Paper

Characterization and Sintering of MgO-Doped β -Alumina Powders Prepared by the Hydrolysis of Metal Alkoxides

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金属アルコキシドの加水分解で合成された MgO 添加 β アルミナ粒子の性質と焼結

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Platelike β -alumina particles with an average size of 0.3 μm were formed at 1100°C from alkoxide-derived amorphous powder with the chemical composition (wt%) 9.3 Na₂O, 1.0 MgO, and balance Al₂O₃. No β'' -alumina formed from the gel of mixed alkoxides. The particle size of the β -alumina increased with increasing MgO content. Aggregation of the platelike particles in green compacts caused a tendency toward the formation of pores surrounded by flat planes, and pores of this type remained in the sintered samples. Densification of the β -alumina powders was inhibited by MgO, and Al₂O₃ dissociated from the β -alumina during sintering in an Na₂O-poor atmosphere. The Na₂O loss from green compacts in a semi-closed Pt container reached a constant value after a short sintering time and was suppressed in an Na₂O-rich atmosphere. In addition, the evaporation behavior of MgO, measured during sintering at 1600°C, followed Henry's law in the MgO-Al₂O₃ system of β -alumina.

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1. Introduction

Metal alkoxides have great potential as ceramic precursors, giving ceramic powders with high purity, fine size, and narrow particle size distribution.¹⁾⁻⁴⁾ Most of the alkoxides react with water at low temperatures to form hydroxides or oxides. The physicochemical properties of the resultant oxide or hydroxide powders are affected by the hydrolysis rate of the alkoxides (temperature and catalyst)^{5), 6)} and the molar ratio of alkoxide to water.^{7), 8)} Powder preparation through the use of alkoxides is especially effective for achieving high chemical homogeneity among particles in multicomponent systems.⁹⁾⁻¹¹⁾ In this method, uniformly small amounts of one metal source can be mixed easily with large amounts of a second metal source in the same atomic-length range.

The present study applies the alkoxide method to the preparation of β -alumina powders and investigates the physicochemical properties and sintering behavior of the derived β -alumina powders. Beta alumina with an ideal composition Na₂O·11 Al₂O₃ is well known as an efficient sodium-ion conductor that can be used as the solid

electrolyte of an Na-S battery.¹²⁾⁻¹⁹⁾ Previous attempts at sol-gel formation of β -alumina were reported by Tseng et al.²⁰⁾ and Yoldas and Partlow.²¹⁾ In the present study, mixtures of NaOC₂H₅, Al(O-*i*-C₃H₇)₃, and Mg(OC₂H₅)₂ in a refluxed benzene-ethyl alcohol solution were hydrolyzed slowly with water diluted with ethyl alcohol. Changes in phase, chemical composition, and particle size caused by heating the as-produced β -alumina powders were analyzed, and the sintering behavior of the heat-treated powders was studied at temperatures up to 1600°C.

2. Experimental procedure

2.1 Hydrolysis of mixed alkoxides

Three powders, with the chemical compositions shown in Table 1, were prepared by the hydrolysis of mixed alkoxides of NaOC₂H₅, Al(O-*i*-C₃H₇)₃, and Mg(OC₂H₅)₂. The alkoxides (32 to 35 g of Al(O-*i*-C₃H₇)₃ (>99 wt%), 2.1 to 2.3 g of NaOC₂H₅ (98.6 wt%), and 0.6 to 2.8 g of Mg(OC₂H₅)₂ (99.9 wt%)) were dissolved at room temperature into 250 ml of benzene (99.5 wt%) and 100 and 50 ml of ethyl alcohol (99.5 wt%),

Table 1. Chemical composition of as-produced powders from mixed alkoxides.

