APPLICATION OF ULTRA－POROUS CERAMICS PREPARED BY GELATION FREEZING METHOD TO REFRACTORIES

Tomohiro Nakane*, Pengfei JIA, Mikako Fujii, Ayumi Matsuoka, Yosuke Tanaka, and Fumihito Ozeki
MINO CERAMIC CO., LTD.

ABSTRACT

Porous ceramics have been used in various fields such as thermal insulators, filters, and catalyst carriers because of their properties such as low thermal conductivity, high permeability, and high specific surface area. Porous ceramics made by gelation freezing method have a relatively high strength and porosity. Therefore, they can contribute to energy saving of high temperature firing furnace as an insulating refractory. In addition, it is necessary to select the heat insulating material to be used depending on the operating temperature and atmospheric conditions of the high temperature firing furnace.

In this study, we made porous ceramics from alumina, mullite, and zirconia by gelation freezing method, measured the porosity, thermal conductivity, and flexural strength required for properties of insulating refractories, and observed the microstructure with an electron microscope. Moreover, in order to get manufacturing guidelines of porous ceramics with the desired thermal conductivity, we compared the relationship between the porosity and thermal conductivity of porous ceramics with two theoretical models, the Maxwell-Eucken model and the Landauer model. The experimental results of thermal conductivity showed intermediate values between the Maxwell-Eucken model and the Landauer model for porous ceramics of any material. This result suggests that porous ceramics made by the gelation freezing method do not have the completely closed pore structure as expected by the Maxwell-Eucken model, and not have a structure that causes percolation with high porosity as expected by the Landauer model.

INTRODUCTION

Porous ceramics have been used in various fields such as thermal insulators, filters, and catalyst carriers because of their properties such as low thermal conductivity, high permeability, and high specific surface area. A number of fabrication methods such as polymer foam replication method have been established for porous ceramics. On the other hands, the porous ceramics fabricated by those methods often have poor mechanical properties. In order to solve this problem, the fabrication method of a porous ceramics by the gelation-freezing (GF) method was studied. Fig. 1 shows the process of GF method. In the GF method, raw powder is firstly dispersed into water with a gelation agent. After gelation, the wet gel is immersed into cold solvent, and ice crystals are formed, which results in the subsequent formation of pores. A vacuum freeze drier is used to dry the frozen gel so that ice is sublimated without shrinkage of the green body. The green body is then sintered to obtain a porous ceramic.

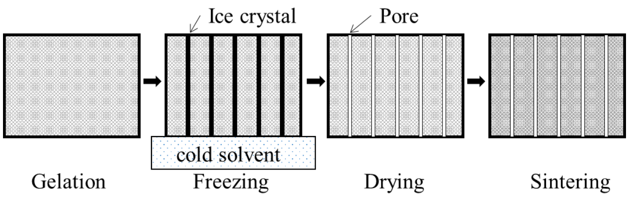

Fig. 1 Schematic diagram of process for porous ceramics by GF method.

The ultra-high porosity ceramic fabricated by the GF method has a high porosity and relatively high strength[1]. However, coarse ice crystals may be formed in freezing, which may eventually result in coarse defects of the ceramic and cause variations on quality.

To solve the problem, we tried replacing

This UNITECR 2022 paper is an open access article under the terms of the Creative Commons Attribution License, CC-BY 4.0, which permits use, distribution, and reproduction in any medium, provided the original work is properly cited.

Downloaded from bulletin-archive.ceramics.org

some of the water with foam (new method). Fig.2 shows the cross-sectional microstructures of porous ceramics fabricated by GF method (a) and new method (b). While the sample fabricated by (a) had a honeycomb structure with large coarse pores due to abnormal growth of ice crystal, the sample fabricated by (b) had small uniform pores without large columnar pores.

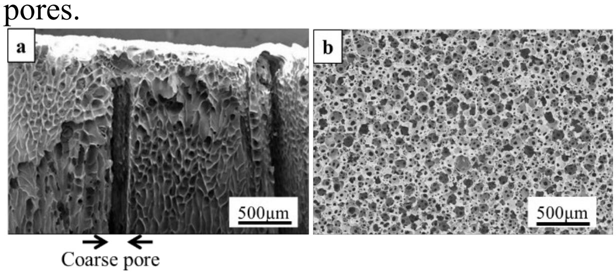

Fig.2 Cross-sectional microstructures of porous ceramics fabricated by GF method (a) and new method (b).

