Advanced Powder Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Fabrication of highly porous honeycomb-shaped mullite–zirconia insulators by gelation freezing

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ARTICLE INFO

Article history:
Received 26 August 2015
Received in revised form 2 February 2016
Accepted 10 February 2016
Available online xxxx

Keywords:
Insulators
Mullite
Freeze casting
Thermal conductivity
Compressive strength

ABSTRACT

Highly porous mullite-based thermal insulators were fabricated using a gelation freezing technique. In this process, a honeycomb-like arrangement of pores is created by forming ice crystals within a gel containing dispersed mullite particles, followed by sublimation of the ice under vacuum and subsequent sintering. The uniform arrangement of pore channels and cell walls results in a mullite insulator with a very high compressive strength, even for porosities of up to 91.5 vol%, together with low thermal conductivity. The mechanical strength of this insulator was found to be strongly influenced by the amount of antifreeze protein, the sintering additive in the raw mixture, and the sintering temperature. The use of 0.25 wt% antifreeze protein with the additive 8Y–ZrO_2 gave a compressive strength of 11.3 MPa, a porosity of 89.1 vol%, and a thermal conductivity of 0.28 W/m K. This approach can be used to produce macrocellular insulators with specific porosity, thermal conductivity and mechanical properties, suitable for a variety of industrial applications.

1. Introduction

Energy consumption by the ceramics industry is generally higher than that for other industries, because heating, calcination and sintering of powders at elevated temperatures are required. In fact, while the overall shipping cost associated with the ceramics industry is just 2.2% of the total value for all Japanese industry, the energy consumption is much higher, at 5.4% [1]. In the furnaces that are typically used for heating or sintering, 40% of the energy consumed is stored in and then released from thermal insulators, and only a very small fraction (about 2–3%) is actually used to make products [2]. This wastage of heat results from the poor thermal insulation provided by the low-porosity firebricks that are often used as structural components such as linings for industrial furnaces [3,4]. Refractory fibrous insulators have a very low thermal conductivity of approximately 0.1 W/m K or less, but do not have sufficient mechanical strength or shape rigidity. In addition, according to the World Health Organization, ceramic fibers are now classified as Group 2B materials, meaning that they are possibly carcinogenic to human. Therefore, these materials should be used with extreme caution, and safer alternatives pursued. Current research is focused on the development of structural thermal insulators that have a similar thermal conductivity to that of ceramic fibers, and a similar strength to that of insulating firebricks.

It may be possible to overcome the above problems by using a freeze casting method to fabricate thermal insulators, because porous ceramics prepared by this route have exhibited improved mechanical strength and structural rigidity, despite their very high porosity [5–8]. Typical approaches involve freeze drying of a water-based slurry, during which pore formation is closely correlated with the growth of ice crystals in the slurry, followed by sublimation of the ice under vacuum and subsequent sintering. Fukasawa and Ohji have reported pioneering work in this field [9–11]. Deville et al. [12–14] studied the anisotropic interfacial kinetics at the solid/liquid boundary during the freeze casting process, along with the morphological features of the resulting macrocellular structure. Combined freeze drying and gel casting techniques have also been frequently applied to the fabrication of cellular ceramics [15–21]. Our group has focused on gelation freezing to create unique honeycomb-like microstructures that are unlike the dendritic, ellipsoidal, and lamellar microstructures obtained via conventional aqueous freeze casting. Gelation freezing can produce a microstructure with highly interconnected pores, and porosities ranging from 79% to 98% [6,7,22–25]. Due to the unique unidirectional honeycomb structure, the mechanical strength of porous ceramics fabricated using this method can be substantially higher than that for ceramics prepared by

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http://dx.doi.org/10.1016/j.apt.2016.02.015
0921-8831/

conventional aqueous freeze casting, despite the fact that the porosity is higher [23]. The purpose of the present study is to fabricate thermal insulators with a very high porosity using gelation freezing, so as to obtain insulators exhibiting both high strength and low thermal conductivity. In a separate paper, we will report on preliminary investigations into the defect-free morphology achieved using antifreeze protein additives to retard the formation of ice lenses, the variations in cell size and orientation obtained under different freezing conditions, and the relationship between porosity and initial slurry concentration [8].

2. Materials and methods

2.1. Mullite powder synthesis

Kaolinite (Eckalite-1, Imerys Japan Co. Ltd., Tokyo, Japan) with an average particle size of 0.4 μm, and aluminum hydroxide (Higilite 43M, Showa Denko Co. Ltd., Tokyo, Japan) with an average particle size of 0.7 μm, were used as raw materials. High-purity mullite powder with an average particle size of 0.7 μm was employed as a seeding material (KM101, KCM Corporation Co. Ltd., Nagoya, Japan) and was blended at a mass ratio of 1:50 with a mixture of kaolinite and aluminum hydroxide (which itself had a kaolinite-to-aluminum hydroxide mass ratio of 45:55) to obtain the stoichiometric composition of mullite ($3Al_2O_3{\cdot}2SiO_2$). This mixture was blended for 24 h by ball milling with Al_2O_3 balls, and then dried and calcined at 1300 °C. X-ray diffraction (XRD) patterns for the calcined powder indicated a well-crystallized mullite phase without any other phases. The calcined powder was used to prepare mullite insulators via a gelation freezing method.

