Transactions of the Materials Research Society of Japan 29 [8] 3383-3386 (2004)

Fabrication of Oriented β - Alumina from Porous Bodies by Slip Casting in a High Magnetic Field

Atsushi Honda, Yoshio Sakka*,Tohru S.Suzuki* and Yusuke Moriyoshi
Faculty of Technology, Hosei University, 3-7-2, Kajinocho, Koganei, Tokyo 184-0002, Japan
FAX:81-042-387-6381,e-mail:HONDA.Atsushi@nims.go.jp
*National Institute for Materials Science, 1-2-1, Sengen, Tsukuba, Ibaraki, 305-0047, Japan
Fax:81-029-854-2401,e-mail:SAKKA.Yoshio@nims.go.jp

Developing texture is one possible way for improving the electrical, chemical, mechanical and other properties of ceramics. We have reported that oriented α-alumina was obtained by slip casting in a high magnetic field and then sintering. β-alumina is well known as a sodium ion conductor used in a sodium-sulfur battery. β-alumina consists of spinel blocks and ion conducive planes. Since the direction of the ion conductive plane of polycrystalline β-alumina is random, the ionic conductivity of polycrystal is lower than that of a single crystal. The purpose of this study is to prepare oriented β-alumina to enhance the sodium ion conductivity. Oriented β-alumina was prepared by the following method: (1)oriented α-alumina green bodies were prepared by colloidal processing in a high magnetic field, (2)the oriented α-alumina green bodies were infiltrated with Na_2O and MgO, and (3)the oriented β-alumina bodies were synthesized by reaction sintering at 1600-1700℃. The reaction product and orientation of the β-alumina were confirmed by XRD.

Key words: β-alumina, High magnetic field, Slip casting, Infiltration

1. INTRODUCTION

The controlled development of texture is one possible way of improving the electrical, chemical, mechanical and other properties of ceramics.(Especially, the controlled orientation is required for a fine structure.)

In previous studies, we have reported that oriented α-alumina was obtained by slip casting in a high magnetic field and then sintering.[1] Recently we can easily use a high magnetic field such as 10T without liquid helium due to the development of superconducting magnets and magnet refrigerator technology. Alumina is known to be a feeble magnetic material and its magnetic susceptibility is very small. However, we have shown that textured alumina can be produced by slip casting under a high magnetic field followed by sintering.[1)・3)]

A well-dispersed suspension of powder is necessary for the effective utilization of the magnetic field, because a strong interaction between the agglomerated particles in a suspension prevents each particle in the suspension from rotating during application of a high magnetic field. We use colloidal processing that helps maximize the particles dispersion and prevent reagglomeration using ultrasonication and a polyelectrolyte.[4)]

β-alumina is a Na^+ ionic conductor and used in the Na-S battery. However, the polycrystalline β-alumina has conduction planes that are randomly orientated. Therefore, the ionic conductivity of this polycrystalline material is lower than that of a single crystal. If it is possible to prepare a texture developed β-alumina polycrystallite, β-alumina with a high ion conductively is expected.

The purpose of this study is the preparation of crystallite oriented β-alumina by infiltrating Na_2O and MgO into the pores of oriented α-alumina and then reaction sintering of α-alumina, Na_2O and MgO [5)・7)]

2. EXPERIMENTAL

The starting materials were two kinds of high-purity single crystalline α-alumina powders (Sumitomo Chemical Co., Ltd., AKP-50, average particle size of 0.2 μm and AKP-15, average particle size of 0.8 μm). Sodium formate (HCOONa, Kanto Chemical) and magnesium acetate tetrahydrate ($(CH_3COO)_2Mg \cdot 4H_2O$, Kanto Chemical) were used as the sources of the Na_2O and MgO, respectively.[5)・6)] Each α-alumina powder was dispersed in distilled water and the suspensions with 30vol% solids were prepared by adding the appropriate amount of poly (ammonium) acrylate (Toagosei Co., Ltd., A-6114)[1)・8)]

