Thermal insulators with macroscopic and microscopic pore anisotropy created by gelation–freezing with alumina platelets

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Thermal insulators were fabricated by freezing and drying gelatin gels containing calcined kaolinite with various amounts of hexagonal alumina platelets, followed by sintering. Unidirectional macroscopic porosity was created via the freezing process, with accompanying pore walls composed of the platelet grains microscopically longitudinally oriented. The relationship among different platelet contents, microstructure, compressive strength, and thermal conductivity was examined. Varying the platelet content in the initial gels enabled effective control of the porosity and properties of the resultant insulators. The use of a gel with a high content of platelets led to a larger porosity because of reduced shrinkage during sintering, resulting in decreased thermal conductivity and strength. The overall morphology and properties of the insulators prepared by gelation–freezing were investigated.

Key-words : Porous, Freeze casting, Porosity, Compressive strength, Thermal conductivity

1. Introduction

Porous ceramics exhibit various attractive engineering properties, such as low density, good fluid permeability, low thermal conductivity, and high surface area. The pores in ceramics act as fracture defects and degrade the structural reliability. Therefore, creating an anisotropic porous structure such as unidirectional porosity is one methodology to overcome the disadvantages of reduced mechanical properties. Among various proposed fabrication routes, the freezing of slurries that contain raw ceramic powders is a promising technique for the formation of unidirectional cellular structures, in which pores can be produced via the formation of unidirectional ice, sublimation under vacuum drying, and subsequent sintering.¹⁻⁷ The properties of freeze-casting-derived porous ceramics can result from unidirectionally aligned porosity. The anisotropy can be used in several industrial applications at elevated temperatures. One promising application of such materials is a ceramic thermal insulator because the mechanical strength parallel to the pore orientation is substantially improved, whereas the thermal conductivity in the opposite direction is very low. Thus, when insulators are used in a furnace, such anisotropy is highly desirable because good mechanical strength is required in the direction in which the insulators are stacked, whereas reduced thermal conductivity is favored in the horizontal direction because of heat transfer from inside the furnace to outside.

Continuous research trends in ceramic insulators prepared by freeze casting⁸⁻¹³ indicate that macroscopic porosity created by the formation of a cylindrical ice column has been widely attempted, whereas microscopic anisotropy created by raw particles oriented during freezing has seldom been investigated. Thus, several issues need to be overcome, particularly limitations related to the shape of raw materials: (1) isotropic raw particles have been used far more frequently than anisotropic particles; (2) the combination of unidirectional pore anisotropy formed by freezing and anisotropic raw particles oriented by freezing has not been well studied; and (3) the properties of strength and thermal conductivity have usually been discussed on the basis of macroporosity and sintered pore walls, not microporosity.

Regarding the orientation of anisotropic particles,¹⁴⁻¹⁷ several authors have reported improved mechanical properties of aerogels with oriented nanocellulose and sodium-montmorillonite platelets, enhanced thermal conductivity of polymer composites composed of unidirectionally oriented boron nitride (BN), super-elasticity and very low dielectric properties of BN aerogels with oriented structures, and very high thermal conductivity of graphene/BN aerogels. These works suggest some possibilities for effectively controlling various properties of porous materials by utilizing both macroscopic and microscopic anisotropy because the freeze-casting route can simultaneously create
such combined morphologies. One purpose of the present paper is thus to examine the effect of the freezing process and anisotropic raw materials on the macro- and microscopic pore architectures created by the gelation freezing process. In this paper, we used calcined kaolinite, which is a typical raw material of thermal insulators, and hexagonal alumina platelets as an additive to create microscopic anisotropy. We also investigated the strength and thermal conductivity of the prepared insulators.

