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Synthesis and mechanical properties of porous alumina from anisotropic alumina particles

S. Hashimoto [a,*], S. Horita [a], Y. Ito [a], H. Hirano [b], S. Honda [a], Y. Iwamoto [a]

[a] *Department of Environmental and Engineering Materials, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya-shi 466-8555, Japan*
[b] *Towa Refractory Engineering, Co., Ltd., Research and Development Division, 21-1 Nakaedo, Kani-shi 509-0202, Japan*

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Abstract

A porous alumina body was synthesized from anisotropic alumina particles (platelets). The uniaxial pressure in fabricating the green compact body had an influence on the relative density of the alumina body after heating. When green compacts, which had been uniaxially pressed at 1 and 3 MPa, were heated at 1400 °C for 1 h, the relative densities of the resulting alumina bodies were 25.0% and 35.5%, respectively. The compressive strength of compacts that were uniaxially pressed at 1 and 3 MPa were 0.8 and 4.3 MPa, respectively. In an attempt to increase the compressive strength of these porous alumina bodies, aluminum nitrate and magnesium nitrate solution treatments were performed, followed by reheating to 1400 °C for 1 h. When a 0.5 mol/l aluminum nitrate solution was used, the compressive strength of the porous alumina body uniaxially pressed at 1 MPa changed from 0.8 MPa (without solution treatment) to 1.5 MPa. Furthermore, when 0.1 mol/l magnesium nitrate solution was used, the compressive strength of the porous alumina increased to 1.7 MPa. Thus, solution treatment of the porous alumina body had a strong positive effect on its mechanical strength.

Keywords: A. Powder-solid state reaction; B. Platelets; C. Strength; D. Al_2O_3; Insurators

1. Introduction

Porous ceramics have many desirable properties such as their light weight, high chemical stability, and low thermal conductivity, so that their application is extending into various fields, such as environmental, energy, biotechnology, and others. Several methods for the fabrication of porous alumina ceramics have been studied for a variety of applications.[1–5] Recently, to enable energy savings, porous alumina ceramics have been proposed for use as high temperature insulators, for instance, as a porous clinker in steel refractories. Such refractories are able to easily maintain a high temperature in the furnace, which leads to lowered energy cost of making steel. A castable refractory requires alumina porous clinkers with approximately 75% porosity (1.0×10^3 kg/m^3), since castable materials are mixed with water, and then finish forming inside the steel furnace. In addition, the porous clinker requires some mechanical strength. In order to obtain a uniform porous structure, high porosity, and sufficient mechanical strength, uniform anisotropic alumina particles (platelet in shape) should be suitable. Until now, scientific reports of fabrication methods based on alumina platelets have been limited.[6–8] However, the authors have developed a novel synthetic method for alumina platelet particles.[9,10] These new alumina platelet particles were employed for the fabrication of novel porous alumina ceramics.

In this study, a porous alumina body composed of anisotropic alumina particles (platelets) was fabricated using a simple heating method. Initially, the effect of varying the uniaxial pressure applied to the green compact body on the porosity and mechanical properties of the resulting porous alumina was studied. Since it is very difficult to fabricate porous bodies from only alumina platelet particles, fine alumina particles were added as a sintering additive and corn starch was added as a pore foaming agent. Furthermore, in order to strengthen the porous alumina, an aluminum nitrate solution or magnesium nitrate solution treatment was performed on the resulting porous alumina body. The strengthening mechanism of the porous alumina will be discussed in a later section.

* Corresponding author.
E-mail address: hasimoto.shinobu@nitech.ac.jp (S. Hashimoto).

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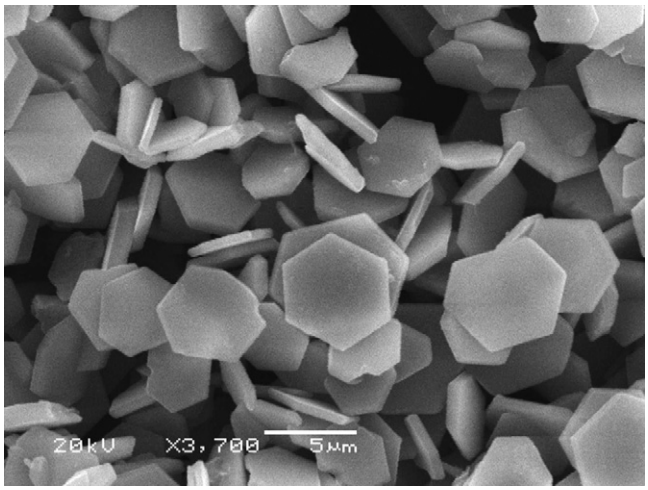

Fig. 1. SEM micrograph of the formed α-alumina platelets using the sodium sulfate flux method.

