodies. Manners of cutting are illustrated in Fig. 1. In this figure, dotted lines represent the hypothetical parallel planes perpendicular to the hot pressing direction. The dimensions of these three kinds of test pieces are all the same, 2 × 7 × 0.5 mm. Test piece (1) was cut so as to make its plane with the maximum surface area normal to the hot pressing direction. In the other test pieces, (2) and (3), the maximum surface are planes parallel to the hot pressing direction. The longest sides are parallel and perpendicular to the hot pressing direction in test pieces (2) and (3), respectively.

3. Results and discussion

Figure 2 shows the XRD patterns of Na β -alumina samples derived from only α -alumina and the mixture of α -alumina and gibbsite. Orientation degrees (fs) of the *c*-plane

Fig. 1. Manners of cutting of hot-pressed bodies (dotted lines represent the hypothetical parallel planes perpendicular to the hot pressing axis).

Fig. 2. XRD patterns of Naβ-alumina ceramics parallel to hot-pressing direction.

were 0.35 and 0.58, respectively, by Lotgering's method. Hereafter, these samples are referred to as low-oriented and highly oriented ones, referred to as. The orientation degree is large in the sample derived from plate-like gibbsite powder while the sample made from α-alumina shows a small but non-negligible orientation degree. The flat surface of the plate-like grain is the (001) plane of gibbsite, which changes to the (0001) plane of Naβ-alumina during the reaction with sodium carbonate. The oriented gibbsite (001) plane during uniaxial pressing would be maintained by the hot pressing, resulting in a highly oriented Naβ-alumina ceramics.⁷⁾ Although the compact body derived from spherical α-alumina powder was isotropic, a small degree of orientation came about due to the pressing during the sintering because the formed Naβ-alumina has a flat plate shape to some extent.

Figure 3 shows the conductivity parallel and perpendicular to the hot pressing axis for both highly and low-oriented samples. In the case of highly oriented samples derived from the powder mixture containing gibbsite, the ionic conductivity perpendicular to the hot-pressing direction was five times higher than that parallel to the hot-pressing direction. Such a conductivity difference along the different directions should be attributed to the connection of the con-

Fig. 3. Arrhenius plots of ionic conductivity in hot-pressed Naβ-alumina ceramics.

▲ perpendicular to hot-pressing direction of low-oriented sample,
● perpendicular to hot-pressing direction of highly oriented sample,
△ parallel to hot-pressing direction of low-oriented sample,
○ parallel to hot-pressing direction of highly oriented sample.

duction pathway oriented parallel to the hot-pressing direction. On the other hand, the conductivity difference is relatively very small in the low-oriented sample and its conductivities in both directions are located between conductivity plots parallel and perpendicular to the hot-pressing direction in the highly oriented sample. In such a low-oriented sample, conduction pathways are thought to connect rarely even in the direction perpendicular to the hot pressing, and as a result conductivity anisotropy becomes small.

Three-point bending strengths (span length: 5 mm) were measured for three types of test pieces cut from the highly and low-oriented hot-pressed bodies. Strength measurements were conducted fourteen times for each data point. The results are illustrated in Fig. 4, where (1), (2) and (3) are the configurations of the test pieces as presented in Fig. 1 and the error bar represents the standard deviation. In both highly and low-oriented samples, test pieces (1) and (3) show almost identical bending strengths, which are larger than that of test piece (2). These results can be ascribed to the crystal structure of Naβ-alumina and/or its grain morphology. Because the present Naβ-alumina consists of flat plate-shaped grains, the formed cracks would propagate perpendicular to the cleavage plane as well as to the flat-plate shaped grains in test pieces (1) and (3). As a result, crack propagation was inhibited by the grains and the test pieces did not break immediately. In test piece (2), on the other hand, the crack propagation plane is parallel to the cleavage plane and the flat surfaces of grains, resulting in a sudden fracture.

When the mechanical strengths of highly and low-oriented samples with the same test piece configuration are compared, test pieces (1) and (3) show almost the same mechanical strength irrespective of the orientation degree. In test piece (2), mechanical strength of the highly oriented sample is much smaller than that of the low-oriented one. This result can be ascribed to the decrease in fracture resistance due to the grain and crystallographic orientation.

The bending strength ratios of test piece (2) against test pieces (1) and (3) in the highly oriented samples are 0.75, and 0.85 in the low-oriented ones. The anisotropy of ionic conductivity is much larger, about one half order in the highly oriented samples and almost two in the low-oriented ones. Thus, ionic conductivity should be considered to a greater

Fig. 4. (a) Dependence of bending strength of highly oriented samples on manner of cutting, (b) dependence of bending strength of low-oriented samples on manner of cutting.

extent than the mechanical strength when designing electrochemical devices using Na β -alumina ceramics with preferential orientation and microstructural features similar to the present work.

4. Conclusions

The contradiction in separation walls cut from preferentially oriented Na β -alumina ceramics with orientation degrees (fs) of 0.35 and 0.58 was confirmed, that is, a separation wall with high ionic conductivity in the longitudinal direction had only small mechanical strength and another wall with high mechanical strength had low ionic conductivity. It was suggested that orientation-dependent electrical and mechanical properties should be considered when designing electrochemical devices using a solid electrolyte.

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References

- 1) Weber, N. and Kummer, J. T., *Proc. Ann. Power Sources Conf.*, **21**, 37-40 (1967).
- 2) Whittingham, M. S. and Huggins, R. A., *J. Chem. Phys.*, **54**, 414-16 (1971).
- 3) Yuzaki, A. and Kishimoto, A., *Solid State Ionics*, **116**, 47-51 (1999).
- 4) Yuzaki, A. and Kishimoto, A., *Solid State Ionics*, **109**, 273-77 (1998).
- 5) Oe, K., Kikkawa, K., Kishimoto, A., Nakamura, Y. and Yanagida, H., *Solid State Ionics*, **91**, 131-36 (1996).
- 6) Hitchcock, D. C. and De Jonghe, L. C., *J. Am. Ceram. Soc.*, **66**, C204-05 (1983).
- 7) Nishikawa, T., Nishida, T., Okamoto, Y. and Inoue, K., *J. Ceram. Soc. Japan (Yogyo-Kyokai-Shi)*, **83**, 394-400 (1975) [in Japanese].