Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 39 (2013) 3881–3884
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

The effects of pore structures on the air permeation properties of sintered diatomite

Jang-Hoon Ha*, Eunji Oh, Rizwan Ahmad, In-Hyuck Song

Powder and Ceramics Division, Korea Institute of Materials Science, 797 Changwondaero, Seongsan-gu, Changwon, Gyeongnam 642-831, Republic of Korea

Received 24 September 2012; received in revised form 21 October 2012; accepted 21 October 2012
Available online 26 October 2012

Abstract

In this study, we discussed the pore structure-property relationships by comparing the pore characteristics and air permeation properties of sintered diatomite specimens, with the same densities, prepared by the particle-stabilized direct foaming method and by the sacrificial polymer template method. Although the porous matrix, induced by irregular diatomite particles, of sintered diatomite specimens provided the paths of air permeation, the air permeation properties of the sintered diatomite specimen not only depended on the effective volume for air to pass through, but also on the pore structure. The pore characteristics of the diatomite specimens were investigated by scanning electron micrographs, mercury porosimetry, and capillary flow porosimetry.

Keywords: A. Sintering; B. Porosity; E. Membranes

1. Introduction

In recent years, there has been increasing interest in porous ceramics due to their unique properties such as high melting point, high corrosion resistance, high wear-resistance, low thermal conductivity, low density, and low dielectric constant. A challenging area among applications of porous ceramics is how to control and tailor their pore structure and emphasis has been placed on versatile and simple approaches that allow control over the microstructural features that ultimately determine the properties of porous ceramics [1]. Although the topic of processing routes to produce porous ceramics has been well-documented in the literature, the pore structure-property relationships have not yet been established.

If a sintered porous ceramic consists of a dense matrix such as alumina, the air permeation properties will depend on the pore characteristics of the specimen having either closed pores or open pores, because the major path of gas phases is open pores that travel through the dense matrix. However, in the case of a porous ceramic that consists of a porous matrix, the porous matrix itself also can act as a path for the gas phase. It is thus not clear whether the air permeation property depends on the pore structure. Therefore, in this study, spherical pore structures in sintered diatomite specimens were obtained by two different approaches, the sacrificial polymer template method and the particle-stabilized direct foaming method. The processing conditions such as the starting material, sintering temperature, and sintering time were controlled, and the specimens were designed to have similar bulk densities to each other. The sacrificial polymer template method usually involves the preparation of a continuous matrix of ceramic particles and a dispersed sacrificial phase that is homogeneously distributed throughout the matrix and is ultimately extracted to generate pores within the microstructure. However, this method has two main drawbacks: (i) micro-cracks can be generated within the microstructure and act as an escaping paths of the gas phase that is generated during pyrolysis of the polymer beads, and (ii) longer sintering time is required for complete pyrolysis [1]. If the sintering conditions of the two approaches are different, the sintering behavior of the diatomite matrix

*Corresponding author. Tel.: +82 55 280 3350; fax: +82 55 280 3392.
E-mail address: hjhoon@kims.re.kr (J.-H. Ha).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.10.231

and related properties will be varied. Hence, we adopted diatomite as a model material to investigate the pore structure-property relationship, because diatomite is a sedimentary rock resulting from the siliceous fossilized skeleton of diatoms, which are composed of rigid cell walls called frustules [2]. We speculated that the inter-particle voids induced by irregular shape of sintered diatomite might act as a partial escaping path of the gas phase. Furthermore, hollow spheres were adopted as a sacrificial polymer template to minimize both the amount of gas phase and the time to complete pyrolysis. The particle-stabilized direct foaming method was also used. With rapid progress in the area of colloidal chemistry, ceramic foams can now be fabricated by incorporating air into an aqueous suspension containing surfactant molecules and then drying and sintering the resulting sample. These processing methods have been extensively studied [3–8] as a promising route for the processing of porous materials because of their exceptional stability. Particles irreversibly adsorbed at a liquid–gas interface impede the coalescence or shrinkage of bubbles, stabilize the liquid foam, and also do not assemble to yield aggregates, in the same manner that surfactant molecules form micelles.

