Fabrication of highly isotropic porous alumina refractory clinkers consisting of platelets using a gelatin-sol

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ABSTRACT
Porous alumina bodies are expected to find application as refractory materials to reduce energy consumption during the manufacture of inorganic products. The porosity of such bodies can be efficiently increased by using alumina platelets to form a so-called “house-of-cards” structure. This technique was employed in the present study, together with a gelatin-sol (as binder) and freeze-drying. The porosity, compressive strength, and thermal conductivity of a porous alumina body made in this manner and heat-treated at 1600°C were 80.2%, 1.7 MPa, and 0.94 W/m·K, respectively. These physicochemical properties would allow this alumina to be used as a thermal insulation refractory clinker material.

1. Introduction
In recent years, numerous methods have been developed for the fabrication of novel porous alumina bodies [1–4]. These materials are expected to have various applications, including as filters, thermal insulators, catalyst carriers, and refractory clinkers [5–11]. Porous alumina refractory clinkers must have several specific characteristics, such as a high degree of porosity, suitable mechanical properties, and low thermal conductivity. To date, α-alumina platelets, which readily form “house-of-cards” structures, have been used to increase the porosity of ceramic bodies. In a “house-of-cards” structure, each platelet has a random orientation, i.e. not oriented or stacked in a certain direction, but with an isotropic and homogeneous structure at the macro level. However, porous alumina bodies made of highly crystalline platelets with minimal contact area tend to be weak, and are thus often treated with chemical solutions to increase their mechanical strength after reheating [12–14]. In addition, a yeast fungus that has been investigated as a pore former can be added to green bodies made of alumina platelets to enhance their porosity [15].

In the present work, a novel method for increasing both the porosity and mechanical strength was developed by using α-alumina platelets, a gelatin-sol as a binder, and a freeze-drying technique. The alumina platelets used in this study have good wettability with water, and the individual particles are separated naturally in the slurry. The dispersion of platelets in the high concentration slurry was expected to be closest to the ideal “house-of-cards” structure. Therefore, the freeze-drying method was chosen to fix the relative position of the platelets in the high concentration slurry before removal of the solvent. There are many studies on the production of porous bodies using plate-like ceramic particles and freeze-drying technology [16–19]. However, in most cases, these studies aimed to achieve both high porosity with a honeycomb structure and improvement in mechanical strength in a specific direction, and were not suitable for refractory clinker applications. This is because the refractory clinker receives force from all directions during the refractory manufacturing process, and inevitably breaks in the direction with the weakest mechanical strength. To the best of our knowledge, this combination of ceramic platelets and freeze-drying techniques has never before been applied to thermal insulation refractory clinker fabrication. The freeze-drying method easily produces a house-of-cards structure from the alumina platelets, and the application of a gelatin-sol maintains this structure, resulting in increases in both mechanical strength and porosity. The mechanical strength and thermal conductivity of the resulting house-of-cards structured porous alumina were investigated and compared with those of honeycomb structured porous alumina and porous alumina produced by using yeast as a pore former.

2. Experimental
In these trials, 0.2 g of a commercially available gelatin was mixed with 9 g of pure water and the solution was maintained at 50°C to form a gelatin-sol. This solution was subsequently combined with 8–12 g of commercially available α-alumina platelets (Kinsei Matec Co.,...
Ltd., Japan; SERATH YFA10030, purity: 98.9%, average grain diameter: 10 μm; average grain thickness: 0.3 μm; specific surface area: 3.13 m$^2$·g$^{-1}$ with stirring at 300 rpm for 20 min to form a slurry. This slurry was subsequently transferred into a cylindrical mold 15 or 30 mm in diameter, and the cylinder was immediately immersed in liquid nitrogen for 5 min to fix the platelets in the sol. When using only water, coarse ice crystals were found to separate from the platelets, so 0.45, 0.9, 1.35, or 1.8 g of additional ethanol was added to the slurry as a cryoprotectant. After removing the cylindrical mold from the liquid nitrogen, the hardened specimen was extricated from the mold. In order to compare and evaluate the structure of the alumina porous body, a honeycomb porous body in which ice crystals were anisotropically grown was also produced. After the slurry was poured into a mold whose bottom surface was an iron plate, it was stored at −20°C for 24 h in a freezer while the side and upper surfaces were thermally insulated with expanded polystyrene.