The suspensions were mixed with a magnetic stirrer and then ultrasonicated (Shimazu Inc., USB-600, 20kHz) for 10 min to homogeneously disperse the powder. The suspensions were degassed in a vacuum, then consolidated by slip casting. A high magnetic field of 10T was applied during the slip casting. The direction of the magnetic field was parallel to the casting direction. The prepared green bodies were calcined at 800℃ for 2h to provide enough strength for handling during the following infiltration treatment. An aqueous solution of

sodium formate and magnesium acetate, prepared in about a 80~90% saturated solution, were then infiltrated into the pores of the calcined α-alumina compacts. After this treatment, the solutions were concentrated and dried at 50℃. The alumina compacts containing Na^+ and Mg^{2+} were heated at the rate of 8℃/min to 800℃ for 2h in air. Na_2O is an element of β-alumina and promotes the densification by the liquid phase, and MgO increases the thermal stability of the β-alumina at high temperature. The obtained samples were embedded in the produced powdered alumina to prevent the loss of Na_2O and sintered at 1600℃ and 1700℃ for 2h in air.[9] The synthesis and orientation of the β-alumina were confirmed by X-ray diffraction (XRD). The X-ray conditions are 30KV and 300mA with Cu Kα radiation. The XRD data were analyzed by an orientation index using the three main peaks of (004), (110), and (220). The orientation index on each cut plane was calculated based on the XRD patterns that is defined as Eq. (1)

$$OI=F_{hkl}/F^0_{hkl} \quad (1)$$

where F_{hkl} is the intensity fraction of the (hkl) plane and defined by Eq.(2), and F^0_{hkl} is the standard data for the JCPDS value.

$$F_{hkl}=I_{hkl}/(I_{004}+I_{110}+I_{220}) \quad (2)$$

The orientation index indicates that the value of 1 shows that the sample is not oriented and that the value far from 1 shows that the sample is highly oriented.

3. RESULTS AND DISCUSSION

The textured porous α-alumina bodies of AKP-50 and AKP-15 were prepared by the slip casting of well-dispersed α-alumina suspensions followed by heating at 800℃. The porous alumina bodies were settled in the sources of Na and Mg at the initial compositions (molar ratio) of Na_2O: MgO: Al_2O_3 =1:0.1:0.25 and Na_2O: MgO: Al_2O_3=1:0.05:0.25. After infiltration and calcination, the molar ratio of Na_2O: MgO: Al_2O_3 for the calcined compacts were calculated from the weight loss. The results of the infiltrated amounts in the pores of the α-alumina compacts were Na_2O: MgO: Al_2O_3=0.12~0.2:0.019~0.024:1 when the starting solutions of the prepared Na_2O: MgO: Al_2O_3=1:0.1:0.25, and Na_2O: MgO: Al_2O_3 =0.1 ~ 0.14:0.004 ~ 0.007:1 when the starting solutions of the prepared Na_2O: MgO: Al_2O_3 =1:0.05:0.25.

Fig. 1 shows the XRD patterns of the AKP-50 and AKP-15 porous bodies that were infiltrated with the initial composition of Na_2O: MgO: Al_2O_3 =1:0.1:0.25 and reaction sintering at 1600℃. Each sample was confirmed to be β-alumina by the reaction of α-alumina and Na_2O, but α-alumina did remain. Fig. 2 shows the XRD patterns for the same infiltration conditions but with reaction sintering at 1700℃. It is noted that the amount of remaining α-alumina decreased. For each reaction temperature, when using the α-alumina of AKP-50 , the residual α-alumina deceased due to the increase in the reaction by using the small particle size.

From Figs. 1 and 2, it is seen that on the T plane perpendicular to the magnetic field, the diffraction peaks of the planes (004) and (008) (β-alumina) and (10$\bar{1}$0) (α-alumina) at the interplanar angle of 17.5° with the

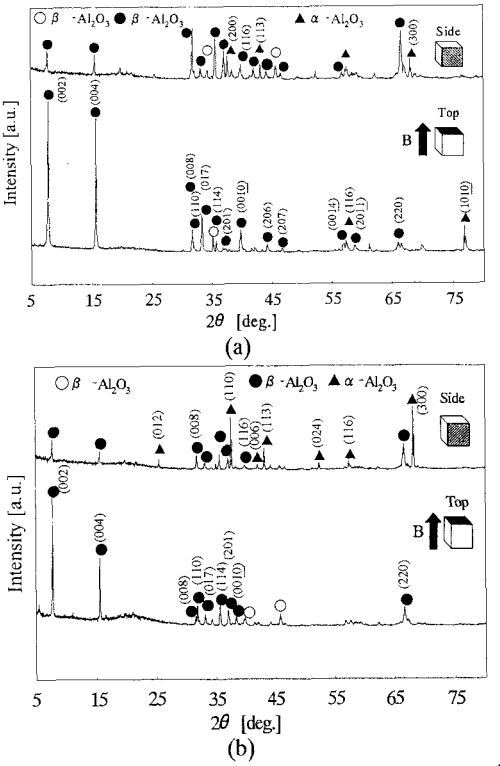


Fig. 1 XRD patterns of the products reaction-sintered at1600℃ for the oriented α -alumina green bodies infiltrated with Na_2O and MgO for the conditions of Na_2O:MgO=1:0.1(a)AKP-50 (b)AKP-15