2. Material and methods

Diatomite (Celite 281, Celite Korea Co. Ltd., Korea) was used for the preparation of sintered diatomite specimens. To prepare the sintered diatomite specimens by the particle-stabilized method, distilled water was used as a solvent and the slurry was ball-milled for 24 h with a ball to powder ratio of 2:1. Fig. 1(a) shows that the diatomite particles maintained both the unique shapes and inherent pores of the fossilized skeleton of diatoms in the case of the specimens ball-milled for 24 h. After ball milling, 105 mmol/L of hexylamine ($CH_3(CH_2)_5NH_2$, 99% pure, Sigma-Aldrich, USA) was added. Foaming was carried out by using a direct driven motor at a speed of 1000 rpm. The prepared particle-stabilized diatomite wet foams were dried for 24 h in a humidity and temperature controlled chamber at 20 °C with humidity of 90%. After 24 h, the temperature was increased to 30 °C under the same humidity conditions. After drying the specimens, sintering was carried out at 1000–1200 °C for 1 h. Diatomite particles with 30 vol% of Expancel (Hollow sphere, Expancel-092-DET-80-d25, Eka Chemicals AB, Sweden) as a sacrificial polymer template, distilled water, and a polyethylene glycol binder were mixed, wet-pressed at 18.7 MPa, and dried for 24 h, and then the same sintering procedures as applied in the particle-stabilized direct foaming method were followed. Bulk densities were calculated by measured dimensions and weights. Pore characteristics of the diatomite foam were investigated by scanning electron micrographs (JSM-5800, JEOL, Japan), mercury porosimetry (Autopore IV 9510, Micromeritics, USA), and capillary flow porosimetry (CFP-1200-AEL, Porous Materials Inc., USA).