Figure 1 illustrates the texture of a porous body composed of platelets undergoing different freeze-drying conditions. Following the freezing step, the sample was held at 10 Pa and 30°C for 24 h to remove water by sublimation. Organic components derived from the gelatin were then removed by heating at 400 °C for 2 h, after which the specimen was heated at a rate of 200°C/h to a temperature of 1400 to 1600°C and held at that temperature for 2 h. The sample was then cooled at the same rate. In addition, for a comparative sample, we made a porous material using yeast as a pore former. Rotating granulation was performed by adding 30 to 50 wt.% water to a powder of alumina platelets and yeast mixed at a ratio of 7:3 [15]. The granulated sample was dried and fired in the same way as the freeze-dried sample. Samples prepared by the freeze-drying method were essentially cylindrical, 13 to 15 mm in diameter and 25 to 30 mm in height. Samples of 25 to 30 mm in diameter and 20 to 25 mm in height were also prepared for measuring the thermal conductivity. Regarding the honeycomb structured porous body, a cube having sides of 15 to 20 mm was cut out from a cylindrical sample 35 mm in diameter and used to evaluate the difference in characteristics depending on the orientation. A sample using yeast as a pore former was evaluated by preparing a cube having sides of 15 to 20 mm.

The relative density (which reflects the porosity) of each alumina body was measured using the Archimedes method. The compressive strength was determined using a specialized test apparatus (SHIMADZU Co., Ltd., Japan; Autograph AG-Xplus). The pressing speed was 0.1 mm per minute. At least three specimens were tested for each set of conditions. The shrinkage rate was calculated from the height of the cylindrical sample before and after heating. The microstructure of the porous alumina bodies was observed by scanning electron microscopy (KEYENCE; SEM VE8800). The specific surface area of the samples was measured with a Brunauer-Emmett-Teller surface area analyzer (MOUNTECH Co., Ltd., Japan; Macsorb HM-1201). The sample for surface area measurement was crushed and classified to a size of 1.5–0.5 mm due to restrictions of the apparatus. Finally, the room-temperature thermal conductivity of each body was measured using the hot-disk technique (Hot Disk AB; TPS500). A 3.189 mm radius hot disk sensor coated with polyimide was used. The sensor was sandwiched between two samples prepared under the same conditions, and a weight of 75 g was placed on it and fixed. The measurement was performed four times while changing the sample and the measurement surface.

Figure 1. Schematic diagram of the texture of platelets porous body undergoing different freeze-drying conditions.
3. Results and discussion

Figure 2 shows a photograph of porous alumina bodies (a) with and (b) without the addition of gelatin after freeze-drying. In the freeze-drying process, moisture can be removed without causing damage to the frozen body by directly vaporizing ice. However, when no binder is added, the dried sample is brittle because the structure is supported only by the adhesive force of the particles. In the case of the alumina platelets used in this test, since the number of contact points between the particles is smaller than that of the ground fine particles, the sample without added gelatin could not support its own weight and collapsed. Figure 3 shows SEM photographs of (a) the raw material for alumina platelets and (b) the sample with added gelatin after freeze-drying. In Figure 3(b), it can be seen that a gelatin film is formed that connects the alumina platelets. Further, the surface of the alumina platelets in Figure 3(a) is relatively smooth. Therefore, the irregularities confirmed on the surface of the alumina platelet in Figure 3(b) are also considered to be a gelatin film that covers the surface of the platelets. When only the gelatin-sol is freeze-dried, the gelatin moves outside the ice crystals to form a gelatin layer, such that a porous structure with a gelatin film is obtained after drying \([20]\). For this test, this gelatin layer is expected to exist in the vicinity of the alumina platelets. Because of the growth of ice crystals, the nearby alumina platelets would also move outside. Alternatively, if the alumina platelet is already fixed with another ice crystal or alumina platelet, it can be predicted that ice crystal growth would physically stop at that position. As a result, a gelatin film forms on the surface of the alumina platelets after freeze-drying. Since this gelatin film connected and supported the platelets as a binder, the gelatin-added sample maintained its structure even after freeze-drying.