2. Experimental procedure

The starting α-alumina platelets were prepared using a flux method reported by Hashimoto and Yamaguchi.[10] In short, γ-alumina was obtained by heating $Al_2(SO_4)_3$ at 900 °C for 3 h with Na_2SO_4 flux. The resulting 5–10 μm diameter and 5–10 aspect ratio platelets are shown in Fig. 1. The purity of the α-alumina platelets was over 99.9%. Fine alumina was used as a sintering additive, with purity and diameter of 99.9% and 0.14 μm, respectively. Since anisotropic particles (platelets) were used, approximately 10 mass% corn starch, 10 μm in diameter, was added as a pore foaming agent. Subsequently, the resultant powder mixture consisting of 85 mass% α-alumina platelets, 5 mass% fine alumina, and 10 mass% corn starch were uniaxially pressed at 1–3 MPa to a green compact 20 mm × 20 mm × 10 mm in size. A porous alumina body was synthesized by heating the compact at 1400 °C for 1 h in air. In order to strengthen the porous alumina body, it was immersed in an aluminum nitrate solution of either 0.25 or 0.50 mol/l for 30 min in vacuum. The aluminum nitrate solution was prepared by first dissolving aluminum isopropoxide (regent grade: $Al[OCH(CH_3)_2]_3$) in hot water (80 °C), and then nitric acid was added to the solution in order to reach in pH = 2 and precipitate aluminum hydrate sol. After solution treatment and drying for 24 h at room temperature, the resultant compact was reheated at 1400 °C for 1 h. As an alternative solution treatment, a magnesium nitrate solution made from magnesium nitrate, 6-hydrate (regent grade) of 0.10 or 0.25 mol/l was used. Other process details were the same as those used with the aluminum nitrate solution. The crystal phases of the porous alumina were examined using X-ray diffraction (XRD), and its microstructure was observed using scanning electron microscopy (SEM). The compressive strength of the porous alumina was also examined. Several samples were used to determine the compressive strength for each set of preparation conditions. In compressive strength figures, the error bar means the maximum and minimum value of the relative density and the compressive strength. Black and white dots inside the error bars mean an average value of the relative density and the compressive strength, respectively.

3. Results and discussion

3.1. Normal heating fabrication

Fig. 2 shows the changes in the relative density and compressive strength of the fabricated porous alumina after heating at 1400 °C for 1 h with varying uniaxial pressure during fabrication of the green compact. Both the relative density and compressive strength of the porous alumina body increased with increasing uniaxial pressure. However, the compressive strength of this porous alumina body with high porosity seems not to have an influence on the direction of uniaxial pressing at the range 1–3 MPa. That is, the compressive strength with parallel and perpendicular to the direction of pressing almost showed the same value. In this case, the compressive strength with perpendicular to the direction of pressing was performed. At 1 MPa uniaxial pressure, the average relative density and the compressive strength of the porous alumina body were 25.0% and 0.76 MPa, respectively. In contrast, at 3 MPa, the relative density and compressive strength increased to 36.0% and 4.2 MPa, respectively. Thus, the uniaxial pressure had a pronounced effect on the compressive strength of the porous alumina body. However, the relative density should be maintained, at approximately 25% (porosity 75%) for use in a steel-making refractory as a clinker. Therefore, the uniaxial pressure was fixed at 1 MPa in subsequent experiments.

3.2. Solution treatment for further strengthening

In order to strengthen the porous alumina body while maintaining a high porosity, solution treatment was performed. The fabricated porous alumina body with approximately 75% porosity was immersed in an aluminum nitrate solution or magnesium nitrate solution of various concentrations for 30 min in a vacuum. Subsequently, the porous alumina body was removed from the solution and dried. After drying for 24 h at room temperature, the

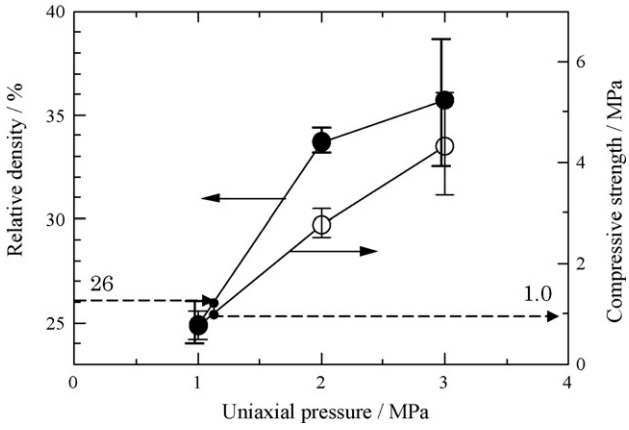

Fig. 2. Change of the relative density and compressive strength of the fabricated porous alumina versus uniaxial pressure during fabrication of the green compact, after heating at 1400 °C for 1 h.

