JOURNALOF

Ceramic Processing Research

Sintering of porous ceramic of diatomite according to molding pressure and PEG content

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Diatomite powder, a naturally occurring porous raw material, was used to make ceramic materials with porosity and high strength. The sintering behavior of the diatomite powder at various sintering temperatures suggests that diatomite monoliths with a high porosity and strength can be prepared at 1100 °C. The compressive strength of the sintered diatomite monoliths increased as the sintering temperature increased, and the molding pressure of 2 MPa and the binder of 18.6 wt.% were excellent. When the sintering temperature rises, the diatomite powder is melted, and its pores gradually disappear. SEM images show that strengthening begins with the formation of inter-particle bonds at a low sintering temperature.

Key words; Diatomite, SiO₂, Molding pressure, PEG content, Sintering, Compressive strength.

Introduction

Porous materials are generally classified as micro porous materials if the pores have a diameter of less than 2 nm, a meso porous material if the pores have a diameter from 2 nm to 50 nm, and a macro porous material if the pores having a diameter of more than 50 nm. The pores of the porous material are defined as open pores if they are connected to the surface and closed pores if they are isolated from the surface. Open pores play a role in catalyst storage and in expansion of the specific surface area. Closed pores are lightweight and have insulation properties.

In every country, environmental regulations, such as CO_2 emission regulations and automobile exhaust regulations are being put in place to deal with problems caused by such emissions [1-3]. In addition, due to the increase in quality of life, interest in the environment has increased, and the demand for purifying the volatile organic compounds (VOCs) generated in living spaces is increasing [4-6]. In addition, purification of wastewater and sewage is also becoming more important [7-16].

Therefore, the porous material is used as a very good filter aid, adsorbent, additive, carrier, abrasive, and insulation. However, the general application of porous ceramics is limited because of the high cost of the material and high production costs. Therefore, in order to replace these, research is needed into methods of low cost and low temperature production. Methods for consolidation of diatomite powders for producing porous ceramics are seldom studied, and the few studies that have been conducted have dealt with methods in which porosity [17-19], microstructure, and mechanical properties depend on sintering temperature [20-22].

This study was carried out to fabricate a porous ceramic by dry pressing and atmospheric pressure sintering using a low cost diatomite. In order to better understand the strengthening and melting behavior of the diatomite, the microstructure, porosity, and compressive strength of porous diatomite monoliths are studied with regard to molding pressure, amount of binder, and sintering temperature.

Materials and Experimental Method

The diatomite powder was manufactured by Linjiang Imerys Diatomite Co. Ltd. China. Table 1 shows the chemical composition of diatomite powder.

The diatomite powder was mixed with polyethylene glycol solution (Daejung Chemicals Co., Ltd., molecular weight 4,000, hereinafter referred to as PEG). PEG solution was used with 18.6 wt.% (A type) and 22.2 wt.% (B type). The mixture of diatomite and PEG solution was dried for 12 hrs in a drier of 60 °C. PEG. 0.8 g of the dried powder was poured into a cylindrical mold with a diameter of 10 mm. The molding was compressed to three types of pressures of 2, 5, and 8 MPa to make a cylindrical shape having a diameter of 10 mm. The PEG binder was removed from the cylindrical specimens by maintain of 2 hrs at

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Table 1. Chemical composition of as-received diatomite powder.

Compound	wt.%
SiO2	92.43
Na2O	2.47
A12O3	1.63
Fe2O3	1.50
K2O	0.53
CaO	0.30
MgO	0.21
TiO2	0.11
Cl + SO3	0.82

a maximum temperature of 600 °C. The heating rate is 30 °C/min. The atmospheric pressure sintering was subsequently carried out at with the temperature increasing from 900 to 1,400 °C at a heating rate of 10 °C/min. It was maintained at the maximum temperature of each temperature for 1 hour and was cooling in furnace for 24 hrs. Binder removal and sintering was carried out in air in a tube furnace (Lenton, Model: LTF-180).