When freeze-drying a low-solid-content slurry, large pores are easily formed by solute rejection along with the growth of ice crystals. Such large pores reduce the mechanical strength of the sample because they act as fracture initiation sites. In order to decrease the number and size of large pores left behind by the ice crystals that form during freeze-drying, cryoprotectants can be used to reduce the effects of solute rejection and crystallite size on the solidification of water in ceramic slurries \([21,22]\). In this study, we chose ethanol as a cryoprotectant, because it is nontoxic, easy to obtain, and vaporizes readily.

Figure 4 shows the side and cross-sectional photographs of porous alumina bodies (a) with and (b) without the addition of 1.35 g ethanol after freeze-drying. The cross-sectional images were taken by cutting cylindrical samples vertically. In Figure 4(a), with 1.35 g ethanol, it...
can be seen that the structure was homogeneous with no major defects. In contrast, in Figure 4(b), without ethanol, the formation of crevices associated with the development of ice crystals was confirmed. From the shape of the crevices, the ice crystals were plate-like with a thickness of 50–300 μm, and the ice plates appeared to be parallel to each other on the side-surface. From the cross-sectional image, multiple discontinuous crevices with the same thickness and length of 500–5000 μm were observed. Furthermore, since the crevices were small and the crevice direction was slanted in the lower part compared to the upper part of the sample, it was considered that ice crystals grew from the most cooled upper surface that was not covered with the mold. In the case where ethanol was not added, these coarse ice crystals were the starting points for destruction, such that the mechanical strength of the sample was reduced.

Figure 5 summarizes the porosity and compressive strength of porous alumina bodies made with 8 g of alumina platelets and 0–1.8 g ethanol with heating at 1600°C for 2 h. Both the porosity and compressive strength were higher for the samples prepared with ethanol than for the samples prepared without ethanol. In order to exclude the effect of porosity on compressive strength, a sample with the addition of 10.35 g of water...
is also described. The 10.35 g water-added sample and 9 g water and 0.45 g ethanol-added sample had similar porosities, but the ethanol-free sample showed a significant decrease in compressive strength.

Thus, it was confirmed that adding more than 0.45 g ethanol to the starting slurry prevented the growth of ice crystals. With increases in the ethanol content, the porosity of the alumina bodies increased, and the specimen made with 9 g water and 1.35 g ethanol exhibited a porosity and compressive strength of 80.2% and 1.7 MPa, respectively. On the other hand, these tests also revealed that samples made using 1.8 g ethanol could not be hardened because they collapsed upon freeze-drying. Because the goal was to maximize the porosity, 1.35 g ethanol was employed in subsequent experiments.

The cause of the suppression of coarse ice crystal formation by ethanol is presumed as follows. First, the freezing point of the aqueous ethanol solution decreases as the ethanol concentration increases. For example, the freezing points of aqueous solutions of 10, 20, and 30 wt. % ethanol are about −4.6, −11.2, and −20.9°C, respectively, and the freezing point of ethanol is −114.5°C [23]. In general, when ice crystals are formed at lower temperatures, the frequency of nucleation increases and the crystals become finer. When formed at relatively high temperatures, the crystal growth rate increases and the crystals become coarser. In addition, ethanol (C₃H₇OH) is composed of a hydrophilic hydroxyl group (-OH) and a hydrophobic ethyl group (-C₃H₇). Since the ethyl groups are bonded to each other in an aqueous ethanol solution, bonding between water molecules and ethanol molecules hardly occurs [24,25]. Upon rapid cooling with liquid nitrogen, ice crystal nuclei are formed. At this time, ethanol as an impurity is discharged out of the ice. As a result, the surrounding ice crystals are surrounded by an aqueous ethanol solution having a higher concentration and a lower freezing point, which reduces the growth rate of the ice crystals. Furthermore, the individual ice crystal sizes remain small because the ethanol is sandwiched between the ice crystals, and the ice crystals are not integrated with each other.

Many studies on alumina porous bodies fabricated by freeze-drying have investigated the formation of the characteristic honeycomb structure by controlling ice crystals growth [16–19,26–30]. Whether the porous body takes on a house-of-cards structure or a honeycomb structure upon freeze-drying is determined by the cooling rate and the cooling direction during freezing. When the cast slurry is instantaneously frozen in liquid nitrogen, it forms a house-of-cards structure, as shown in Figure 1. When, however, the casting mold is thermally insulated and then gently frozen from the lower surface of the sample in a freezer at −20°C, it forms a honeycomb structure.