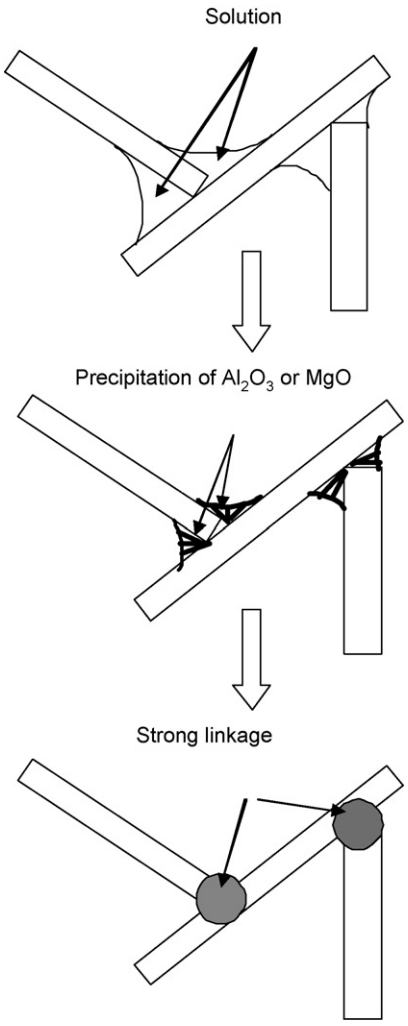

Fig. 3. Schematic drawing of the strengthening mechanism of the porous alumina body during solution treatment.

resultant porous body was reheated to 1400 °C for 1 h. During this reheating process, increased linkage among platelets led to a higher strength. Thus, the mechanical strength of the porous alumina body increased, while maintaining a high porosity. Fig. 3 shows a schematic drawing of the strengthening mechanism of the porous alumina body during solution treatment.

3.2.1. Aluminum nitrate solution treatment

Fig. 4 shows the changes in relative density and compressive strength of the porous alumina body with varying concentration of aluminum nitrate solution after reheating to 1400 °C for 1 h. The relative density of the porous alumina body after reheating increased slightly to 25.8%. On the other hand, the compressive strength increased with increasing concentration of aluminum nitrate solution. With 0.5 mol/l aluminum nitrate solution, the compressive strength of the porous alumina body reached 1.5 MPa. Compared to the porous alumina body with no aluminum nitrate solution treatment, the strength was improved by 50%, as shown in Fig. 2. Furthermore, according to Fig. 2, for a relative density of the porous alumina body of approximately 26%, the compressive strength would be estimated as 1.0 MPa,

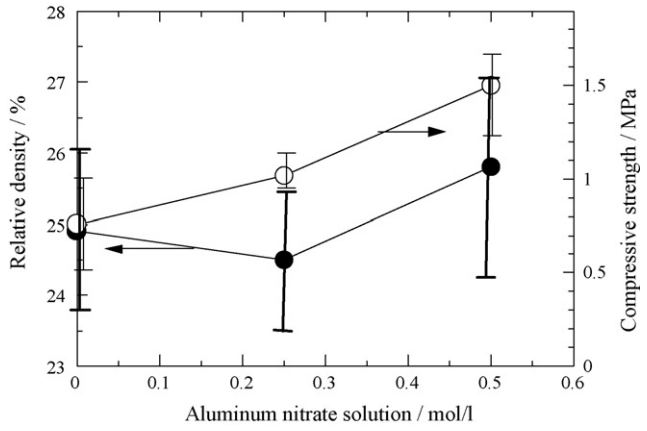

Fig. 4. Change of the relative density and compressive strength of the porous alumina body versus concentration of aluminum nitrate solution, after reheating at 1400 °C for 1 h.

based on the ideal line (indicating doted line in Fig. 1). Thus, the aluminum nitrate solution treatment increased the strength of the porous alumina body. When aluminum isopropoxide dissolved in hot water, and then nitric acid was added to the solution, an aluminum hydrate sol formed, according to the following hydrolysis Eq. (1):

$$Al[OCH(CH_3)_2]_3 + 3H_2O \rightarrow Al(OH)_3 + 3CH(CH_3)_2OH \quad (1)$$

Upon heating, the formed $Al(OH)_3$ gel remaining at points of contact between platelets, as shown in Fig. 3, changed to Al_2O_3 crystal to strongly link the alumina platelets.