Powder	Na ₂ O(wt%)	MgO(wt%)	Al ₂ O ₃ (wt%)
A	9.34	0.99	89.67
	(Na ₂ O 0.163MgO 5.83Al ₂ O ₃)*		
B	9.74	2.05	88.22
	(Na ₂ O 0.324MgO 5.51Al ₂ O ₃)*		
C	6.52	3.29	90.19
	(Na ₂ O 0.776MgO 8.41Al ₂ O ₃)*		

* : molar ratio

respectively. These nonaqueous alkoxide solutions were stirred in a 500 ml flask and then refluxed at 70° to 72°C for 4 h under a 200 ml/min flow of dried N₂ to ensure mixing. After 4 h of reflux, enough distilled water (≈ 11.4 g, pH 5) to cause the formation of hydroxides was diluted with 90 ml of ethyl alcohol and added to the refluxed benzene-ethyl alcohol solution at a rate of 2 ml/min. The reflux was continued for 4 h to complete the hydrolysis of the mixed alkoxides. The as-produced powders in the flask then were removed from the solution, by evaporating the solvent on a hot plate at 188°C, and heat-treated in a covered Pt container at 1000° to 1400°C for 3 h in air. Phases in the as-produced and heat-treated powders were identified by X-ray diffraction (Cu K α , Model No.2013, Rigaku Corp., Tokyo, Japan) at a scanning rate of 2°/min. The chemical compositions of the powders were examined by X-ray fluorescence (Rh) at 50 kV (System 3080-E, Rigaku Corp., Tokyo, Japan). About 300 mg of the powders were mixed with 3 g of Li₂B₄O₇ and the mixture melted to form 35-mm-diameter glass spheres, which were chemically analyzed for Na, Al and Mg content. The shape and structure of the particles were observed by transmission electron microscopy at 200 kV (H-700H Type, Hitachi Ltd., Tokyo, Japan). The as-produced and heat-treated powders were then ultrasonically dispersed in water, settled onto a colloidal membrane (amyl acetate), and finally coated with sputtered carbon for TEM observation. The powders were also examined by scanning electron microscopy at 75 kV.

2.2 Sintering of MgO-doped β -alumina powders

The heat-treated powders were compacted into disks 9 to 10 mm in diameter and 2 to 3 mm thick by isostatic pressing at 294 MPa after preliminary uniaxial pressing at 37 MPa. Green densities

were calculated from measured dimensions (± 0.01 mm) and compact weight. These green compacts were embedded into the as-produced powders in a covered Pt container (15 by 13 by 8 mm) and heated in air at 5°C/min to above 1500°C. Bulk densities after sintering for 10 to 120 min were measured by the Archimedes method using distilled water. The relative densities of the green and sintered samples for series A, B and C (Table 1) were calculated from the true densities 3.46, 3.45, and 3.41 g/cm³ of MgO-doped β -alumina powders with the chemical compositions Na₂O·0.189 MgO·6.23 Al₂O₃, Na₂O·0.315 MgO·5.72 Al₂O₃, and Na₂O·0.817 MgO·9.02 Al₂O₃, respectively, that were formed by heat treatment at 1200°C for 3 h. The phases and chemical compositions of the sintered samples were investigated as described previously (see Section (2.1)). The samples were next polished and etched at 70°C for 10 to 120 s by a 17% H₃PO₄ aqueous solution; the microstructures were observed by SEM.

3. Results

3.1 Phases and chemical compositions of heat-treated powders

All as-produced powders with the chemical compositions shown in Table 1 were amorphous under X-ray diffraction. Figure 1 shows the phase change of powder A with heating. The as-produced powders changed to mixtures of β -alumina, γ -alumina, and mullite-type alumina at 1000°C, and no phase but that of β -alumina formed above 1100°C. It has been reported^{(22)–(24)} that mullite-type alumina (i) is a metastable phase that appears in powders prepared through gelation from an aqueous solution containing Na and Al and (ii) forms from γ -alumina and Na adsorbed onto the defect spinel structure and decomposes to β -alumina at high temperature ($\sim 1200^\circ\text{C}$). As shown in Fig. 1, phase relations for

Fig. 1. Phase change with heating of the as-produced powder A with the composition shown in Table 1. The β , γ and m mean β -alumina, γ -alumina and mullite type alumina, respectively.