The crystal structure of the diatomite powder was analyzed by an X-ray diffractometer (X-Ray Diffractometer: UltimaIV, Rigaku, Japan). Thermal gravimetric analysis (Thermogravimetric Analyzer, TGA 7 PerkinElmer, USA) of diatomite powder was performed in air at a heating rate of 10 °C/min. The component of the sintered diatomite monoliths was determined by EDX (energy dispersive X-ray spectrometer, Horiba, Japan). SEM (scanning electron microscope: Hitachi S-2700, Japan) was used for the characterization of the original diatomite particles and the fracture surface.

Compression testing of the sintered diatomite specimens was carried out by applying a compressive load on the cylindrical specimen until a crack formed, causing a fracture of the specimen. The compression tests were carried out under atmospheric conditions using a universal testing machine at a constant crosshead displacement rate of 0.5 mm/min. A minimum of three specimens were tested for each sintering temperature under the same conditions.

Results and Discussion

As seen in Fig. 1 the appearance of the diatomite reveals its unique porous structure. Diatomite is a naturally obtained raw material. Table 1 shows the chemical composition of the diatomite powders used, which has a silica content of 92.43%. A diatomite powder having a silica content of 85% or more is considered to be a high silica diatomite powder. This is often used as commercially available celite filter. The other impurities in the diatomite powder are Na₂O, Fe₂O₃, K₂O, CaO, MgO, and TiO₂.

The TGA of the diatomite powder is shown in Fig. 2. As can be seen, the diatomite powder contains little volatile impurities. That is, the diatomite powder



Fig. 1. SEM of the as-received diatomite powder.



Fig. 2. TGA curve of diatomite powder.

showed a weight loss of about 0.4% at 800 °C. From this, diatomite powder used in this study can be said to be high purity material. In general, volatile impurities make secondary pores and can affect the original shape of the diatomite shell during the consolidation process.

Fig. 3 shows the XRD of the diatomite powder. The images reveal that the calcination treatment has transformed the amorphous silica of the diatomite into cristobalite. Cristobalite is used in applications more frequently than amorphous silica, due to its excellent chemical and thermal stability.

Fig. 4 shows the sintering density according to the sintering temperature. The measured density after PEG binder removal was 1.0 g/cm³. The sintering temperature was from 900 °C to 1,400 °C. The sintered density of diatomite increased as the sintering temperature increased, regardless of the type, and it could be divided into two stages. The first stage increased slowly from 900 °C to 1,200 °C. The second stage increased sharply from 1,200 °C to 1,400 °C. A sharp increase may be associated with the formation of a melt phase, which promotes liquid phase sintering. The formation of a melt phase can be determined from the fracture surface (Fig. 7). B type with high PEG content has a higher



Fig. 3. XRD pattern of diatomite powder.



Fig. 4. Sintered density depending on sintering temperature.

density than A type. This is also related to melting (Fig. 8). As is demonstrated in Table 2, the two types of compositions were injected into a cylindrical mold for a compression test and molded at three different pressures.

Fig. 5 shows the compressive strength of fabricated specimens at two different ratios. PEG has 18.6 wt.% of A type and 22.2 wt.% of B type. When the PEG concentration was less than A type, it was not molded, due to insufficient viscosity. When the PEG concentration was more than B type, diatomite powder was aggregated because of high viscosity, so that fine powder could not be obtained. Compressive strength increased as the sintering temperature increased, regardless of PEG content. The A type diatomite monoliths sintered at 1,100 °C show a compression strength as high as 18 MPa. This is sufficient for applications like water and air filtration. However, B type was about 10 MPa, which was smaller than A type. The A type diatomite monolith sintered at 1,400 °C showed a high compressive strength of $73 \sim 84$ MPa, while the B type showed $48 \sim 70$ MPa. Diatomite powder is melted as the sintering temperature increases, and the pores of the diatomite gradually disappear. That is, the volume of the molding specimen gradually decreases. This shows



Fig. 5. Compressive strength of diatomite monoliths as a function of sintering temperature.