Additionaly the sample made by (b) had higher strength than that made by GF method[2]. From this result, the light weight and high strength porous ceramics fabricated by (b) is expected to be used as high performance insulating refractories. In addition to low thermal conductivity, chemical stability and higher maximum service temperature are also required properties depending on the object to be fired. In those cases, not only mullite but also alumina and zirconia are used as material of insulating refractories

Regarding the thermal conductivity of porous ceramics, the relationship between porosity and thermal conductivity can be treated as a conduction problem in a classical two-phase mixed system. Several models have been proposed for the problem depending on the shape of the pores and the state of connection between the pores. According to the Maxwell-Eucken model represented by Eq. (1) and the Landauer model represented by Eq. (2), the thermal conductivity of the porous ceramics (λ) are determined from the thermal conductivity of the pores (λ_p), the porosity (v_p), and the thermal conductivity of the solid phase (λ_s)[3].

$$\lambda = \lambda_s \frac{\lambda_p + 2\lambda_s + 2v_p(\lambda_p - \lambda_s)}{\lambda_p + 2\lambda_s - v_p(\lambda_p - \lambda_s)} \qquad (1)$$

$$\lambda = \frac{1}{4}\Big[\lambda_p(3v_p - 1) + \lambda_s(2 - 3v_p) + \Big\{\big[\lambda_p(3v_p - 1) + \lambda_s(2 - 3v_p)\big]^2 + 8\lambda_s\lambda_p\Big\}^{1/2}\Big] \qquad (2)$$

As suggested in these models, the porous ceramics of alumina, mullite, and zirconia may have some difference in thermal conductivity even with the same porosity due to the difference in thermal conductivity of the solid phase. Thus, we actually prepared alumina, mullite, and zirconia porous ceramics by the GF method. We measured their porosity, thermal conductivity, flexural strength, observed microstructures, and compared the relationship between porosity and thermal conductivity with theoretical models.

EXPERIMENTAL PROCEDURE

Sample preparation

We used commercially available alumina powder (D_{50} = 0.5 μm), mullite powder (D_{50} = 4 μm) and 3 mol% yttria-stabilized zirconia powder (D_{50} = 0.1 μm) as raw materials. The mullite powder was milled with a wet ball mill to D_{50} = 1 μm. The porous ceramics were made through slurry preparation, casting, gelation, freezing, drying and sintering. The raw material powder, water, and gelling agent were mixed and then mixed with the foam prepared from the surfactant until they become uniform. At this time, the slurry solid content concentration and the amount of foam added were adjusted so that the porosity of the porous ceramics after firing was 75-95%. The gelation was performed by keeping under ambient atmosphere to obtain a powder dispersed gel. The metal mold was then immersed from bottom into cold solvent. After freeze-drying in vacuum, the green bodies with

Downloaded from bulletin-archive.ceramics.org

320x180x20mmh were sintered in an electric furnace. Alumina and mullite ones were sintered at 1650 °C and zirconia ones were sintered at 1400 °C for 3h. In addition, in order to determine the thermal conductivity of the solid phase in the theoretical models, the same raw material as the porous ceramics was press-molded and sintered under the same conditions to prepare dense ceramics.

Sample Characterization

The porosity, microstructure, flexural strength and thermal conductivity of the obtained porous ceramics and the thermal conductivity and flexural strength of the dense ceramics were measured. Porosity was calculated from the weight and volume of the porous ceramics and the theoretical densities of alumina, mullite and zirconia. The flexural strength and the thermal conductivity were measured at room temperature. The cross-sectional microstructures were observed with scanning electron microscope (JEOL, JSM-IT200, Japan). The flexural strength was measured using the universal testing machine (SHIMADZU Corporation, AUTO GRAPH, Japan) with a crosshead speed of 0.5mm/min. The size of the flexural test pieces were 120x40x15 mmh for the porous ceramics and 40x4x3mmh for the dense ceramics. The thermal conductivity was measured by QTM-500 (KYOTO ELECTRONICS MANUFACTURING, Japan) for porous ceramics and TCi (C-THERM TECHNPLOGIES, Canada) for dense ceramics.