Fig. 2. SEM and TEM pictures of the as-produced powder A (a, b) and powders heat-treated at 1000°C (c, d), 1100°C (e, f) and 1400°C (g, h).

Fig. 3. TEM pictures and electron diffraction patterns of the powders A (a, a'), B (b, b') and C (c, c') heat-treated at 1200°C.

the powders heat-treated at 1000°C and thermal stability of the mullite-type alumina and γ -alumina were in accordance with findings from previous studies.²²⁾⁻²⁴⁾ When powders B and C were heat-treated at 1200°C, only β -alumina formed. Ritter and Frase²⁵⁾ reported that at 1100°C alkoxide-derived powders in the system $\text{Na}_2\text{O-MgO-Al}_2\text{O}_3$ with β'' -alumina compositions yield a "distorted solid solution of β -type structure" that is not produced by a solid state reaction and that Mg substitution in the Al-O layers is ordered in the β'' structure but random in the solid solution β structure. No β'' -alumina formed in heat-treated

powders A, B, and C, in agreement with observations by Ritter and Frase²⁵⁾ and Hodge.²⁴⁾ The molecular mixing of Na, Al, and Mg through alkoxide media tends to produce the β structure rather than the β'' structure. The actual density (3.41 to 3.46 g/cm³) of β -alumina particles formed at 1200°C was higher than the reported value (3.24 g/cm³)²⁶⁾ for β -alumina without MgO; this higher density may be related to the distorted solid solution β structure.

Changes in the chemical composition of the as-produced powders (A, B, and C) with heating were examined by X-ray fluorescence. The molar

ratio of MgO to Al_2O_3 was nearly constant up to 1400°C . At higher temperatures, however, MgO evaporation was detected, as described in detail in section (3.4). The evaporation of Na_2O occurred above 1000°C , and 3.7 to 6.7% of the Na_2O was lost at 1200°C .

3.2 Shape and size of β -alumina particles

Figure 2 shows SEM and TEM photos of as-produced and heat-treated powder A. As-produced amorphous powders consisting of sub-micrometer-sized agglomerates shown in Fig. 2 (a) changed to platelike β -alumina with an average particle size of $0.3\ \mu\text{m}$ after heat-treatment at 1100° to 1400°C . Those particles shown in Figs. 2(f) and (h) provided spot patterns of electron diffraction, indicating single crystal β -alumina. In addition, the β -alumina particles experienced little grain growth in the temperature range of 1100° to 1400°C . In the powders heated at 1000°C , wedge-type crystals that formed in the spherical agglomerate powders of γ -alumina appeared to be mullite-type alumina. Figure 3 shows the compositional dependence of shape and structure for β -alumina particles produced at 1200°C . Powders B and C revealed fine particles (smaller than about $0.08\ \mu\text{m}$), in addition to platelike β -alumina; the electron diffraction patterns of the single crystals corresponded to those of the platelike particles. The average size of the platelike β -alumina particles in powder B was $0.6\ \mu\text{m}$, larger than that in powder A; the particle size of the β -alumina thus increased with increasing MgO content. Powder C, with the highest MgO content, contained the highest concentration of fine particles.

3.3 Sintering of alkoxide-derived β -alumina powders

3.3.1 Effect of calcination temperature

Green compacts of heat-treated powders A, B, and C were sintered in an Na_2O -rich atmosphere

Fig. 4. Densification behavior with sintering temperature for the powder compact A, covered with the as-produced powder A.

by embedding the green compacts into the as-produced powders in a covered Pt container. Figure 4 illustrates densification behavior as a function of sintering temperature for powder compact A, with green densities of 51 to 59%, covered with as-produced powder A. The higher green density of the powder heat-treated at 1000°C was due to greater weight gain from moisture absorbed into the mixed phases (γ , mullite-type, and β). That is, the weight loss of the compacts after sintering at 1500°C was 13.6% for the powder heat-treated at 1000°C and 4.1–5.8% for the powders heat-treated at 1100° to 1400°C before sintering. Water absorbed into powder A after heat-treatment at 1000° to 1400°C was also detected by IR spectroscopy, which showed the maximum amount of absorbed water in the powder heat treated at 1000°C .^{27),28)} On the other hand, the ratios of the measured weight loss against the weight loss calculated from Na_2O and MgO content after sintering at 1600°C for 2 h were 0.7–1.2 for powders B and C heat-treated at 1200°C , and 1.8–3.2 for powder A heat-treated at

Fig. 5. Microstructures of β -alumina sintered at 1600°C for 20 min (a) and 120 min (b) from the powder A calcined at 1200°C .