Figure 6 shows micrographs of porous bodies with house-of-cards and honeycomb structures. Figure 6(a) is a top view of a cylindrical sample with a house-of-cards structure, and Figure 6(b) is a side view of the same sample. Similarly, Figure. 6(c,d) show, respectively, top and side views of the honeycomb porous body. Figure. 6(a,b) reveal that the house-of-cards porous body has an isotropic structure that does not vary with the observation direction. This structure was formed because the random arrangement of platelets in the slurry is fixed by rapid freezing, and the relative position of the individual platelets is maintained by the gelatin film after the solvent is removed by freeze-drying. In contrast, it can be seen in Figure 6(d) that in the honeycomb porous body, elongated pores are formed along the vertical direction. These holes, which have a width of 10 to 20 μm, are formed by plate columnar ice crystals produced during slow cooling from the bottom of the sample. The plate-like continuous pores and lamellar walls are generated in parallel in a plurality of layers, which are macroscopically aligned vertically. On the other hand, in the horizontal...
direction, as shown in Figure 6(c), it can be seen that units composed of several layers of parallel plate-like pores exist in various orientations so as to be random or branched. The greatest difference between the honeycomb structure porous body sample (Figure 6(c,d) and the ethanol-free sample (Figure 5(b))) is the size of the generated pores. In the case of a honeycomb structure porous body, the size of the plate-like pores is small and constant, and the pores exist uniformly throughout the sample. Therefore, there is no unevenness in the structure or mechanical strength as in the case of an ethanol-free sample, and a stable porous body is obtained.

3.1. Characteristics of porous alumina bodies

3.1.1. Compressive strength

Figure 7 shows the relationship between the porosity and compressive strength for porous alumina bodies made under various conditions. The house-of-cards porous body produced by freeze-drying varied with the amount of alumina platelets (8, 10, 12 g) in the raw material slurry and the firing temperature (1400, 1500, 1600°C). The honeycomb porous body was produced using 8 g of alumina platelets and a firing temperature of 1600°C, and its compressive strength was measured in the vertical and horizontal directions as shown in Figure 6. For reference, house-of-cards porous alumina bodies were fabricated by heating green bodies consisting of the same starting alumina platelets and yeast fungus as a pore former. In Figure 6, the compressive strengths of the porous alumina bodies fabricated by heating with a pore former are also shown. At each temperature, a lower amount of alumina platelets resulted in a higher porosity. The use of a lower processing temperature also increased the porosity, such that a specimen made with 8 g of alumina platelets at 1400°C had a porosity of 84%.

However, temperatures up to and including 1500°C gave a compressive strength of less than 1 MPa, which is insufficient for use as a clinker during the processing of a castable refractory. In such processes, various raw materials are mixed and, if the mechanical properties of the porous alumina clinker are poor, the clinker will be easily broken. In addition, during steel production, refractories are typically exposed to temperatures above 1500°C, and thus the alumina bodies fabricated below 1500°C in the present work would undergo sintering, i.e. their porosity would decrease during use. Hence, a fabrication temperature of 1600°C is desirable. On the other hand, in the honeycomb porous body, the compressive strength was higher in the vertical direction than in the horizontal direction. However, the compressive strength in the vertical direction was about 1.3 MPa, which was lower than that of a house-of-cards porous body produced under the same compounding slurry and firing conditions. The compressive strength of the honeycomb structure alumina porous body produced in this research is in a low class even compared to the reported values in similar research [16–18]. This is presumably because control of the freezing conditions is insufficient and many columnar pores are formed in the oblique with the vertical direction by the crystal growth of ice. However, since the honeycomb porous body is inevitably weaker in the lateral (or oblique) direction, it is not suitable as a material to which force is applied in all directions, such as a fireproof aggregate.

A porous alumina body made with 12 g of alumina platelets and heating at 1600°C reached a porosity and compressive strength of 74.7% and 3.4 MPa, respectively. When porous alumina made with yeast fungus as a pore former and heating at 1600°C was examined, the compressive strength of the porous body with 75.6% porosity was 0.9 MPa. This indicates that the alumina porous material produced by freeze-drying...
can achieve much higher strength than the porous material produced using the pore former.