2. Experimental

Kaolinite (Eckalite-1, Imerys Japan Co. Ltd., Tokyo, Japan) with an average particle size of 0.4 μm was calcined at 1000 °C. The obtained powder was pulverized for 24 h using a ball mill with Al<sub>2</sub>O<sub>3</sub> balls in water. After mixing, the slurry was dried. The calcined kaolinite screened through a 125mesh sieve was then mixed with α-alumina hexagonal platelets (SERATH YFA10030, Kinsei Matec Co. Ltd., Osaka, Japan) with an average particle size of 10 μm and an aspect ratio of approximately 25–30, and a warm gelatin solution (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan); the resulting mixture was allowed to set at 50 °C. As ice binding additives to avoid rapid ice growth, antifreeze glycoprotein (AFP, Nichirei Foods Inc., Chiba, Japan) was used; the AFP was mixed with a gelatin solution in a ratio of 0.1/99.9 by weight. Details of the effects of AFP on growing ice crystals has been reported elsewhere. The mixture ratios of calcined kaolinite/alumina platelets were 100/0, 90/10, 70/30, 30/70, and 0/100 by weight. According to their platelet content, these samples are represented as A0, A10, A30, A70, and A100, respectively. The solid loading in the gelatin solution was maintained at 5% with a gelatin content of 0.1/99.9 by weight. Details of the effects of AFP on growing ice crystals has been reported elsewhere. The mixture ratios of calcined kaolinite/alumina platelets were 100/0, 90/10, 70/30, 30/70, and 0/100 by weight. According to their platelet content, these samples are represented as A0, A10, A30, A70, and A100, respectively. The solid loading in the gelatin solution was maintained at 5/95. The slurry was stirred using a planetary homogenizer (ARE310, Thinky, Tokyo, Japan). Ammonium polyacrylate was used as a dispersant to obtain a homogeneous slurry. The slurry was poured into a centrifuge container, which was revolved (800 rpm) while rotating (2000 rpm). After being deformed under vacuum, the slurry was poured into a plastic mold and maintained at 7 °C to induce gelation. The mold containing the gel was cooled from the bottom by immersion into an ethanol bath at −40 °C. After demolding, the frozen bodies were dried under vacuum in a freeze drier (model FDU-40, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) at −10 to 30 °C to sublimate the ice crystals in the frozen gel. The green bodies were finally sintered at 1550 °C for 2 h.

The porosity, microstructure, thermal conductivity, and compressive strength of the resultant thermal insulators were characterized. Open porosities were measured using the Archimedes method with water displacement. The pore morphologies were observed by scanning electron microscopy (SEM; JEOL, JSM-5600, Tokyo, Japan). The thermal conductivities of insulators were measured using the hot-disk method (TPS1500, Kyoto Electronics Manufacturing Co. Ltd., Kyoto, Japan) with a transient plane source (TPS) and a polyimide sensor with a radius of 3.189 mm; isotropic modes were measured at room temperature. The output power and measurement time were varied in the ranges of 0.02–0.08 W and 20–40 s, respectively, depending on the thermal characteristics of the insulators. X-ray diffraction (XRD) patterns (SmartLab, Rigaku, Tokyo, Japan) were collected using monochromatic Cu Kα radiation (40 kV/30 mA) to analyze the phase compositions of powder mixtures, gelation–freezing-derived green bodies, and sintered bodies. The compressive strength was measured using a universal testing machine (MTS Systems Corp., Sintech 10/GL, Minnesota, USA) with a crosshead speed of 0.5 mm/min. The cylindrical specimens with a diameter of 4.8 mm and a height of 12 mm were loaded on the top and bottom surfaces such that the load was parallel to the freezing (pore) direction. At least five samples were fractured to obtain the average strength.

3. Results

Figure 1 shows the porosities of the prepared insulators as a function of their platelet content. The porosities were approximately 79.4, 81.5, 87.1, 92.3, and 90.8% for samples A0, A10, A30, A70, and A100, respectively, corresponding to relative densities of 20.6, 18.5, 12.9, 7.7, and 9.2%, respectively. The porosities were thus found to be dependent on the platelet content in the initial slurry.

Figure 2 shows typical microstructures of the polished surfaces of prepared insulators (A) A0, (B) A30, and (C) A70, where the microstructures were observed in a section perpendicular to the freezing direction (channel direction). The observed morphologies are typical of the cellular structures produced by gelation–freezing and consist of uniformly distributed micrometer-sized cylindrical cells. Cell sizes and wall thicknesses slightly decreased with increasing platelet content.

Figure 3 shows typical microstructures of fractured surfaces in samples (A and D) A10, (B and E) A70, and (C and F) A100, as observed parallel to the freezing direction and indicated by arrows. Longitudinal anisotropic pore morphologies were observed, where the cells were portioned by thin channel walls macroscopically oriented along the freezing direction but the orientation gradually became less linearity with increasing platelet addition. The platelets remained, and needle-like grains embedded in the skeleton were observed in (B) and (C). As observed from the struts at high magnification (E and F), the porous skeleton still remained, with highly anisotropic platelets.
Figure 4 shows the XRD patterns of the sintered bodies of (A) A100, (B) A70, (C) A10, and (D) A0. Only peaks due to alumina were detected in sample (A) A100, whereas the patterns of the other samples included peaks ascribed to (B) mullite and alumina and to (C and D) mullite and cristobalite.

