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The fabrication and characterization of sintered diatomite for potential microfiltration applications

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

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

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Abstract

Porous ceramic membranes have lately become a subject of special interest due to their outstanding thermal and chemical stability. We investigated whether a sintered diatomite support layer could also serve as a separation layer to minimize any processing difficulties, and investigated whether the support layer and the separation layer could be made from the same material to avoid a thermal mismatch during a high-temperature sintering process. We prepared sintered diatomite as a porous ceramic membrane for microfiltration, as diatomite particles are inherently porous and irregular. The pore characteristics of the sintered diatomite specimens were studied by scanning electron micrography, mercury porosimetry, and capillary flow porosimetry.

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

1. Introduction

The importance of porous ceramics has recently been recognized as researchers seek to exploit their unique properties, such as their high melting point, high corrosion resistance, high wear resistance, low density, low thermal conductivity, and low dielectric constant. In particular, porous ceramic membranes are feasible materials for the creation of porous ceramics. The driving force behind the development of porous ceramic membranes is mainly the need to produce membranes with greater levels of thermal and chemical stability, as most polymeric membranes cannot withstand operating temperatures above 200 °C or exposure to organic solvents such as benzene or toluene [1].

In general, the most important aspects of a porous ceramic membrane are its permeation and separation properties. Therefore, precise control of the average pore size, and the largest pore size, while retaining acceptable permeation capabilities is important. A challenging area in the application of ceramic membranes is how to control, tailor, and characterize the pore characteristics; emphasis has been placed on various approaches that afford control over the microstructural features of both the separation layer and support layer, which ultimately determine the permeation properties of porous ceramic membranes. Although processing routes to produce porous ceramics have been extensively documented in the literature [2], the relationship between the pore characteristics and the membrane properties of porous ceramic membranes has not yet been established.

Moreover, ceramic membranes are usually composites consisting of several layers of one or more different ceramics. A porous ceramic membrane is thus usually fabricated through multiple steps. A support layer is initially prepared to provide mechanical strength for the membrane, if needed, followed by the coating of one or more intermediate layers on the support layer, after which a final separation layer is deposited. Each step involves a high-temperature sintering process, making the ceramic membrane fabrication procedure expensive and challenging. If the support layer can also serve as a separation layer, or if the support layer and separation layer can at least be made from the same material to avoid a thermal mismatch

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

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during the sintering process, processing becomes easier and the time and cost issues associated with processing are mitigated.

The applications and separation mechanisms of porous ceramic membranes correspond to the pore size of the membranes. As it is difficult to create a support layer with microporous or dense materials due to their low permeation characteristics, it is worthwhile to investigate porous ceramic membranes that consist of a support layer only or a support layer and a separation layer composed of the same macroporous material. Among the methods of reverse osmosis, nanofiltration, ultrafiltration, and microfiltration, we focused on microfiltration in this study, as the largest and smallest pore sizes of membranes for microfiltration are roughly several μm and 0.1 μm, respectively.

Recent developments in porous ceramic membranes have heightened the need to investigate mass transport through a separation layer deposited on a support layer, as the overall permeation capabilities and reliability of the pores on separation layer are critical to porous ceramic membrane applications. In general, the permeability of a separation layer on a support layer governs the overall permeation capabilities of the membrane. Although there have been various reports on commonly used materials for ceramic membranes, including Al_2O_3, TiO_2, ZrO_2, SiO_2, and composites of these materials, there have been few studies on 'porous and irregular' starting particles such as diatomite. Diatomite is a sedimentary rock originating from the siliceous fossilized skeletons of diatoms, which are composed of rigid cell walls called frustules. To date, no detailed studies on the use of a separation layer made with inherent porous and irregular particles have been published.

The present study investigated the following areas. First, we investigated whether a sintered diatomite support layer could simultaneously serve as a separation layer, within a sintering temperature range of 900–1200 °C. The basic properties of the sintered diatomite support layer and the processing conditions for additional experiments were obtained during these experiments. When a sintered porous ceramic is used as a surface membrane filter as a support layer, the largest pore size of the sintered layer is inconsequential. The important factors that must be considered for the sintered porous ceramic support layer are the mass transfer resistance, mechanical strength, and chemical resistance.

Second, to enhance the permeability of the sintered diatomite support layer further, spherical pores were incorporated using a sacrificial polymer template method. This type of 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. Hollow spheres were adopted as a sacrificial polymer template to minimize both the amount of the gas phase and the time to complete the pyrolysis process. However, because micro-cracks can be generated within the microstructure and act as escape paths for the gas phase generated during the pyrolysis of the polymer beads despite the adoption of hollow spheres instead of solid spheres to minimize micro-cracks, the largest pore size on the surface can fluctuate. Thus, we introduced a diatomite separation layer via a dip-coating process. We then investigated whether such a layer can suppress the fluctuation of the largest pore size of the diatomite support layer.

2. Material and methods

Diatomite (Celite 499, Celite Korea Co. Ltd., Korea) was used for the preparation of the sintered diatomite specimens. To reduce the average particle size of diatomite to less than 5 μm, distilled water was used as a solvent. The slurry was ball-milled for 24 h with a ball-to-powder volume ratio of 2:1. The diatomite particles maintained both the unique shapes and inherent pores of the fossilized skeleton of diatoms after being ball-milled for 24 h. For the support layer, green bodies of diatomite particles with a polyethylene glycol binder were dry-pressed at 18.7 MPa, after which sintering was carried out at 900–1200 °C for 1 h.

To enhance the permeability of the sintered diatomite support layer, spherical pores were incorporated into the layer by a sacrificial polymer template method. Diatomite particles ranging in quantity from 0 vol% to 25 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. Next, they were sintered at 1200 °C for 1 h. To suppress the fluctuation of the largest pore size of the sintered diatomite support layer, a dip-coating process was carried out. For the separation layer, diatomite particles ball-milled for 24 h, distilled water, organic binder (HS BD-25, San Nopco Korea, Korea), and inorganic binder (AS-40, Sigma-Aldrich, USA) were mixed, dip-coated on a sintered diatomite support layer, dried at room temperature for 24 h, and then sintered at 1200 °C for 1 h.

The flexural strengths of the sintered diatomite specimens were measured by a three-point bending test (Instron 4206, Instron, USA). The pore characteristics were investigated by scanning electron micrography (JSM-5800, JEOL, Japan), mercury porosimetry (Autopore IV 9510, Micromeritics, USA) and capillary flow porosimetry (CFP-1200-AEL, Porous Materials Inc., USA).

3. Results and discussion

Typical scanning electron microscope (SEM) images of the diatomite support layers sintered at 1000 °C and 1200 °C for 1 h are shown in Fig. 1(a) and (b), respectively. These sintered diatomite specimens showed similar microstructures and maintained the unique shapes of the fossilized skeleton of the diatoms when sintered at temperatures up to 1200 °C. As shown in Fig. 2(a), the average pore size of the sintered diatomite increased slightly as the sintering temperature was increased from 900 °C to 1200 °C. Unlike the isolated pores in dense ceramics, in porous ceramics both the grains and the pores normally increase in size while decreasing in number. Generally, coarsening is used to describe the progress by