1200°C. These results suggest that the heat-treated powders with higher MgO content (powders B and C) absorb less moisture, so that most of their weight loss during sintering corresponds to the evaporation of Na_2O and MgO.

As shown in Fig. 4, relative densities of sintered samples were almost independent of the calcination temperatures of the powders. This result suggests that the molar ratio of Na_2O to Al_2O_3 in the range 1:5.6 to 1:7.0 for the heat-treated powders does not affect densification rate. Density of the sintered sample related closely to the calcination temperature when particle shape, size, and green density of the heat-treated powders were similar (Fig. 2). Densities after sintering at 1570° and 1600°C were lower than those extrapolated from the data at lower temperatures. Increased density from suppressing Na_2O loss during sintering was expected for sintering times below 2 h at 1600°C, but the actual experimental results showed a small increase of 2 to 3% in relative density after 10 to 40 min of sintering. The microstructures of β -alumina sintered at 1600°C are shown in Fig. 5. The SEM photos seem to indicate that the low relative density (<90%) is mainly due to the aggregation of platelike particles, forming pores surrounded by flat planes, and which could not be eliminated by sintering. The pores formed between non-oriented platelike particles would be more difficult to eliminate than those between spherical particles at a given sintering temperature.

3.3.2 Effect of MgO content

Figure 6 shows the effect of the MgO content of powders heat-treated at 1200°C on densification at 1600°C. Those green compacts were embedded in as-produced powders A, B, and C, respectively, and sintered for 2 h. The relative density apparently decreased with the increasing MgO

Fig. 6. Effect of MgO content of the powders calcined at 1200°C on the densification at 1600°C. Green compacts were covered with the as-produced powders A, B and C respectively in a Pt container and sintered for 2 h.

content of the heat-treated powders. In the sintered samples from powders of 2.0 wt% MgO covered with powders B and C, and in the sintered samples from powder of 3.3 wt% MgO covered with powder C, α -alumina formed in addition to β -alumina. The lower sinterability of β -alumina powders with high MgO content was also reported by Kennedy and Sammells.²⁹⁾ The higher green density with higher MgO content can be explained by powder packing in the bimodal particle-size system, which suggests the homogeneous distribution of fine particles in the spaces among the larger platelike β -alumina particles.³⁰⁾⁻³²⁾

Figure 6 also represents the influence of the chemical composition of the as-produced powders covering the green compacts. Higher sintered density was achieved with cover powder A than with powder B or C. This result is related to the partial pressure of the NaO gas released from the cover powder during sintering in the Pt container. As-produced powder A lost more Na_2O with heating than did B or C. This Na_2O -rich atmosphere suppressed the evaporation of Na_2O from the green compacts during sintering and increased the densification rate; producing the Na_2O -rich atmosphere is thus very important to the sintering of β -alumina. Similar results were also reported by Francis et al.³³⁾

Figure 7 summarizes the $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ ratio of the sintered samples as a function of relative density. Figure 6 shows that green compacts of β -alumina powders with lower MgO content reached higher density in an Na_2O -rich atmosphere, and that the evaporation of Na_2O from the compacts during sintering was suppressed by increasing the partial pressure of NaO gas in the Pt container. These conclusions allow the following interpretation of Fig. 7. Since the low-density porous compact has a high surface area, its $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ ratio would decrease during sintering because of greater Na_2O loss by evapor-

Fig. 7. Relation between chemical compositions and densities of samples sintered at 1600°C.

ation. The amount of Na_2O lost from the compacts of course depends on the partial pressure of NaO in the atmosphere. The molar ratio of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ for the samples thus increased with higher relative density.

