FULL PAPER

Fabrication of mullite fiber porous ceramics with even structures by filtration freeze-drying

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In this study, mullite fibrous porous ceramics (MFPCs) were fabricated by freeze-drying wetted bodies formed using vacuum filtration. The effects of freezing temperatures on the microstructure and mechanical properties were investigated. The investigations revealed that freeze-drying could effectively stop silica sol migration and obtain a uniform porous ceramic microstructure in which the binder covered the fiber surfaces and bonded the fibers at nodes. Owing to the homogeneous microstructure, the compressive strength of the obtained MFPCs with open porosity of 85.4% was more than 2.0 MPa, and there were two elastic regimes and one plastic regime in the stress–strain curve of the MFPCs, moreover, which revealed that the MFPCs fractured step by step under compression. In addition, the freezing temperatures affected the properties of the MFPCs because of the formation of plates derived from the binder.

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Key-words: Mullite fibrous porous ceramics, Freeze-drying, Microstructure, Mechanical properties

1. Introduction

Fibrous porous ceramics for use as structural and functional materials have received considerable attention due to the interesting combination of mechanical, chemical and physical properties.¹ Porous ceramics are widely applied in various fields for such purposes as hot gas filtration,² high-temperature thermal insulation³,⁴ and catalyst supports.⁵ Since fibers are soft materials, some method of bonding the fibers at overlapping points is required to give the fiber-based porous ceramic bodies rigidity and strength. Generally, these overlapping points, which are tightly bonded by binder, are called nodes. The nodes greatly stiffen this kind of porous ceramics.⁶ The quantity, distribution and morphology of the nodes therefore play significant roles in determining the mechanical properties of fibrous porous ceramics. It is thus essential to control the distribution and morphology of the nodes to fabricate desired fibrous porous ceramics.

The formation method is one of the factors that affects the distribution of the nodes in a sample. Fibrous porous ceramics can be fabricated by a variety of methods, including gel-casting,⁷,⁸ freeze-casting,⁹,¹⁰ vacuum filtration¹¹,¹²) compared with gel-casting and freeze-casting, vacuum filtration is more suitable for obtaining light weight and high-strength fibrous porous ceramics. During the filtration process, the fibers form a three-dimensional (3D) skeleton, and appropriate amounts of the binders are trapped at the intersections of pairs of fibers due to the blockage by fibers.¹³) The drying process after filtration is another important factor affecting the distribution of binder. At present, the drying methods for high moisture ceramic bodies include free convection drying, forced convection drying, radiation drying, and microwave drying.¹⁴) The main drying process in the above drying methods is migration of moisture from inside a wet body to the surface and vaporization of the moisture from the surface, which may result in binder particles moving from the interior to and aggregating on the sample surface, which leads to uneven distribution of the binder.¹⁵)

Herein, we demonstrate an effective strategy for solving the uneven distribution of the binder by using freeze-drying.¹⁶) In the freeze-drying process, the wet body was solidified by turning the liquid growing in the body into ice crystals by placing it in a low temperature environment.¹⁷,¹⁸) Binder particles were fixed and retained in the original distribution positions after sublimation of the ice crystals.

In this study, fibrous porous ceramics with mullite fibers as substrates and silica sol as binder were fabricated by filtration formation and freeze-drying. In addition, the microstructures and compressive behavior of fibrous porous ceramics frozen at different temperatures were investigated to determine the effects of the freezing temperature on
the microstructures, thermal conductivity and mechanical properties.

2. Experimental procedure

2.1 Raw materials

In this study, commercially available polycrystalline mullite fibers (99.5%, Zhejiang Hongda Crystal Fiber Co., Ltd., China) with an average diameter of 10 µm were chopped to lengths of 500–800 µm. Aqueous silica sol (30 wt %, Tongda Weipeng Electric Co., Ltd., Zhejiang, China) was used as a high-temperature binder. Polyacrylamide (PAM) (AR, Kemiou Chemical Reagent Co., Ltd., Tianjin, China) was used as a low-temperature binder. Polyacrylamide (PAM) (AR, Kemiou Chemical Reagent Co., Ltd., Tianjin, China) was used as a low-temperature binder to improve the strength of the green bodies. Boron carbide powders (Mudanjiang Chenxi Boron Carbide Co., Ltd., China) were used as sintering additives.