RESULTS AND DISCUSSION

Thermal conductivity

The measured thermal conductivity of the dense ceramics was as follows, alumina : 24.7 W・m^{-1}・K^{-1}, mullite : 5.6 W・m^{-1}・K^{-1}, zirconia : 4.1 W・m^{-1}・K^{-1}. Substituting these thermal conductivity and 0.0257 W・m^{-1}・K^{-1} which is thermal conductivity of air at 20 °C into λ_s and λ_p in Eq.(1) and (2), the relationship between the porosity and thermal conductivity of each porous ceramic is shown in Fig. 3.

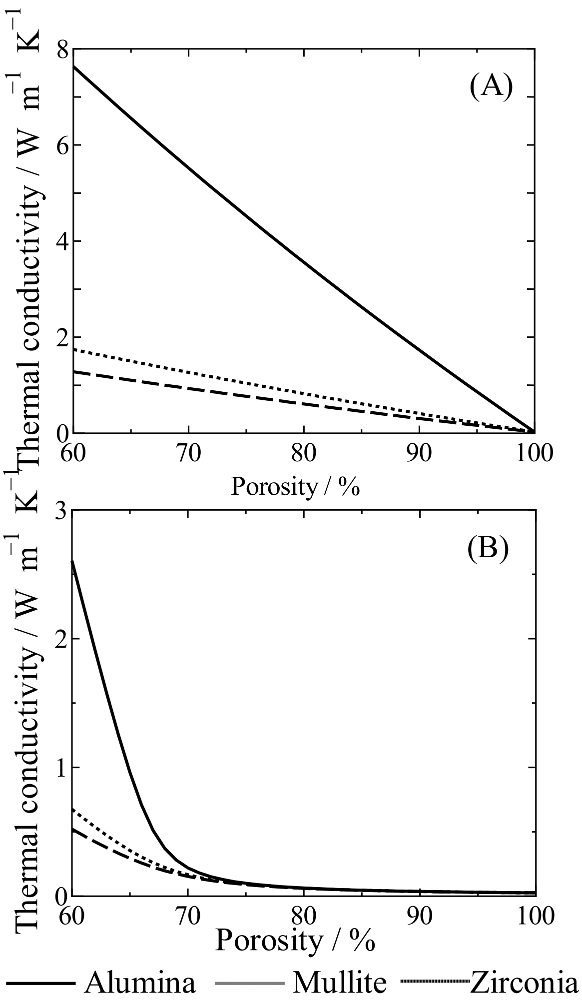

Fig. 3 Relationship between porosity and thermal conductivity of porous ceramics predicted from Maxwell-Eucken model (A) and Landauer model (B).

In both models, the absolute value of thermal conductivity with the same porosity in each porous ceramics made of different materials was ranked alumina > mullite > zirconia. The Maxwell-Eucken model was expected to show a difference in thermal conductivity even at high porosity, while the Landauer model was expected to show no significant difference in thermal conductivity at high porosity of over 70%. The relationship between the porosity and thermal conductivity of the prepared porous ceramics is shown in Fig .4.

Downloaded from bulletin-archive.ceramics.org

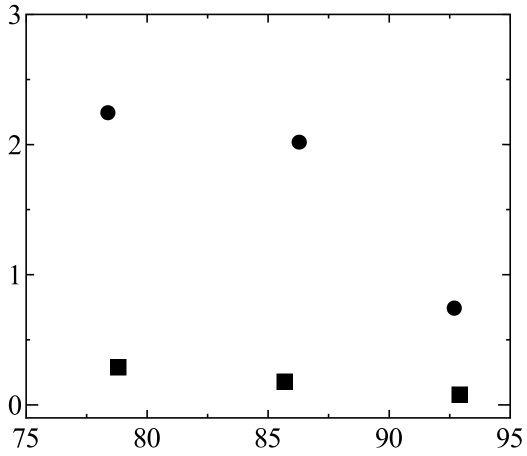

Fig. 4 Relationship between porosity and thermal conductivity of porous ceramics.

The magnitude relation of the thermal conductivity at the same porosity in each porous ceramics made of different materials was consistent with the theoretical model. There was a difference in the thermal conductivity even at high porosity, and the behavior was similar to that of the Maxwell-Eucken model. Comparing the thermal conductivity obtained in this experiment with the thermal conductivity of the two models from Fig. 5, the thermal conductivity of any porosity was ranked Maxwell-Eucken model > experimental value > Landauer model.