3.4 Chemical compositions and phases of the sintered samples

The relation between chemical composition and phase was studied mainly for the samples sintered at 1600°C . Loss of Na_2O from the powder compacts occurred mostly with short sintering time (<10 min at 1600°C) or during heating to sintering temperature. The vapor pressure of NaO gas thus should reach equilibrium within a relatively short time in the covered Pt container

Fig. 8. Mol% of MgO in the $\text{MgO}-\text{Al}_2\text{O}_3$ system of as-produced powders and amount of MgO lost during sintering at 1600°C for 2h.

Fig. 9. Chemical compositions and phases of compacts sintered at 1600°C and powders heat-treated at 1200°C . Region I and II illustrate the formation region of β -alumina from alkoxides at 1400°C ²⁵⁾ and by solid state reaction at 1700°C ,³⁴⁾ respectively. The compositions a, b, c, d, e and f correspond to β -alumina ($\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$), β'' -alumina without MgO ($\text{Na}_2\text{O} \cdot 5.33 \text{Al}_2\text{O}_3$), β'' -alumina with MgO ($\text{Na}_2\text{O} \cdot \text{MgO} \cdot 5 \text{Al}_2\text{O}_3$), β''' -alumina ($\text{Na}_2\text{O} \cdot 3 \text{MgO} \cdot 7 \text{Al}_2\text{O}_3$), β''' - Al_2O_3 ($\text{Na}_2\text{O} \cdot 4 \text{MgO} \cdot 15 \text{Al}_2\text{O}_3$) and spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$), respectively.

containing the green compacts and cover powders; that is, the covered Pt container should be a semi-closed system. Evaporation of MgO from the compacts was also detected, increasing with sintering time. Figure 8 shows the amount of MgO lost after sintering at 1600°C for 2h as a function of mol% of MgO in the system $\text{MgO}-\text{Al}_2\text{O}_3$ for the as-produced powders. The high linearity in Fig. 8 suggests Henry's law concerning the evaporation of MgO . The chemical composition of the cover powder had little effect on MgO evaporation.

Figure 9 summarizes the relation of chemical composition and phase for compacts sintered at 1600°C for 2h and powders heat-treated at 1200°C for 3h and shows the formation region for β -alumina from alkoxides at 1400°C as postulated by Ritter and Frase.²⁵⁾ The present study showed a good agreement with previous studies for X-ray diffraction analysis. The β -alumina region in Fig. 9 is located inside the triangle represented by dashed lines, based on the spinel block structure. The formation of β -alumina by solid state reaction at 1700°C is also presented.³⁴⁾ A comparison of both reactions indicates that the hydrolysis of mixed alkoxides yields a larger formation of β -alumina.

4. Discussion

The relation between phase and chemical composition of samples in the system $\text{Na}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3$ heated at 1100° to 1600°C was analy-

Fig. 10. $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio dependence of concentration of Al vacancy (x) and substituted amount of Mg for Al (y) in the assumed equation of β -alumina solid solution, $\text{Na}_{2+3x+y}\text{Mg}_y\text{Al}_{22-x-y}\text{O}_{34}$.

zed assuming the β -alumina solid solution formula $\text{Na}_{2+3x+y}\text{Mg}_y\text{Al}_{22-x-y}\text{O}_{34}$, where x and y indicate the concentration of Al vacancies and the amount of Mg substituted for Al in the spinel block of β -alumina, respectively. This solid solution equation gives the composition of ideal β -alumina $\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$ for $x=y=0$, ideal β'' -alumina $\text{Na}_2\text{O} \cdot 5.33 \text{Al}_2\text{O}_3$ for $x=0.667$ and $y=0$, and ideal MgO-doped β'' -alumina $\text{Na}_2\text{O} \cdot \text{MgO} \cdot 5 \text{Al}_2\text{O}_3$ for $x=0$ and $y=2$.³⁵⁾ Figure 10 shows the values x and y calculated from the chemical compositions of heat-treated powders and sintered samples, as a function of the molar ratio of Na_2O to Al_2O_3 . Alpha alumina was not identified by X-ray diffraction above the value of 0.0909 for the $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ ratio for ideal β -alumina. The minus sign before the x represents the precipitation of excess MgO above the solubility limit at $x=0$ in the solid solution equation. This excess MgO may form an $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel, especially in the samples with an $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ ratio lower than 0.0909.^{36), 37)} No MgO or $\text{MgO} \cdot \text{Al}_2\text{O}_3$ was detected by X-ray diffraction when MgO content was low (0.8 to 3.3 wt%) in the heat-treated powders or the sintered samples.