### 3.1.2. Thermal conductivity

Figure 8 shows the relationship between the porosity and the room-temperature thermal conductivity of porous alumina bodies made with varying amounts of alumina platelets as a function of processing temperature. In the house-of-cards porous body produced by freeze-drying, the thermal conductivity decreased with a decreasing amount of platelets and heating temperature, owing to increased porosity. A porous alumina body made from 8 g of alumina platelets and heated at 1600°C exhibited a thermal conductivity of 0.94 W·m⁻¹·K⁻¹. On the other hand, in the honeycomb porous body, the thermal conductivity in the vertical direction was 1.04 W·m⁻¹·K⁻¹, which was comparable to that for the house-of-cards porous body fired at 1600°C, while the thermal conductivity in the horizontal direction was 0.64 W·m⁻¹·K⁻¹, i.e. significantly lower. In the case of porous alumina made with yeast fungus as a pore former, the thermal conductivity was lower than that of porous alumina prepared by the freeze-drying method having the same heating temperature and similar porosity.

At room temperature, the influence of convective and radiative heat transfer can be ignored, so it is only necessary to consider material heat conduction. Since all samples produced in this study used the same alumina platelets, it is expected that the parameters affecting the room-temperature thermal conductivity would be the porosity, number of contacts between alumina platelets, and contact strength (neck thickness). Naturally, the higher the porosity, the lower the thermal conductivity. As the amount of alumina platelets in the slurry increases, so does the number of contacts between the particles, leading to a higher thermal conductivity. Furthermore, sintering between particles is promoted by raising the firing temperature, and the thermal conductivity increases as the necks thicken. These basic relationships hold for the porous alumina bodies using the same sample preparation method, but not for the different sample preparation methods that were used. The thermal conductivity in the horizontal direction for the honeycomb porous body decreases because the heat transfer path is longer in the horizontal direction than in the vertical direction due to the structure [31]. Thus, the honeycomb porous body may function better as a bulk thermal insulation material than the house-of-cards porous body. However, in order to effectively utilize the honeycomb structure, it is necessary to produce a large block or board in which the columnar pores are parallel to the thermal gradient, which is problematic in terms of manufacturing cost and mass production. In the case of a house-of-cards porous body, the particle size should be about 5 mm at most in order to ensure usability as a thermal-insulating refractory aggregate, and the freezing process can proceed faster, which is conducive to mass production.

Various equations and strategies for the evaluation of thermal conductivity in porous materials have been reported to date [32–41]. The raw material particles used in this study are high aspect ratio (AR) alumina platelets, so it is necessary to consider the anisotropy of the particles. Kanari’s equation is a generalization of the Bruggeman equation to accommodate any particle shape, and can be expressed as follows [39–41]:

\[
1 - V_f = \frac{\lambda_c - \lambda_f}{\lambda_m - \lambda_f} \left( \frac{\lambda_m}{\lambda_c} \right)^{\frac{1}{3}}
\]

where \(V_f\) is the volume fraction of alumina, and \(\lambda_c, \lambda_f,\) and \(\lambda_m\) are the thermal conductivities of the alumina porous body, dense alumina, and air (pores), respectively. In the present study, the thermal conductivities were assumed to be \(\lambda_f = 38\) W·m⁻¹·K⁻¹ and \(\lambda_m = 0.025\) W·m⁻¹·K⁻¹.

**Figure 8.** Relationship between the porosity and the room-temperature thermal conductivity of porous alumina bodies.
Furthermore, "n" is the particle shape factor proposed by Hamilton and Crosser, and is expressed as in equation (2) using the sphericity $\Psi$ of the particle [42].

$$n = \frac{3}{\Psi} \quad (2)$$

Here, $\Psi$ is a value obtained by dividing the surface area of a sphere having a volume equal to the raw material particle volume by the actual particle surface area. In Figure 8, the ideal thermal conductivities calculated based on Kanari's equation for AR = 20, 40, and 60 for the platelets are shown as solid curves. It was found that the thermal conductivity of the porous alumina produced using the freeze-drying method is close to the calculated value of Kanari's equation for AR = 60. The average aspect ratio of the alumina platelets used in this study is approximately 33, but as shown in Figure 3(a), the particle size varies widely and there are many particles with diameters $\geq 20 \mu m$ (AR $\geq 60$). In the house-of-cards structure, since the skeleton is mainly formed from these relatively large platelets, it was considered that they were approximated by Kanari's equation under relatively large AR conditions.