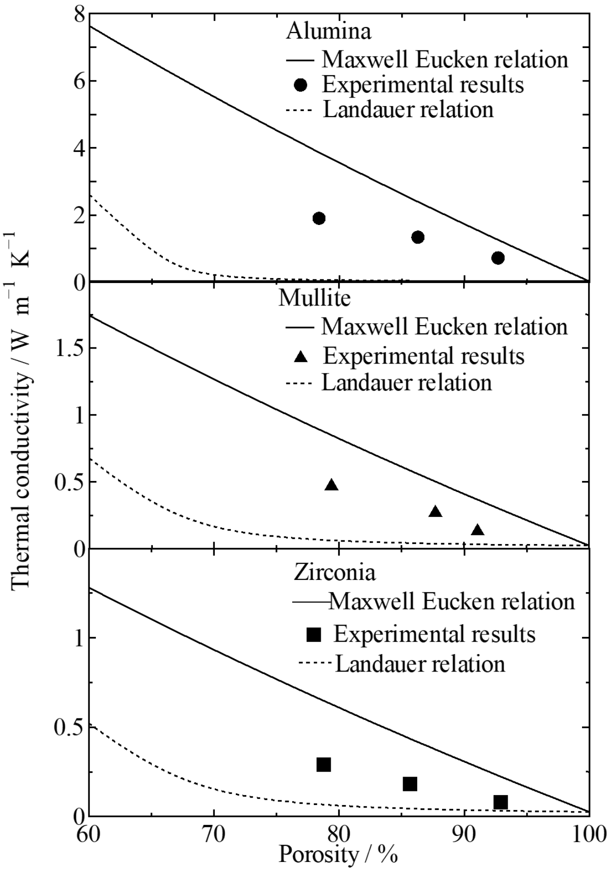

Fig. 5 Comparison of experimental results and theoretical models in relationship between porosity and thermal conductivity of porous ceramics.

Flexural strength

Table. 1 shows the relative density and flexural strength of the prepared dense ceramics, and Fig. 6 shows the relationship between the porosity and the flexural strength of the porous ceramics prepared.

Table I Relative density and flexural strength of the dense ceramics.

	Alumina	Mullite	Zirconia
Relative density / %	94.2	97.5	98.6
Flexural strength / MPa	253	266	928

Downloaded from bulletin-archive.ceramics.org

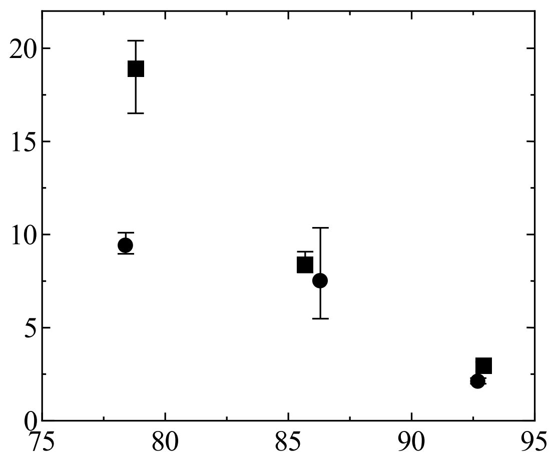

Fig. 6 Relationship between porosity and flexural strength of a porous ceramics

In Fig. 6, the error bars show the maximum and minimum values in the three tests. At a porosity of about 78%, the strength of the zirconia porous ceramics was higher than that of the alumina and mullite ones, this result was also consistent with the result of dense ceramics, but as the porosity increased, almost no difference was observed.

Microstructure

Fig. 7 shows the cross-sectional microstructure of the prepared porous ceramics having a porosity of about 78%. Porous ceramics of any material have spherical pores with a size of about 100 to 200 μm derived from the added foam, and the walls of the pores have communication holes smaller than the spherical pores that connect to the adjacent spherical pores. The diameter of the spherical pores differs depending on the raw material, and the order is zirconia > alumina> mullite. We consider that this is because the difference in pH and viscosity of the slurry due to the difference in the raw material affected the stability of the mixed foam. In addition, all porous ceramics sometimes have coarse pores than other spherical pores as seen in the microstructure of the porous ceramics of mullite in Fig. 7. The coarse pores seem to cause variations in the strength of porous ceramic.