Figure 5 shows the thermal conductivities of the prepared insulators as a function of (A) platelet content and (B) porosity; the effective conductivities of alumina (dotted line) and mullite (solid line) are included, as calculated by Maxwell–Eucken model I:

\[
k_e = \frac{k_s + k_g - 2(k_s - k_g)v_g}{k_s + k_g + (k_s - k_g)v_g}
\]  

where \(k_s\), \(k_g\), and \(v_g\) are the thermal conductivity of the solid phase (skeleton), the thermal conductivity of air, and the volume fraction of air in the insulator (porosity), respectively. We used 0.025, 5, and 33 W m\(^{-1}\) K\(^{-1}\) as reference values for the thermal conductivities of air, dense mullite, and dense alumina, respectively. The thermal conductivity of insulators A0, A10, A30, A70, and A100 was 0.32, 0.33, 0.23, 0.15, and 0.38 W m\(^{-1}\) K\(^{-1}\), respectively. The trend shows a decrease in thermal conductivity with increasing platelet content, except for the A100 sample, which exhibits the highest thermal conductivity. Figure 5(B) shows that the thermal conductivity decreases with increasing porosity, again with the exception of the A100 sample. Those were always lower than those of efficient thermal conductivities.

Figure 6 shows compressive strength of the prepared insulators as a function of (A) platelet contents and (B) porosity. The compressive strength of the A0, A10, A30, A70, and A100 insulators was 25.5, 15.4, 4.8, 0.6, and 0.6 MPa, respectively. The strength was thus found to decrease with increasing platelet content and increasing porosity.

4. Discussion

One purpose of this paper is to investigate the relationship between anisotropic additive platelets, porosity, and pore morphologies created through the freezing process. As previously reported, green porosities are dependent on the solid loading in the initial slurry because the ratio of shrinkage during vacuum drying tends to be negligible. In the present study, the green porosities of all samples were approximately constant at 94–96%, irrespective of the platelet content; these porosities correspond to relative densities of approximately 4–6%, which are close to the initial solid content of 5%. Thus, shrinkage is reasonably deduced to have occurred during the sintering process and to have affected the porosities because the porosities of the sintered samples (Fig. 1) are consistently lower than those of the green bodies. The effect of platelets on shrinkage will be discussed in detail later.

Cell (ice) sizes were observed to decrease with increasing platelets content, as shown in Fig. 2, because the thermal conductivity of alumina is higher than that of kaolinite. The thermal conductivities of fully dense sintered kaolinite and alumina have been reported to be 3.2 and 33 W m\(^{-1}\) K\(^{-1}\), respectively. As we previously reported, the size of ice crystals grown is closely correlated with the transfer of latent heat generated during the phase change and with the number of ice nuclei, i.e., the freezing rate. Materials with higher thermal conductivity can become a good heat-transfer path and promote the conduction of latent heat from the grown ice toward the cooling medium, eventually leading to smaller ice crystals (a smaller cell size). The effects of the freezing rate and/or ice recrystallization on the size of ice crystals is considered negligible here because all samples have been frozen at the same temperature of \(-40^\circ\text{C}\), which is sufficiently low so as not to cause recrystallization. Thus, the different cell size means that the platelets could lead to the formation of
smaller ice crystals because of the platelets’ higher thermal conductivity.

During the freezing process, the particles that form the cell walls are rejected by ice crystals growing along the temperature-gradient direction in the gel body, as shown in Fig. 3. The skeleton of sample A10 shown in Fig. 3(D) appears almost dense; however, no platelets are observed. In this case, the platelets are assumed to be consumed to form mullite (discussed later), supported by the observations of needle-like grains embedded in the skeleton and the peak identification of mullite but not alumina in the XRD pattern in Fig. 4(C). Figures 3(B), 3(C), 3(E), and 3(F) and 4(A) and 4(B) show that the platelets oriented vertically remain in samples A100 and A70, even after the sintering process. To obtain the stoichiometric ratio for mullite, mixtures with a calcined kaolinite/alumina weight

![Fig. 3. Typical microstructures of fractured surfaces in the prepared insulators (A and D) A10, (B and E) A70, and (C and F) A100, as observed in a section parallel to the freezing direction.](image)

![Fig. 4. XRD patterns of the prepared insulators (A) A100, (B) A70, (C) A10, and (D) A0.](image)
ratio of 52/48 are required according to the following reaction between calcined kaolinite and alumina:

\[ 2\text{SiO}_2\cdot\text{Al}_2\text{O}_3 + 2\text{Al}_2\text{O}_3 \rightarrow 3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2 \]  \(\text{(2)}\)

Thus, as shown in Figs. 3(B) and 3(E), excess and unreacted alumina remained in sample A70. Figures 3(C) and 3(F) shows the porous skeleton with almost all of the platelets highly vertically oriented. This microscopic anisotropy is considered to be formed during the freezing process because the morphologies of sintered samples could generally remain in those of green bodies, although the cell size could be reduced by shrinkage during the sintering process. To further investigate the anisotropy of the platelets caused by the freezing process, the XRD pattern was collected for samples before and after the freezing process.