2.2. Fabrication of insulators

The obtained mullite powder was mixed with the sintering aid 8Y–ZrO_2 at a mullite-to-ZrO_2 mass ratio of 98:2 in order to promote densification and retard grain growth in the mullite phase. The mixture was pulverized for 3 h using a planetary mill consisting of an Al_2O_3 pot and Al_2O_3 balls to obtain fine mullite particles. The resulting slurry was poured into a warm solution of gelatin (Wako Pure Chemical Industries Ltd., Tokyo, Japan) and antifreeze glycoprotein (AFP, Nichirei Foods Inc., Chiba, Japan), at a mullite/ZrO_2-to-gelatin solution volume ratio of 5:95, and AFP-to-gelatin mass ratios of 0.25:99.75, 0.50:99.50, and 1.00:99.00. Note that the detailed molecular structure of AFP has been reported elsewhere [26–29]. The resulting slurry was then poured into a plastic mold and kept at 7 °C to obtain a gel containing dispersed mullite powder. The plastic molds containing the gel were then immersed in an ethanol bath at either −40 or −60 °C. After demolding, ice crystals that had formed in the frozen gels were removed by sublimation in a vacuum freeze drier (Model FDU-2100, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) at a temperature of −12 to 30 °C and a pressure of less than 5 Pa. The resulting green bodies were sintered at 1450 or 1500 °C for 2 h to obtain highly porous mullite thermal insulators.

2.3. Sample characterization

The porosity, microstructure, thermal conductivity, and compressive strength of the prepared insulators were measured. The open porosity of the insulators was calculated using the Archimedes method with water displacement. The microstructure of polished surfaces was observed using a digital microscope (VHX5000, Keyence Co. Ltd., Osaka, Japan). The thermal conductivity was determined via a hot-disk method (TPS1500, Kyoto Electronics Manufacturing Co. Ltd., Kyoto, Japan) with a transient plane source (TPS) and a polyimide sensor with a radius of 3.189 mm. The output power and measurement time were varied over the ranges of 0.02–0.08 W and 20–40 s, respectively, depending on the thermal characteristics of the sample. All conductivities were measured in isotropic mode at room temperature. The compressive strength of insulator samples having a diameter of ∅5 mm and a height of 10 mm was measured using a universal testing machine (MTS Systems Corporation, Sintech 10/GL, Minnesota, USA), applying a crosshead speed of 0.5 mm/min.

3. Results and discussion

Table 1 summarizes the porosities of insulators produced using different ZrO_2 and AFP fractions in the initial slurry, freezing temperatures and sintering temperatures. The porosity of the samples was clearly affected by the processing parameters. Lower porosity were obtained for samples prepared with ZrO_2 than without it, suggesting that ZrO_2 promoted densification of the mullite phase, as will be discussed later. In addition, the porosity increased with decreasing AFP fraction in the initial slurry. In contrast, the freezing temperature had almost no effect on the porosity, which is consistent with our previous findings [6,7,23,25]. Consistently lower porosity was obtained for a sintering temperature of 1500 °C than for 1450 °C. This was due to sample densification by larger shrinkage during sintering at higher temperature.

Fig. 1 shows typical optical micrographs of the polished surfaces of samples A and C in Table 1, prepared by freezing at −60 °C with a ZrO_2 content of 2% and AFP contents of 1% and 0.25%, respectively. These samples were observed in a perpendicular section to the freezing direction (channel direction). The observed morphologies are typical of the anisotropic cellular structures produced by gelation–freezing [6,7,22–24,30], and consist of uniformly distributed micrometer-sized honeycomb-like cells. These cells are of varying sizes in both samples, but are unlike those created by conventional aqueous freeze casting, suggesting that this method inhibits the formation of lamellar or dendritic structures that freely and preferentially grow during conventional freezing. During the freezing process, the particles that form the cell walls are rejected by ice crystals growing along the temperature-gradient direction in the gel body. This occurs because the ice column cannot contain any impurities due to their very low solubility in the crystal lattice, with the exception of HF and NH_3 [20,21]. Thus, the gelatin does not dissolve in the ice and is rejected from the growing ice column. In addition, the preliminary addition of gelatin to the slurry, which causes the gelatin to dissolve in the water without gelation, generates dendritic or lamellar structures as expected. This indicates that the gel state greatly reduces water migration during freezing and is essential to the creation of the honeycomb-like morphology. The water molecules in the initial gel body form a discontinuous network,

Table 1
Processing conditions and porosities for fabricated insulators.

	FSZ content in initial slurry	AFP content in initial slurry	Freezing temperature (°C)	Sintering temperature (°C)	Porosity (vol%)
A	2	1	−60	1450	88.9
B		0.5			89.9
C		0.25			90.8
D			−40		90.7
E		1	−60	1500	85.7
F		0.5			87.9
G		0.25			89.1
H	0				91.0
I	2		−40		88.7
J	0				91.5

Please cite this article in press as: M. Fukushima, Y.-i. Yoshizawa, Fabrication of highly porous honeycomb-shaped mullite–zirconia insulators by gelation freezing, Advanced Powder Technology (2016), http://dx.doi.org/10.1016/j.apt.2016.02.015