The results so far cannot explain that the compressive strength and thermal conductivity of the porous body using yeast as a pore former are smaller than that of the freeze-dried porous body. Therefore, in order to clarify the dependence of the compressive strength and thermal conductivity on the method of fabrication in the case of house-of-cards porous bodies, the microstructure before and after firing alumina porous bodies produced by freeze-drying or a pore former was examined.

### 3.1.3. Influence of pore formers on alumina porous structure

Figure 9 shows SEM micrographs taken at the same position in a house-of-cards structure alumina porous body before and after heating at 1400°C; (a) (a') (b) (b') used the freeze-drying method and (c) (c') (d) (d') used yeast fungi as a pore former.
bodies fabricated by different methods before and after heating at 1400°C. Figure 9(a), (b) and (a’), (b’) are “before” and “after” micrographs of a sample prepared by freeze-drying using gelatin-sol, taken at the same position. Similarly, Figure 9(c), (d) and (c’), (d’) are “before” and “after” micrographs, respectively, revealing the structural changes that occurred at a fixed position of the sample upon heating with a pore former. From Figure 9(a), as in Figure 3(b), it can be confirmed that the alumina platelets were covered with a gelatin gel film after freeze-drying. Representative sections of this film peeling off from the platelets are indicated by white dotted circles in the image to illustrate their appearance. The film was retained on each platelet, helping to maintain the house-of-cards structure before heating. In Fig. 9(a), only the gelatin gel film on the platelets was burned out and the relative positions of the platelets remained largely unchanged, such that the house-of-cards structure formed by freeze-drying was retained after heating. Figure 9(b) and (b’) show a wider range of images, but no noticeable changes were observed before and after heating. Note that the linear cracks in Figure 9(b), (b’), (d), and (d’) are provided as position confirmation marks after the sample was manufactured. On the other hand, in the case of the sample heated with a pore former (Figure 9(c), (c’), (d), and (d’)), the relative positions of the platelets changed upon heating. For example, the platelet aggregation unit enclosed in red in Figure 9(c) has moved to the center of the image in Fig. 9(c’) after heating. This is due to the burning of yeast fungus. As shown by the white dotted circle in Figure 9(c), the yeast fungus used as a pore former consisted of 2 to 4 µm spherical particles, which were often aggregated. Therefore, units such as the platelet aggregation unit surrounded by the red solid line in Figure 9(c) and (c’) that were only in contact with the surroundings through the pore former will lose connection with the surroundings due to the burning of yeast. In extreme cases, few-hundred-micrometer platelet aggregate units as shown in Fig. 9(d’) may form free aggregates. These free agglomerates can move when they are no longer supported (mainly thought to fall due to their own weight) and form bonds with surrounding particles by heating. However, in this case, the free agglomerates and the surrounding bond formation are expected to have few contacts and become inhomogeneous.

Figure 10 shows the shrinkage rate before and after heating of an alumina porous body prepared under different conditions. The shrinkage rate of the house-of-cards porous material after firing at 1400°C was 1 to 2% for the freeze-dried porous material, whereas it showed a large shrinkage of about 5% when the pore former was used. This is because the burn-out of yeast fungus, which is a pore former, forms large voids, whereas the gelatin film used for freeze-drying has a thickness of only several tens of nanometers and hardly forms voids. On the other hand, the shrinkage ratio increased due to the sintering of the alumina platelets as the firing temperature increased. After heating at 1600°C, all the samples had similar shrinkages of 7 to 10%. In the case of a sample prepared by the freeze-drying method, since the structure has a homogeneous and continuous particle indirect point, the sintering shrinkage between the individual particles is integrated and becomes the shrinkage of the whole sample. On the other hand, in the case of a sample using a pore former, the interparticle contraction is unlikely to cause the contraction of the entire sample due to unevenness in the structure. For example, shrinkage of free aggregates only increases the gap between the free aggregates and the surroundings. Further, in the case of a crack as shown by a red dotted circle in Figure 9(d’), the crack expands due to sintering shrinkage, so that it does not lead to shrinkage of the whole sample. Finally, the honeycomb porous body had a small shrinkage in the vertical direction and a large shrinkage in the parallel direction due to the anisotropy of the structure.

