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Fabrication of porous silica ceramics by gelation-freezing of diatomite slurry

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ABSTRACT

Diatomite-derived porous silica ceramics with high porosities of up to 90% were fabricated using a gelation-freezing method, which resulted in unidirectional cellular or random microstructure with micrometer-sized cells. The ice crystals that were formed during freezing of a diatomite powder dispersed gel were removed by sublimation during vacuum drying, and the green bodies were sintered at 1150–1350 °C for 2 h in air. The thermal conductivity of the porous ceramics prepared with initial solid loadings of 5 and 10 vol% ranged from 0.09 to 0.16 W/(mK) at room temperature. The proposed method is therefore promising for the preparation of ceramic thermal insulators with very low thermal conductivity.

1. Introduction

In brittle ceramic materials used for structural applications, pores are generally considered to be an origin for fractures. However, there are many industrial applications in which porosity in ceramics is desirable, such as refractory materials, filtration materials, biomaterials, catalyst supports, thermal insulators and lightweight structural components. In particular, there is growing interest in the field of ceramic thermal insulators. The use of materials with very low thermal conductivity can lead to a reduction of heat loss from high-temperature furnaces and chemical plants, leading to improved energy efficiency. Thus, the development of ceramic thermal insulators with enhanced performance is very important from the viewpoint of industrial energy savings.

Traditional insulating firebricks and ceramic fibrous insulators are frequently used in industrial applications. The thermal conductivity of firebricks is usually high due to their low porosity, and they are used primarily for structural components such as the lining of high-temperature furnaces [1,2]. Firebricks are generally fabricated by partial sintering, where the added sacrificial organic additives are burned away. The thermal conductivity of refractory ceramic fibers (RCFs) is around 0.1 W/(mK), which is much lower than that of firebricks. However, due to their very high porosity, their mechanical strength and rigidity are relatively low. They are also categorized as Group 2 B substances (possible human carcinogens) by the World Health Organization. Consequently, RCFs should be used with caution, and substitutes should be considered. There is therefore a demand for ceramic insulators with a thermal conductivity that is comparable to that of RCFs, and that can be easily fabricated using readily available raw materials and process routes. Although the thermal conductivity can be reduced by increasing the porosity, from the viewpoint of industrial manufacturing, this causes problems with finding suitable materials and handling of the final products.

One promising category of materials is silica based ceramic produced from diatomite using a freezing method. Diatomite particles contain a large number of meso- and micropores which intrinsically reduce the thermal conductivity, and ceramics prepared using the freezing method have exhibited a very high porosity of up to 98%, in addition to structural rigidity [3]. Typical approaches involve freeze-drying of a water-based slurry, in which the pore structure is created by formation of ice crystals in the slurry, followed by sublimation of the ice under vacuum and subsequent sintering [4–6]. The pioneering work in this field was carried out by Nakazawa et al. [7] and Fukasawa and Tsujii [8]. Deville et al. [9–11] studied the kinetics of the anisotropic solid/liquid interface, along with the morphological features of the macrocellular structure. A combination of freeze-drying and gel casting is another frequently employed approach to fabricating cellular ceramics [12–18]. We have been focusing on gelation-freezing to create unique honeycomb-like microstructures, unlike the dendritic, ellipsoidal, and lamellar microstructures obtained using conventional freeze-casting, and have achieved very high porosities ranging from 79 to 98% [3,19–22].

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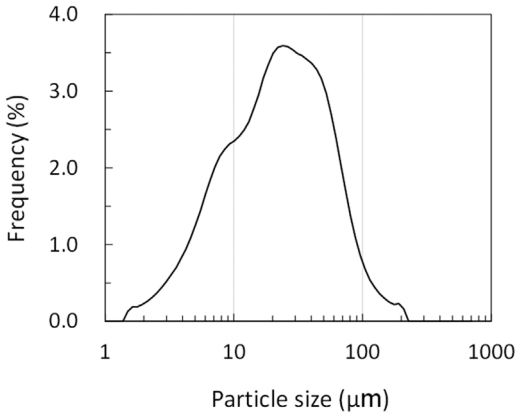

Fig. 1. Particle size distribution for as-received diatomite powder.

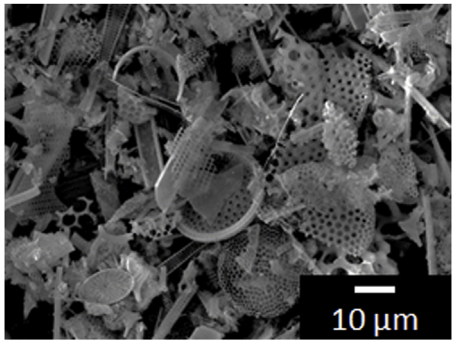

Fig. 2. SEM micrograph of as-received diatomite powder.