In the comparison of the theoretical model and the experimental value in relationship between the porosity and the thermal conductivity, the thermal conductivity of the prepared porous ceramics was about the average value of the Maxwell-Eucken model and the Landauer model. We considered this result as follows. First, the Maxwell-Eucken model assumes that the spherical closed pores are evenly dispersed, whereas the prepared porous ceramics have a spherical pore, but communicates with the communication holes. As a result, it is considered that the prepared porous ceramics have a lower thermal conductivity than the Maxwell-Eucken model. In addition, the Landauer model assumes a rapid decrease in thermal conductivity due to percolation with a high porosity, but the communication holes of the prepared porous ceramics are small and partial, and the solid-phase connection is maintained above a certain level. As a result, it is considered that the prepared porous ceramics did not cause a rapid decrease in thermal conductivity even if the porosity increased.

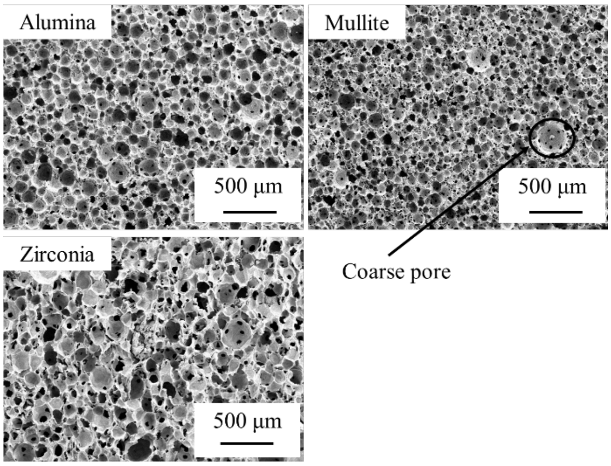

Fig. 7 Cross-sectional microstructure of the prepared porous ceramics.

CONCLUSIONS

We prepared alumina, mullite, and zirconia porous ceramics by the gelation freezing method, measured porosity, thermal

Downloaded from bulletin-archive.ceramics.org

conductivity, and flexural strength, and observed the microstructure with an electron microscope.

The flexural strength reflected the difference in the strength of the dense ceramics at the porosity of 78%, but the influence of the difference in the raw materials became smaller as the porosity increased.

In addition, in order to get manufacturing guideline for producing porous ceramics with the desired thermal conductivity, the relationship between the porosity and thermal conductivity of the porous ceramics was compared between the actual measurement results and the two theoretical models. The experimental results of thermal conductivity were close to the average value of the Maxwell-Eucken model and the Landauer model. We believe that this is because the Maxwell-Eucken model assumes that spherical closed pores are evenly dispersed, and the Landauer model assumes a high porosity and a sharp decrease in thermal conductivity due to percolation, whereas the prepared porous ceramics have partially communicating spherical pores, but most of the solid phase remains connected.

From this result, the relationship between the thermal conductivity of the porosity of the porous ceramics prepared by the GF method can be estimated to some extent from the Maxwell-Eucken model and the Landauer model. For a more accurate estimation, it is necessary to have a model that reflects the structure of the porous ceramics prepared by the GF method, which partially communicated pores and structure that maintains solid-phase connection even with high porosity.

ACKNOWLEDGEMENT

This paper is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

REFERENCES

1. M. Fukushima, M.Nakata, Y. Zhou, T. Ohji and Y. Yoshizawa, “Fabrication and properties of ultra highly porous silicon carbide by the gelation–freezing method”J. Eur. Ceram.Soc., 30 2889 (2010).

2. M. Fujii, A. Matsuoka, Y. Tanaka, F. Ozeki, M. Fukushima and Y. Yoshizawa, “Development of Insulating Firebrick through a Gelation Freezing Method” Proc. UNITECR 2019, pp. 516-519 (2019).

3. DS. Smith, A. Alzina, J. Bourret, B. Nati-Ali, F. Pennec and N. Tessier-Doyen, “Thermal conductivity of porous materials” Journal of Materials Research, 28(17), 2260-2272. (2013)

Downloaded from bulletin-archive.ceramics.org