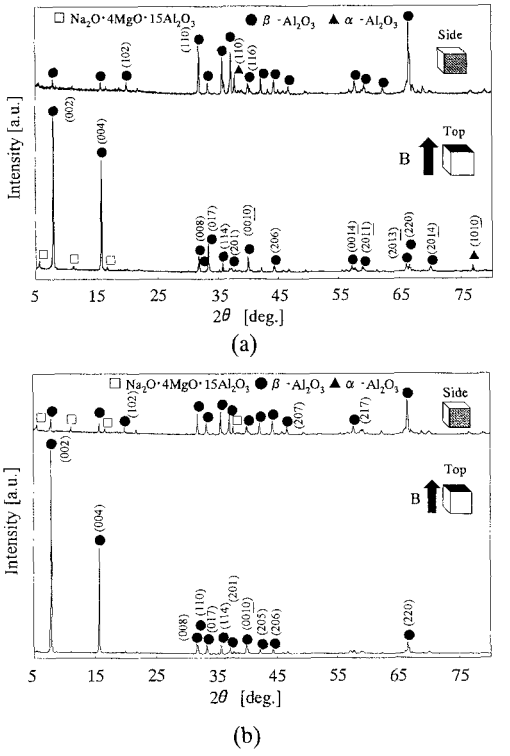
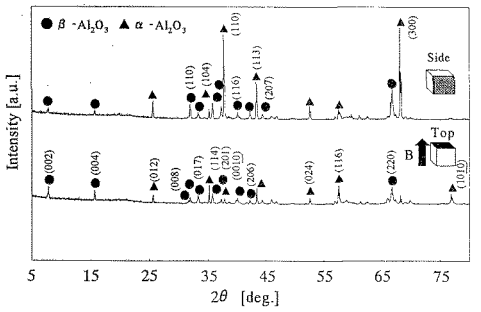


Fig. 2 XRD patterns of the products reaction-sintered at 1700℃ for the oriented α -alumina green bodies infiltrated with Na_2O and MgO for the conditions of Na_2O:MgO=1:0.1(a)AKP-50 (b)AKP-15

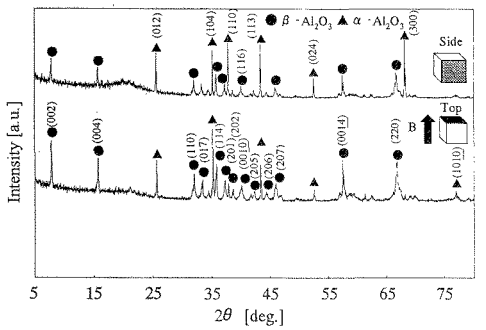
basal plane are very large. In contrast, on the S plane

parallel to the magnetic field, the peaks of the planes (110) and (220) (β -alumina) and (300) (α -alumina) are very large. These results indicate that a crystalline texture with the c axis perpendicular to the magnetic field had been developed by slip casting in a high magnetic field followed by reaction sintering.

Fig. 3 shows the XRD patterns of AKP-50 and AKP-15 that infiltrated with the initial composition of Na_2O: MgO: Al_2O_3 =1:0.05:0.25 and reaction sintering at 1600℃. Fig. 4 shows the XRD patterns for the same condition in Fig. 3 but with reaction sintering at 1700℃. Comparing Fig. 2 with Fig. 4, the diffraction peaks of the α -alumina in Fig. 4 are larger than those in Fig. 2. This result suggests that the infiltrated MgO could not stabilize β -alumina enough when the initial MgO=0.05. When the initial MgO=0.1, we have realized a sufficient β -alumina. β ℃ but was not obtained at 1700℃. This result was in accordance with the phase diagram of the $NaAl_2O$-Al_2O_3 system