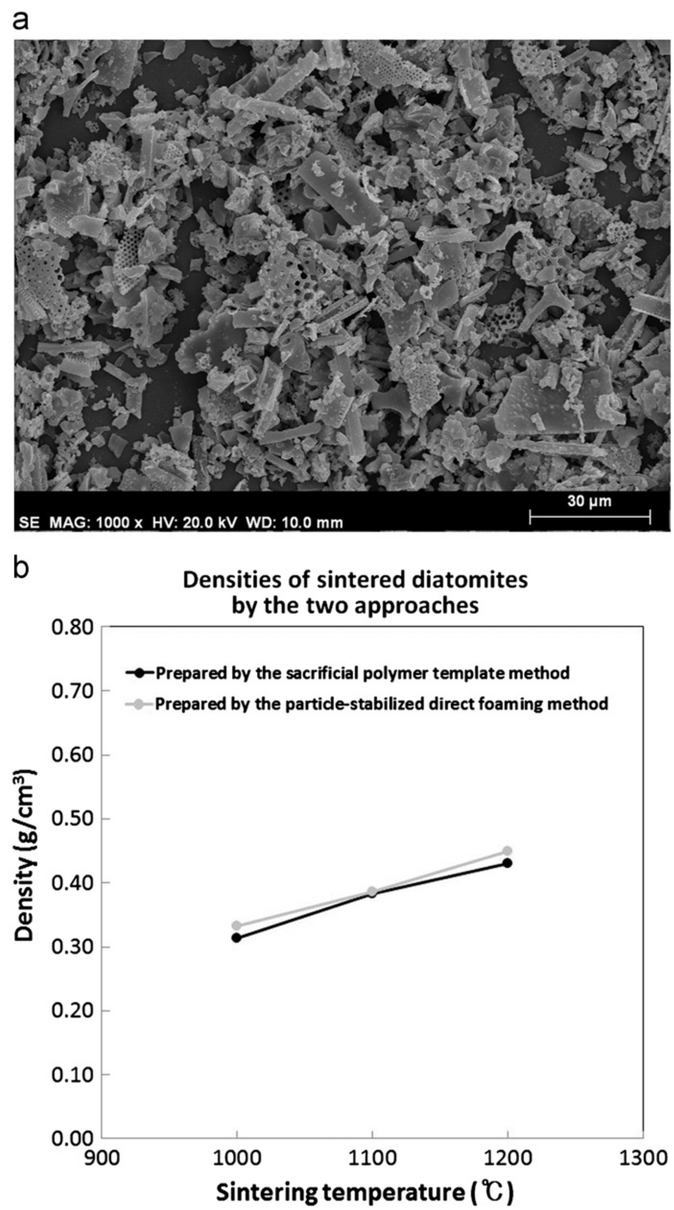

Fig. 1. (a) SEM image of diatomite particles after ball-milling for 24 h, and (b) densities of the diatomite specimens sintered at 1000 °C to 1200 °C, prepared by the sacrificial polymer template method, and by the particle-stabilized direct foaming method.

3. Results and discussion

Taking into consideration the findings of the preliminary experiments and those in the literature [2], we ascertained that sintered diatomite showed similar microstructures at 1200 °C and a clear coalescence of porous diatom frustules and grains in samples occurred at 1300 °C. In this study, we limited the sintering temperature of diatomite up to 1200 °C, because we wanted to focus on the effects of pore characteristics of diatomite on the properties by eliminating unnecessary factors. Fig. 1(b) shows that the densities of the sintered diatomite specimens prepared by the aforementioned two different approaches at sintering temperature

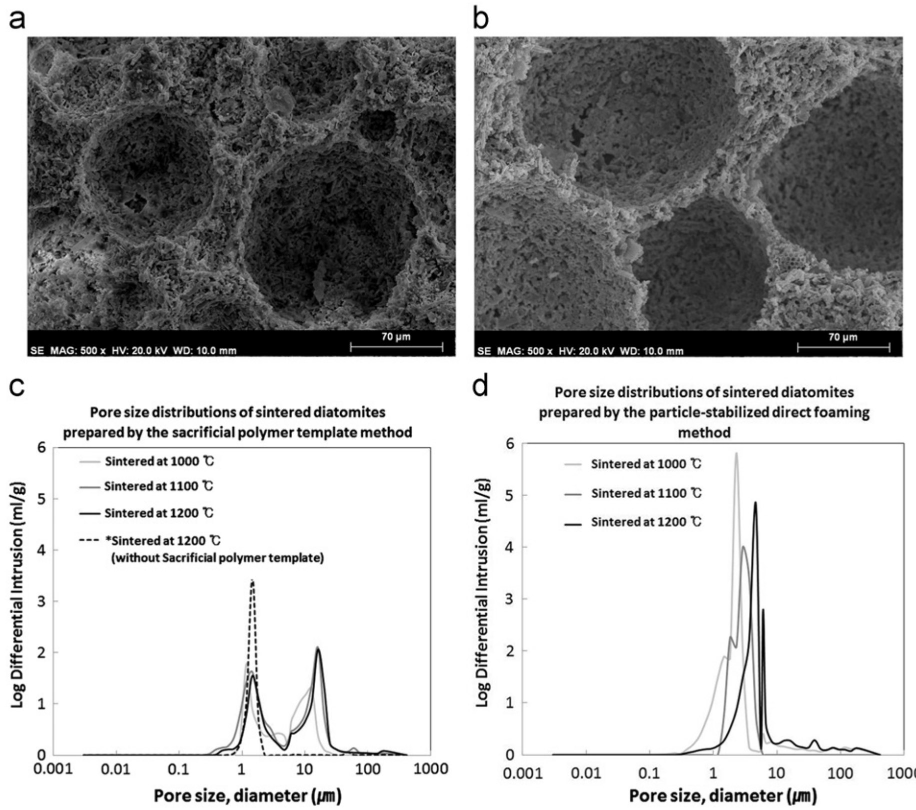

Fig. 2. SEM images of diatomite specimens sintered at 1200 °C for 1 h, prepared (a) by the sacrificial polymer template method, (b) by the particle-stabilized direct foaming method, pore size distributions of diatomite specimens prepared, (c) by the sacrificial polymer template method, and (d) by the particle-stabilized direct foaming method.

from 1000 °C to 1200 °C have a negligible difference as designed.