Figure 10 also suggests the linear relation between the $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ ratio and the Al vacancy concentration. Extrapolation of x to 0 along the line for the powder A indicates the chemical composition $\text{Na}_2\text{O} \cdot 0.167 \text{MgO} \cdot 10.0 \text{Al}_2\text{O}_3$, which contains no Al vacancy and ~ 0.6 wt% MgO. Figure 10 could be used to evaluate the structural stability of β -alumina against Na_2O loss during sintering. The MgO-rich β -alumina would dissociate MgO more easily, by small Na_2O loss, than the MgO-poor β -alumina with the same $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ ratio. The MgO-poor β -alumina with high Na_2O content has a high structural stability against Na_2O loss that is controlled by its Al

vacancy concentration.

Figure 11 illustrates the densities of samples sintered at 1600°C for 2h as a function of the calculated amount of excess MgO above the solubility limit ($x=0$). The plotted data suggest that densification of β -alumina is inhibited by MgO, which cannot dissolve into the β -alumina during sintering. The excess MgO could be decreased by suppressing Na_2O loss from the compacts during sintering (Figs. 6 and 10); that is, an Na_2O -rich atmosphere is needed to prevent the loss of Na_2O and the precipitation of MgO from β -alumina. Some of the MgO evaporates during sintering, but the evaporation rate of the MgO is lower than that of the Na_2O or the rate for the dissociation of MgO from the β -alumina. As a result, the MgO remaining in the compacts decreases the densification rate. Alpha alumina that forms in the samples by Na_2O evaporation would also inhibit β -alumina densification.

5. Summary and conclusions

Alkoxide-derived amorphous powder with the composition $\text{Na}_2\text{O} \cdot 0.163 \text{MgO} \cdot 5.84 \text{Al}_2\text{O}_3$ (~ 1 wt% MgO) changed to platelike single crystals of β -alumina with an average size of $0.3 \mu\text{m}$ at 1100°C through γ -alumina and mullite-type alumina phases. No change was observed in the shape and size of β -alumina particles during heat treatment at 1100° to 1400°C for 3h. The particle size of the β -alumina increased with increasing MgO content. No β'' -alumina formed in the system Na_2O -MgO- Al_2O_3 from alkoxides, in contrast to the solid state reaction. The higher partial pressure of NaO gas in the sintering atmosphere effectively increased the density of sintered sample. In an Na_2O -poor atmosphere, Na_2O evaporation from the compacts caused the precipitation of MgO and Al_2O_3 from the β -alumina. This precipitation of second phases in the β -alumina compacts inhibited densification. Evaporation of MgO from the compacts was also measured at a sintering temperature of 1600°C . The amount of lost MgO followed Henry's law in the MgO - Al_2O_3 system of β -alumina. The particle shape of the β -alumina plays an important role in the densification behavior during sintering. Aggregation of platelike particles caused a tendency toward the formation of pores surrounded by flat planes in the green compacts; pores of this type remained in the sintered samples. Control of both the shape of the starting particles and powder packing in the green compacts is important to producing a fully dense β -alumina body at low sintering temperature.³⁸⁾

Fig. 11. Densities of samples sintered at 1600°C for 2h as a function of calculated amount of excess MgO above the solubility limit in MgO-doped β -alumina solid solution.

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