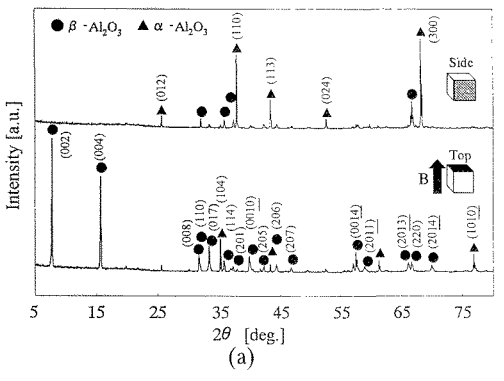


(a)

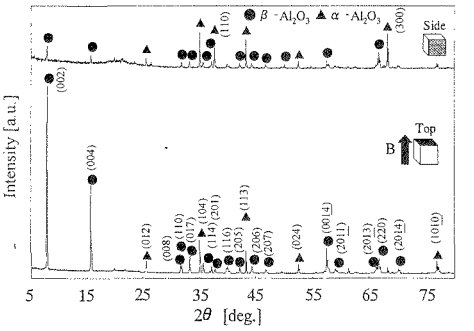


(b)

Fig.3 XRD patterns of the products reaction-sintered at 1600℃ for the oriented α -alumina green bodies infiltrated with Na_2O and MgO for the conditions of Na_2O:MgO=1:0.05(a)AKP-50 (b)AKP-15



(a)



(b)

Fig.4 XRD patterns of the products reaction-sintered at 1700℃ for the oriented α -alumina green bodies infiltrated with Na_2O and MgO for the conditions of Na_2O:MgO=1:0.05(a)AKP-50 (b)AKP-15)

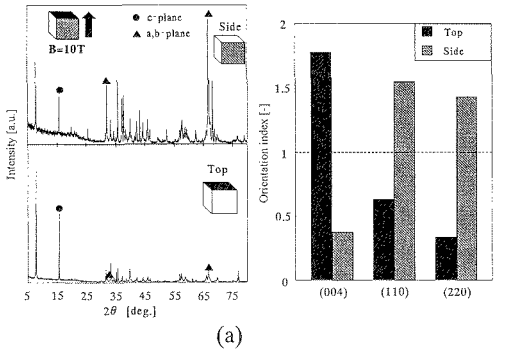
reported by DeVries and Roth [9]. According to the phase diagram, β ℃ as follows :

$\beta \rightarrow \beta + \delta$ -$Na_2O \cdot Al_2O_3$ $\xrightarrow{1580℃}$ β +liquid($Na_2O \cdot 1.86Al_2O_3$).[6)·12)]

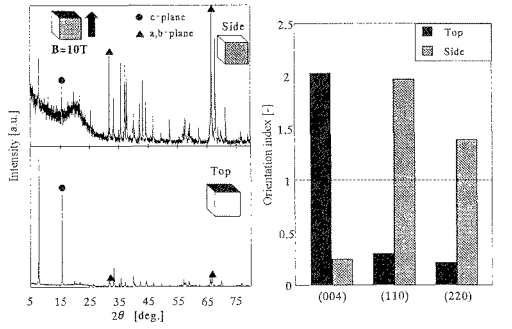
The result also suggests that infiltrated MgO could not completely stabilize the β

℃

and 1700℃ that are estimated from Eq. (1). On the T plane, the orientation index of the (004) plane is larger than 1, and in the S plane, the orientation index of the (110) plane and (220) plane is larger than 1. These results also indicate that the prepared β -alumina with the c axis perpendicular to the magnetic field has been developed.



(a)



(b)

Fig.5 XRD patterns and orientation indices of β -alumina sintered bodies prepared by AKP-50 (Na_2O:MgO=1:0.1) (a)1600℃(b)1700℃

The orientation index of samples sintered at 1700℃ is larger than that of 1600℃. This result suggests that the crystalline texture has significantly increased with the grain growth occurring at the higher sintering temperature.