Fig. 6. Compressive strength of sintered A and B type diatomite monoliths at 1400 °C as a function of molding pressure.

that the pores of the diatomite disappear from the fractured surface (Fig. 7), described later. The compressive strength of A and B types was higher when the molding pressure was smaller. That is, it was 2 MPa > 5 MPa > 8 MPa. High pressures were densely molded the specimens, and the sintered specimen showed a crack propagation rapidly and showed low compressive strength. The low pressure is considered to be due to the formation of many pores between the diatomite powders and the suppression of crack propagation. Regardless of the molding pressure, the compressive strength of type A with small PEG content was higher than that of type B. This is because the porosity increases as the amount of added PEG increases. B type with high PEG content was sintered more densely than A type, resulting in low porosity. As the amount of PEG binder was smaller, more pores were formed, and the formation of the pores interrupted the progress of the cracks. Therefore, the compressive strength of A type was higher than that of B type.

Fig. 6 shows the compressive strength of A and B type specimens sintered at a temperature of 1,400 °C as a function of molding pressure. The compressive strength of type A was 21% (2 MPa), 13% (5 MPa) and 53% (8 MPa) higher than B type.



Fig. 7. SEM from the fracture surfaces of the sintered A type diatomite monoliths at (a) 900 °C, (b) 1000 °C, (c) 1100 °C, (d) 1200 °C, (e) 1300 °C and (f) 1400 °C. Molding pressure of 2 MPa.



Fig. 8. EDX analysis from (a) As-received diatomite powder, and (b) Sintered A type diatomite monoliths at a molding pressure of 2 MPa and a sintering temperature of 1100 °C.

The SEM of diatomite monoliths sintered at 900 °C (Fig. 7(a)) and 1,000 °C (Fig. 7(b)) shows that the diatomite particles bind together without any significant effect on the original pore structure of the diatomite powder. The larger pores in the sintered diatomite monoliths relate to inter-particle voids. This kind of microstructure is typical of porous materials characterized by intra-particle and inter-particle pore, respectively. The diatomite monoliths sintered at 1,100 °C (Fig. 7(c)) and 1,200 °C (Fig. 7(d)) still has much porosity. However, some of the molten phase covers the diatomite particles, and the pores of the diatomite disappeared. The impurities of diatomite, such as Na₂O, Al₂O₃, K₂O, CaO, and MgO (Table 1) promoted the formation of a low-temperature eutectic mixture, and thus they formed a molten state in the silica-rich grains. When the sintering temperature rises above 1,300 °C (Fig. 7(e)), the amount of the molten phase increases. And this could confirm that a small amount of porosity remained in part of the material. The diatomite monoliths sintered at 1,400 °C (Fig. 7(f)) means that the molten of the diatomite appears as particle coarsening and aggregation. A mass transfer by viscous flow was observed during sintering of various silicates at high temperatures. Partial melting of the diatomite grains eliminates the fine porosity of the diatomite, but the amount of the liquid phase may be

insufficient to close the pores between the now dense silica-rich grains. Some pores are still observed at fracture surfaces of the diatomite monoliths sintered at 1,400 °C. This can be seen as the thermally stable cristobalite phase of the original diatomite powder.

Fig. 8 is the EDX analysis. Here, (a) shows the diatomite powder, and (b) shows the A type diatomite monoliths (b) sintered at 1100 °C with the molding pressure of 2 MPa. Diatomite powder (a) has all the elements (O, Si, Al, Na, K, Cl, Fe) of the chemical components shown in Table 1. Four elements (O, Si, Al, and Na) were obtained in the liquid phase of A type diatomite monoliths (b) sintered at 1100 °C. It is judged that the very small amount of others elements are melted and dispersed at high temperature or burned.

Conclusions

Porous ceramic monoliths sintered using low cost diatomite was prepared by dry pressing and atmospheric pressure sintering. It was found that the sintering behavior of diatomite powders at various sintering temperatures and molding pressures can fabricate diatomite monoliths with high porosity and a high compressive strength. The compressive strength of the sintered diatomite monoliths increased as the sintering temperature increased, and the molding pressure of 2 MPa and the binder of 18.6 wt.% were excellent. Diatomite powder with a high porosity and strength can be prepared at 1,100 °C. When the sintering temperature rises, the diatomite powder is melted, and the pores of the diatomite gradually disappear. The impurities of diatomite such as Na₂O, Al₂O₃, K₂O, CaO and MgO promoted the formation of a low temperature eutectic mixture, and thus they formed a molten state in the silica-rich grains. SEM shows that strengthening begins with the formation of inter-particle bonds at a low sintering temperature.

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