Figure 10. Shrinkage rate before and after heating of alumina porous bodies prepared under different conditions.
Figure 11 shows the results of specific surface area measurements of each sample. The surface area of the alumina porous body made by 8 g of alumina platelets and heating at 1400°C was 1.05 m²·g⁻¹, which was the largest, but was decreased to about 1/3 compared with the starting material. In all samples, the surface area decreased with increasing heating temperature. Even in the porous bodies with different amounts of added platelets, the porous bodies had similar surface areas when the heating temperature was the same, so the influence of the porosity of the porous bodies seemed to be relatively small. In addition, compared with the house-of-cards structure freeze-dried porous body, a honeycomb porous body or that created with a pore former tended to have a low specific surface area. As confirmed in Figure 6(d), in the case of the honeycomb porous body, the alumina platelets pushed out by the growth of the ice pillars form lamella walls, so the directions of the alumina platelets are aligned. Therefore, the platelets are stacked such that the surfaces are bonded together, reducing the surface area. In the case of a porous body using a pore former, the entire structure has no anisotropy as shown in Figs. 9(c) and (d). However, from the results shown in Figure 11, it is expected that plate alignment and stacking occurred more than the honeycomb structure. This is presumably due to the fact that the porous body using the pore former is produced by rolling granulation of a wet powder, and therefore, the agglomeration of the surfaces having higher adhesion force occurred.

Figure 12 illustrates the strengthening mechanism for a porous alumina body fabricated by freeze-drying, in comparison to the method of using yeast fungus as a pore former. In the freeze-drying method, individual alumina platelets were non-oriented and homogeneously dispersed in the raw slurry, and the relative position was fixed by rapid freezing to form a house-of-cards structure. However, when it was gradually frozen from a certain direction, a honeycomb structure composed of continuous pores perpendicular to the cooling surface and lamellar walls was formed by the growth of ice crystals. These house-of-cards and honeycomb structures were retained by a gelatin film covering the alumina platelet surface even after freeze-drying. Furthermore, since the gelatin film between the alumina platelets was just several nanometers to several tens of nanometers thick, the structure at the time of drying was maintained, with no gaps forming in the necks as the gelatin film was burned off. Therefore, when using freeze-drying, the alumina platelets are considered to have a continuous and homogeneous neck bond network. In contrast, when using yeast fungus as a pore former, a house-of-cards structure consisting of platelets was formed by supporting yeast fungus between the platelets. The voids after the pore former is burned down are at least several micrometers, and the contact point continuity between the alumina platelets is lost. Consequently, the alumina platelets move so as to fill these gaps, resulting in large shrinkage, but it is thought that the discontinuities generated by the pore former are maintained to some extent. In summary, alumina porous bodies prepared by freeze-drying using gelatin-sol had relatively high mechanical strength and thermal conductivity due to their continuous necks. In contrast, when yeast was used as a pore-forming material, there were many free platelet ends that could lead to fracture, and the particle network was partially discontinuous, resulting in relatively low mechanical strength and thermal conductivity.

4. Summary

Highly porous alumina bodies were successfully fabricated by a freeze-drying technique, using α-alumina platelets and a gelatin-sol. The gelatin-sol played an
important role in the formation of a “house-of-cards” structure consisting of platelets, and subsequent freeze-drying appeared to help maintain this structure during heating. The porous body with a house-of-cards structure had a more isotropic structure than the honeycomb porous body, so the former can readily be used as a refractory clinker since its mechanical strength is relatively high in all directions. It was found that the porosity, compressive strength, and thermal conductivity of the specimens made from 8 g of alumina platelets after heating at 1600°C were 80.2%, 1.7 MPa, and 0.94 W/m\(^{-1}\)K\(^{-1}\), respectively. Hence, the use of alumina platelets and freeze-drying with a gelatin-sol allowed the fabrication of porous alumina clinkers usable for thermal insulation refractories.

### Disclosure Statement

No potential conflict of interest was reported by the authors.

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Figure 12. Schematic diagram of the strengthening mechanism of a porous alumina body made using the freeze-drying method, compared to that of a body formed using yeast fungi as a pore former.