Fig.6 and Fig.7 show SEM images of the β-alumina sintered at 1600℃ and 1700℃, respectively. The grain

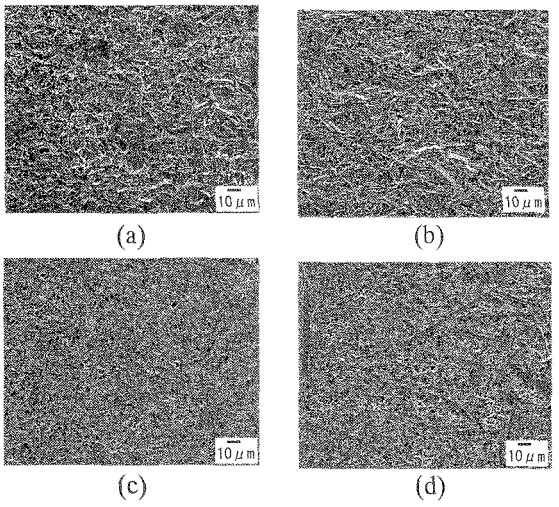


Fig.6 SEM images of sintered bodies at 1600 ℃ (Na_2O:MgO=1:0.1) (a)AKP-50 T plane (b)AKP-50 S plane (c) AKP-15 T plane (d) AKP-15 S plane

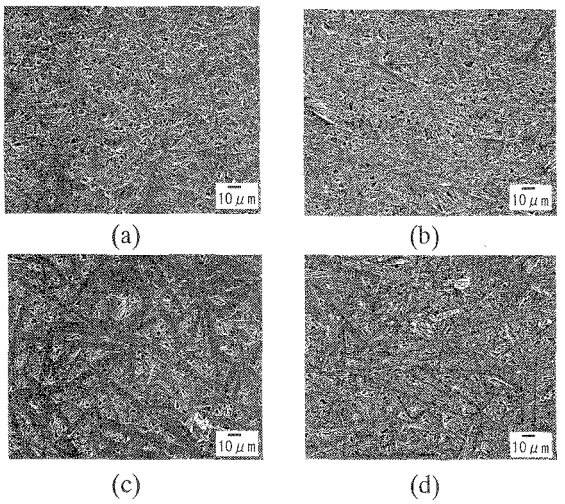


Fig.7 SEM images of sintered bodies at 1700 ℃ (Na_2O:MgO=1:0.1) (a)AKP-50 T plane (b)AKP-50 S plane (c) AKP-15 T plane (d) AKP-15 S plane

size of the sample sintered at 1700℃ is larger than that sintered at 1600℃. Based on these results, we confirmed that oriented β-alumina was prepared by reaction sintering from crystallite oriented porous α-alumina made by slip casting in a high magnetic field.

4. CONCLUSIONS

We have successfully prepared a textured β-alumina using infiltration treatment by Na^+ and Mg^{2+} followed by reaction sintering of the oriented porous α-alumina produced by slip casting in a high magnetic field.

(1) From the XRD patterns, we confirmed that β-alumina was prepared by the infiltration and reaction sintering.

(2) A textured β-alumina was confirmed by the orientation index calculated from the XRD patterns.

(3) The degree of orientation increased with an increase in the grain growth.

REFERENCES

1) T. S. Suzuki, H. Otsuka, Y. Sakka, K. Hiraga, and K. Kitazawa,: J. Jpn. Powder Powder Metal., 47, 1010 (2000)
2) K. Sassa, T. Morikawa, and S. Asai: J. Jpn. Inst. Met., 61,1283 (1997)
3) T. S. Suzuki, Y. Sakka and K. Kitazawa: J. Ceram. Soc. Japan., 109, 886 (2001)
4) F. F. Lange:J. Am. Ceram. Soc., 72, 3 (1989).
5) Y. Hirata and T. Izaku: J.Ceram. Japan., 101,2 68 (1993)
6) Y. Hirata, T. Izaku and Y. Ishihara: J. Mater. Res.,6, 585 (1991)
7) G. E. Youngblood and R. S. Gordon, Ceramurgia International, 4, 93 (1978)
8) Y. Sakka and T. S. Suzuki: Ceramic Data Book, 29, 158 (2001)
9) R. C. DeVries and W. L. Roth: J. Am. Ceram. Soc., 52, 364 (1969)
10) J. D. Hodge: J. Am. Ceram. Soc., 67, 183 (1984)
11) R. Stevens and J.G.P.Binner: J.Mater. Sci., 119, 695 (1984)
12) F. Vandecruys, E. Brauns, J. Vangrunderbeek and R. V. Kumar: Mat. Res. Bull., 35, 1153 (2000)

(Received October 8, 2003; Accepted March 12, 2004)