Typical microstructures of diatomite specimens sintered at 1200 °C for 1 h by the sacrificial polymer method and particle-stabilized direct foaming method are shown in Fig. 2(a) and (b), respectively. These sintered diatomite specimens had similar microstructures and maintained the unique shapes of the fossilized skeleton of diatoms when sintered at up to 1200 °C. The scanning electron microscope (SEM) images of the sintered diatomite specimen prepared by the sacrificial polymer method shows that the spherical pores are distributed in the diatomite matrix in a manner similar to Swiss cheese, whereas the sintered diatomite specimen prepared by the particle-stabilized direct foaming method consists of strut walls of spherical pores similar to soap bubbles that act as the diatomite matrix.

Fig. 3(a) shows that the pore size distributions of the diatomite specimens sintered at 1000 °C to 1200 °C by the sacrificial polymer template method have one peak at around 1–5 μm and another peak at around 10–20 μm. The former corresponds to inter-particle voids between the diatomite particles, whereas the latter corresponds to the throats [9] or entrance openings to spherical pores, because mercury will enter the spherical pores at a pressure determined by the entrance size and rather than actual spherical pore size. Consequently, sintered at 1200 °C without the sacrificial polymer, the specimen shows a unimodal pore distribution. Fig. 3(b) indicates that the sintered diatomite specimen prepared by particle-stabilized direct foaming method also had inter-particle voids between the diatomite particles. However, because the relatively short spacing between the neighboring spherical pores may lessen the ink bottle effect of mercury porosimetry, there was no sharp peak at around 10–20 μm.

Fig. 3(c) and (d) presents the air permeation properties of sintered diatomite prepared by the sacrificial polymer template method. The air permeation properties of the sintered diatomite were proportional to the sintering temperature up to 1200 °C regardless of preparation method. When the specimens were sintered at the same temperature, the air permeable property of the specimen that was prepared by the sacrificial polymer template method was higher than that of the specimen obtained by the particle-stabilized method. This can be explained as follows: the particle-stabilized direct foaming method is intrinsically based on the idea that particles can be used to adsorb irreversibly on the surface of gas bubbles to stabilize wet foams. Upon adsorption, particles lower the overall free energy of the system by replacing part of the high-energetic gas-liquid interfacial area with less energetic interfaces [10]. Therefore, if the particles are uniform and spherical, the surfaces of gas bubbles are fully covered with a single layer of the particles. And if the particles are

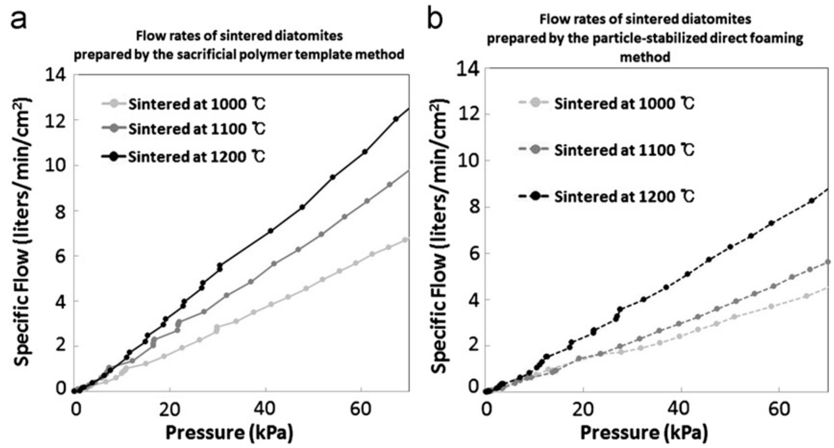

Fig. 3. The air permeation properties of the diatomite specimens, sintered at 1000 °C to 1200 °C, prepared; (a) by the sacrificial polymer template method; and (b) by the particle-stabilized direct foaming method.