Figure 7 shows XRD patterns of powder mixtures of (A) A100, (B) A70, (C) A10, and (D) A0 samples and gelation–freeze-dried bodies of (E) A100, (F) A70, (G) A10, and (H) A0 samples.
increase in intensity was due to the volume effect of the platelets because the platelets in the powder mixture should be randomly distributed. By contrast, as evident in the XRD patterns of (E–H) the gelation–freeze-dried bodies, the (006) peak, representing the basal plane of the platelets, disappeared, whereas the peaks due to the (012), (110), (113), (024), and (300) increased in intensity. These results suggest that the platelets were rotated and oriented vertically along growing ice crystals during the freezing process. In order to estimate the crystalline anisotropy, the orientation degree ($P$), as shown in Fig. 8, was calculated using the peak intensities for (006) and (110), $I_{006}$ and $I_{110}$, respectively, according to Eq. (3):

$$ P = \frac{I_{110}}{I_{006} + I_{110}} \quad (3) $$

The orientation degrees were calculated to be 51 and 49% for the A10 and A70 powders, again suggesting the platelets randomly oriented. On the other hand, those were calculated to be 88 and 90% for the gelation–freezing-derived A10 and A70 bodies, respectively. The orientation degrees of the gelation–freezing bodies were consistently higher than those of the powder mixtures. Thus, the results suggest that most of the platelet particles could be vertically oriented by the freeze-drying process. Also, it is again remarked that the platelets remained are still oriented vertically even after sintering.

In addition to the effect of orientation, the effect of platelets on porosity was also observed in Fig. 1. The observed inhibition in the densification of the samples containing platelets is attributed to (1) lowered packing density and (2) inhibited densification (shrinkage) by the platelets. The packing densities in the skeleton were very low, indicating that the addition of platelets suppresses the packing and sintering of the kaolinite matrix. Interestingly, the porosity of sample A100 is slightly lower than that of sample A70, consistent with the above discussion that the platelets inhibit the sintering of kaolinite itself. Other authors have reported that when a mixture of fine particles and platelets oriented horizontally are sintered, some mismatch of shrinkage between the platelet thickness direction and long-basal-plane directions can occur,

$$ \text{meaning that the addition of the platelets can result in tensile stress generated around that region, followed by retarded densification. Thus, the addition of platelets can provide very high porosity because of reduced shrinkage by microscopic anisotropy.} $$

This porosity remaining in the skeleton could affect the properties of the prepared insulators. As shown in Fig. 5, thermal conductivity was substantially affected by the platelet contents and porosities. In our previous study, the measured conductivities of prepared mullite were consistent with curves calculated using Maxwell–Eucken model

$$ \text{However, the results of conductivity measurements in the current study are lower than the calculated values, clearly indicating that porosity existed in the skeleton. The calculated conductivity is based on dense mullite and alumina used as a reference; porous struts should exhibit lower actual conductivity. Also, with higher platelet contents, the conductivity approaches the calculated value, except in the case of A100, which is affected by unreacted remaining alumina, which exhibits higher conductivity than silica and mullite, as shown in Fig. 3. The decrease in strength depends on the increase in porosity resulting from the addition of platelets. In a compressive test, when a net sectional stress in a surface plane perpendicular to the cell orientation exceeds the fracture strength of a cell wall material, a cellular ceramic will be fractured. As mentioned above, the observed cell walls with increasing platelet contents became highly porous and less linearity, with disordered tortuous with increasing platelet content and some bent, leading to reduced strength of the insulators. Thus, the tension arises because of a moment of force during a compression test, meaning the severe local stress concentrations to become sources of crack initiation and propagation, followed by final failure.} $$

In fact, the wall thickness and the linearity decrease with increasing platelet content, leading to lower strength because of the stress concentration.

These results reveal that the gelation–freezing process and the use of platelets can become the key factor in enhancing porosity and modulating the macroscopic and microscopic pore anisotropy in controlling the engineering properties. The proposed method is expected to be a promising approach for tailoring various pore architectures of different size scales.

5. Conclusion

Pore morphologies were successfully modulated from
macroscopic unidirectional porosity to microscopic anisotropy with highly oriented hexagonal alumina platelets through gelation–freezing of calcined kaolinite and platelets. The platelets enhanced the porosity up to 92.3% and controlled the pore architecture. These microstructures affected the porosity, thermal conductivity, and compressive strength as the platelet contents were varied.

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