In addition, in the case of 0.5 mol/l aluminum nitrate solution treatment, the relative density increased slightly. Precipitation of alumina during reheating had an influence on this densification of the aluminum body.

3.2.2. Magnesium nitrate solution treatment

Fig. 5 shows the change in relative density and compressive strength of the porous alumina body with varying concentration of magnesium nitrate solution after reheating to 1400 °C for

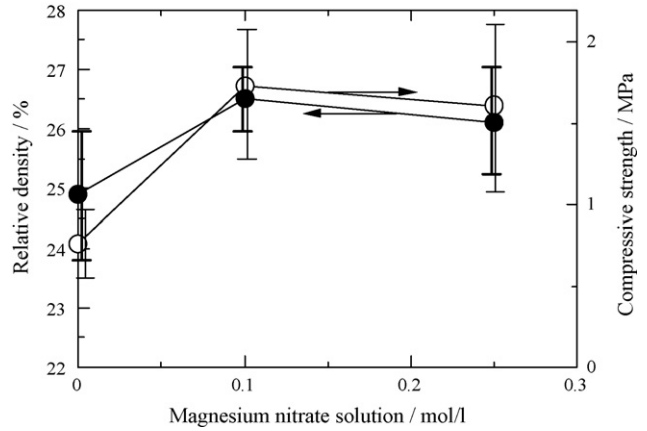

Fig. 5. Change of the relative density and compressive strength of the porous alumina body versus concentration of magnesium nitrate solution, after reheating at 1400 °C for 1 h.

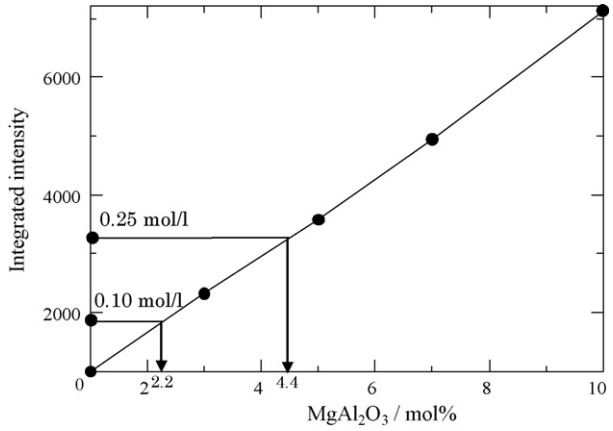

Fig. 6. Calibration curve based on various molar ratios of spinel and alumina using integrated intensity of the strongest refrection from the 303 lattice plane of spinel.

1 h. When 0.10 mol/l magnesium nitrate solution was used, the relative density of the porous alumina body was 26.5%, and its compressive strength increased to 1.7 MPa. With 0.25 mol/l magnesium nitrate solution, the relative density and compressive strength maintained almost the same values: 26.1% and 1.6 MPa, respectively. When magnesium nitrate solution was used, a new crystal phase of magnesium aluminum spinel ($MgAl_2O_4$) was detected in the porous bodies from both 0.10 and 0.25 mol/l magnesium nitrate solution treatment. The formation reaction of the spinel was thought to be as follows:

$$2Mg(NO_3)_2 + 2Al_2O_3 \rightarrow 2MgAl_2O_4 + 4NO_2 + O_2 \quad (2)$$

In order to estimate the amount of spinel formed in the porous alumina body, a calibration curve based on the various molar ratios of spinel and alumina was prepared using the integrated intensity of the strongest refrection from the 303 lattice plane of spinel (see Fig. 6). When 0.10 or 0.25 mol/l of magnesium nitrate solution was used, the integrated intensity was calculated at the point shown in Fig. 6, thus it was concluded that approximately 2.2 or 4.4 mol.% of spinel was included in the porous alumina body, respectively. The formation of spinel with 2.2 mol.% helped increase the compressive strength of the porous alumina body. However, further formation of spinel, as observed when using 0.25 mol/l magnesium nitric solution, did not improve the mechanical properties. Generally, the formation of spinel (ID (intrinsic density): 3.58×10^3 kg/m^3) between alumina (ID: 3.99×10^3 kg/m^3) and magnesia (ID: 3.65×10^3 kg/m^3) shows an increase of volume fraction at 8.58%. This increase in volume fraction with the formation of spinel is considered to be caused by the decrease in compressive strength and relative density. As a consequence, treatment with 0.10 mol/l magnesium nitrate solution led to enhanced mechanical properties while maintaining a high porosity.