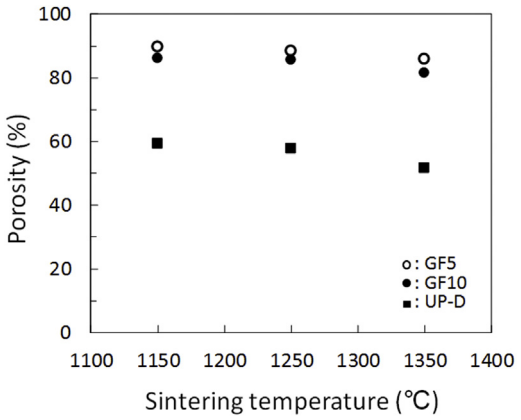

Fig. 3. Porosity of sintered GF5, GF10 and UP-D specimens as function of sintering temperature.

The purpose of the present study is to fabricate thermal insulators with a very high porosity and very low thermal conductivity using the gelation-freezing method, and to determine the relationship between the microstructure and thermal conductivity.

2. Experimental procedure

The starting material was a commercially available calcined diatomite powder (Celite577, Tokyo Kogyo Boyeki Shokai Ltd., Tokyo, Japan) with a wide particle size distribution (Fig. 1) and a 50% cumulative particle size of 21.53 μm. A scanning electron microscopy (SEM) image of the diatomite powder is shown in Fig. 2 and Table 1 gives a breakdown of its composition. The raw powder was mixed with a solution of gelatin at 50 °C at a volume ratio of 5:95 and 10:90; these specimens are hereafter referred to as GF5 and GF10, respectively. As an ice-binding additive to maintain the stable growth of ice, antifreeze glycoprotein (AFP, Nichirei foods Inc., Chiba, Japan) was used without further purification. This contains repeating alanine–alanine–threonine (Ala–Ala–Thr) tripeptide units whose threonyl OH groups are modified with the disaccharide β-D-galactosyl-(1,3)-α-*N*-acetyl-D-galactosamine, with a molecular weight distribution ranging from 2600 to 33,000 [23,24]. This protein has been reported to form either a polyproline type-II helix or a flexible random coil [24–26]. The AFP was mixed with a gelatin solution in a weight ratio of 0.25:99.75. Gels without AFP were not prepared here, because our previous report showed almost no differences among thermal conductivities of samples prepared with and without AFP [27]. The mixture was stirred under vacuum using a planetary homogenizer (ARV-310, Thinky Co. Ltd., Tokyo, Japan). In order to defoam the slurry, it was placed in a container and revolved at 1000 rpm while rotating at 2000 rpm under vacuum. It was then poured into a plastic mold and held at 7 °C to obtain a diatomite powder dispersed gel. The bottoms of plastic molds containing gels with different solid concentrations were immersed in an ethanol bath at a temperature of −40 °C. The contact (immersed) depth with the cooled ethanol was 1–2 mm from the bottom of the mold, in which ice nuclei could be formed at the bottom of gel, and then grow from bottom toward the top along a temperature gradient. After demolding, sublimation of the ice crystals in the frozen gels was carried out in a vacuum freeze drier (Model FDU-2100, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) at −12 to 30 °C at a pressure of less than 5 Pa. After drying, the green bodies were approximately 40 mm in diameter and 18 mm in height. For purposes of comparison, powder compacts of diatomite were pressed uniaxially into disk shapes using a steel mold at a pressure of 40 MPa, and these specimens were denoted UP-D. When diatomite green compacts were sintered at 1400 °C, porosities of sintered diatomite compacts were reported to be 25 vol% [28]. Thus, green bodies prepared by both gelation-freezing and uniaxial pressing were sintered at 1150, 1250 and 1350 °C for 2 h.

Table 1
Chemical composition of as-received diatomite powder (Celite 577).

Compound	Wt.%
SiO_2	91.5
Al_2O_3	4.0
Fe_2O_3	1.1
TiO_2	0.2
CaO	0.6
MgO	0.6
Na_2O/K_2O	1.2
P_2O_3	0.2

The open porosity of the sintered bodies was calculated using the Archimedes principle based on water displacement. The microstructure of the ground surfaces was observed using SEM (JEOL, JSM-5600, Tokyo, Japan). The specimens were first ground to remove the upper and lower end, and were observed in the center region around approximately 11 mm height from the bottom by using SEM. The specific surface area of all specimens was determined using the BET method (Autosorb-3B, Quantachrome Instruments Japan Co., Kanagawa, Japan). The thermal conductivity of the sintered specimens was measured using the hot-disk method (TPS1500, Kyoto Electronics Manufacturing Co. Ltd., Kyoto, Japan) with a transient plane source. A polyimide sensor with a radius of 3.189 mm was used. All thermal conductivities were measured using isotropic modes at room temperature.

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