irregular such as the diatomite particles in this study, the surfaces of gas bubbles are covered with several layers of the particles. Even though there are many inter-particle voids induced by irregular particles, when the surfaces of gas bubbles are covered with the particles as possible as they can, it is energetically favorable. However, in the case of the sacrificial polymer template method, when the mixtures of the diatomite particles and the sacrificial polymer templates are wet-pressed uni-axially, the diatomite particles do not have to cover the surfaces of the sacrificial polymer templates. The diatomite particles and the sacrificial polymer templates are redistributed to increase the overall packing density of the mixtures regardless of whether the diatomite particles cover the surfaces of the sacrificial polymer templates or not.

It is thus noteworthy that the air permeation property, of the sintered diatomite that consists of a porous matrix, depends more the on pore structure than on the effective volume that the air must pass through. Furthermore, the air permeation properties of sintered diatomite could be controlled by the processing conditions. These findings show the feasibility of using sintered diatomite in the filtration area.

4. Conclusions

In summary, using diatomite as a model material, we discussed the pore structure-property relationships of porous ceramics that have a porous matrix. To compare the pore structure-related properties, sintered diatomite specimens were prepared by the particle-stabilized direct foaming method and by the sacrificial polymer template method. The sintered diatomite specimens prepared by the two different approaches had spherical pore structures and maintained the unique shapes of the fossilized skeleton of diatoms when sintered at up to 1200 °C. The air permeation properties of sintered diatomite were proportional to the sintering temperature up to 1200 °C, and the air permeation property of the sintered porous diatomite that consists of a porous matrix depended not only on the effective volume that air must pass through, but also on the pore structure.

Acknowledgments

This study was supported financially by Fundamental Research Program of the Korean Institute of Materials Science (KIMS).

References

[1] A.R. Studart, U.T. Gonzenbach, E. Tervoort, L.J. Gauckler, Processing routes to macroporous ceramics: a review, Journal of the American Ceramic Society 89 (6) (2006) 1771–1789.
[2] N. van Garderen, F.J. Clemens, M. Mezzomo, C.P. Bergmann, T. Graule, Investigation of clay content and sintering temperature on attrition resistance of highly porous diatomite based material, Applied Clay Science 52 (1–2) (2011) 115–121.
[3] J.C.H. Wong, E. Tervoort, S. Busato, L.J. Gauckler, P. Ermanni, Controlling phase distributions in macroporous composite materials through particle-stabilized foams, Langmuir 27 (7) (2011) 3254–3260.
[4] C. Chuanuwatanakul, C. Tallon, D.E. Dunstan, G.V. Franks, Controlling the microstructure of ceramic particle stabilized foams: influence of contact angle and particle aggregation, Soft Matter 7 (24) (2011) 11464.
[5] U.T. Gonzenbach, A.R. Studart, E. Tervoort, L.J. Gauckler, Macroporous ceramics from particle-stabilized wet foams, Journal of the American Ceramic Society 90 (1) (2007) 16–22.
[6] J. Yu, J. Yang, H. Li, X. Xi, Y. Huang, Study on particle-stabilized Si_3N_4 ceramic foams, Materials Letters 65 (12) (2011) 1801–1804.
[7] J.-H. Ha, R. Ahmad, I.-H. Song, A novel method of coating a particle-stabilized alumina foam on a porous alumina substrate, Materials Letters 88 (0) (2012) 40–42.
[8] U.T. Gonzenbach, A.R. Studart, E. Tervoort, L.J. Gauckler, Stabilization of foams with inorganic colloidal particles, Langmuir 22 (26) (2006) 10983–10988.
[9] H. Giesche, Mercury porosimetry: a general (practical) overview, Particle and Particle Systems Characterization 23 (1) (2006) 9–19.
[10] U.T. Gonzenbach, A.R. Studart, E. Tervoort, L.J. Gauckler, Tailoring the microstructure of particle-stabilized wet foams, Langmuir 23 (3) (2007) 1025–1032.