3.3. Microstructure

According to SEM observations, most of the alumina particles retained their platelet shape in the porous alumina body after reheating to 1400 °C for 1 h. At this temperature, the alumina platelet particles seemed to be stable due to their high purity (99.9%). Fig. 7 shows a typical SEM micrograph of the connection between platelets after 0.5 mol/l aluminum nitrate solution treatment. Newly precipitated alumina was observed to form a strong link between platelets. This micrograph shows evidence of the strengthening mechanism of the porous alumina body composed of alumina platelets, as shown in Fig. 3. However, when comparing porous alumina bodies after aluminum nitrate or magnesium nitrate solution treatment, no discernable difference in microstructure was observed. Furthermore, newly deposited $MgAl_2O_4$ (spinel) was not observed on the surface of the platelets. This result is thought to because the amount of the $MgAl_2O_4$ was very small. For example, when 0.25 mol/l magnesium solution was used, the amount of precipitated $MgAl_2O_4$ was estimated to be 4.4 mol% for the whole porous material, as shown in Fig. 6. Therefore, the surface of the platelets mostly seems to remain smooth, although $MgAl_2O_4$ was formed on its surface and interior.

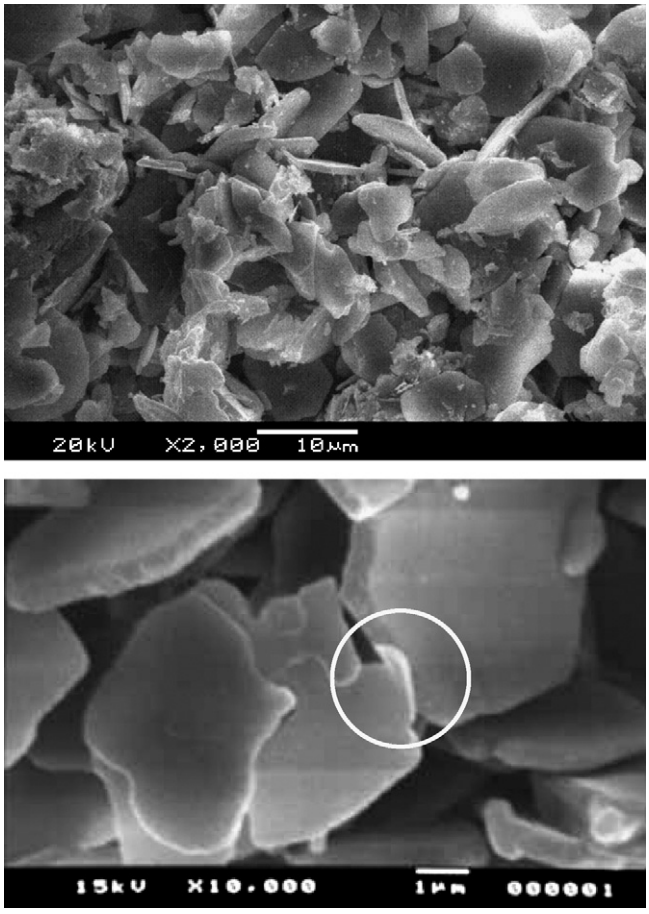

Fig. 7. SEM micrographs of the connection between platelets after 0.50 mol/l aluminum nitrate solution treatment.

4. Summary

Anisotropic alumina platelets 5–10 μm in diameter and 5–10 in aspect ratio were synthesized by a sodium sulfate flux method.

An alumina compact body was formed by uniaxially compressing the alumina platelets at 1 MPa, and then heating at 1400 °C for 1 h. The relative density and the compressive strength of the formed porous alumina body were 25.0% and 0.76 MPa, respectively. Subsequently, after the porous alumina body was immersed in 0.50 mol/l aluminum isopropoxide solution, dried for 24 h at room temperature, and then reheated to 1400 °C for 1 h, the relative density and the compressive strength of the porous alumina were 25.8% and 1.5 MPa, respectively. Similarly, when the porous alumina body was immersed in 0.25 mol/l magnesium nitrate solution, dried for 24 h at room temperature, and reheated to 1400 °C for 1 h, the relative density and the compressive strength of the formed porous alumina body were 26.5% and 1.7 MPa, respectively. These solution treatments had a strong positive influence on the strength of the porous alumina body, while maintaining its porosity.

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