2.2 Preparation procedures

The starting slurry contained 8.25% chopped mullite fibers, 91.57% aqueous silica sol (10 wt %), 0.13% PAM and 0.05% boron carbide powders. As shown in Fig. 1, the processing procedure for MFPCs included the following four steps: slurry preparation, molding, drying and sintering. First of all, ultrafine B₄C powder and PAM powder were added to silica sol. A homogeneous slurry was obtained by stirring mechanically for 5 h at a speed of 180 r/min. Next, chopped fibers were added to the above slurry. The slurry with fibers was stirred with a high-shear sigma blade mixer to form a highly dispersed slurry. Second, bulk was fabricated by pouring the fiber slurry into a cylindrical mold and removing the surplus slurry by filtration. The bulk was frozen at −20, −80 and −196°C using a cryopreservation box (BDF-60V50, Ji’nan Xin Bei Xi Biological Technology Co., Ltd.) and liquid nitrogen. Sublimation of the ice crystals was carried out by freeze-drying at −55°C and 75 Pa for 36 h in a vacuum freeze drier (FD-1A-50, Boyikang Laboratory Instrument Co., Ltd., Beijing, China), and green bodies were obtained. Finally, the green bodies were sintered in air at 1300°C at a heating rate 5 °C/min, and the holding time was set at 2 h.

2.3 Characterization

The microstructures of the MFPCs were observed by scanning electron microscopy (SEM, Nanosem 430, FEI Technologies Inc., Oregon, United States). The bulk densities were obtained from the mass and dimensions and the open porosities were determined by the water-immersion technique using the Archimedes method. The thermal conductivity was measured with a thermal conductivity instrument (C-3000, Xian Xiaxi Electric Co., Ltd., Shaxi, China). Samples were machined to dimensions of 20.0 mm in diameter and 20.0 mm in height to perform compression testing using a universal testing machine (UTM4204, Suns Technology Stock Co., Ltd., Shenzhen, China) with a 5 KN load cell at a constant loading speed of 0.02 mm/min. To ensure the accuracy of the results, five samples were tested for each kind of material. The compressive strength (σ) was obtained from the elastic maximum in the stress–strain curves and the Young’s modulus (Eₛ) was the ratio of the stress (σ) to strain (ε) within the elastic limit of the compressed sample,¹⁷) as:

\[
Eₛ = \frac{σ}{ε}
\]

3. Results and discussion

3.1 Microstructures and mechanical properties of the MFPCs

In this study, wet bodies of MFPCs were fabricated using vacuum filtration. During this process, chopped mullite fibers overlapped to form a 3D network skeleton and binder particles collected at the fiber nodes due to the blocking effect of the fiber network. The drying method played a vital role in the distribution of the high-temperature binder, consequently influencing the mechanical properties of the fibrous ceramics.

3.1.1 Structural uniformity of the MFPCs

Figure 2 shows the morphology of different cross-sections of an MFPC sample (frozen at −196°C). It can be seen that the high-temperature binder is distributed homogeneously at the fiber nodes in the sample. The principle of freeze-drying was that the moisture in the sample was rapidly solidified into ice by cold treatment, and the binder particles were fixed in their original positions. The ice crystals were sublimated under appropriate temperature and vacuum condition, resulting in perfect retention of the original structure (silica sol distribution). During the freezing process of MFPCs at −196°C, the transfer of heat (cold) was mainly through the fibers due to the porous structure. That is to say, the fibers become the local cold

Fig. 1. The MFPCs preparation process.
source, and there was a temperature gradient between the fibers and liquid, leading to formation of a dense, uniform film wrapping on the surface of the fibers and bonding at the nodes of the fibers. The rapid freezing process preserved the uniform liquid distribution in the fiber networks, eventually forming the even microstructures shown in Fig. 2.

### 3.1.2 Density, porosity and compressive behavior of the MFPCs

Figure 3 presents a compressive stress–strain curve of the MFPCs, showing that the peak stress of the MFPCs was up to 2.1 MPa at a strain of 12.5%. The mechanical properties of porous ceramics depend heavily on the microstructure, density and porosity of these materials. According to Rice’s equation,[18] the compressive stress of porous ceramics and porosity show an exponential relationship, as follows:

$$\sigma = \sigma_0 e^{-bp}$$

(2)

where $\sigma_0$ is the zero-porosity compressive stress, $b$ reflects the particle stacking and shape, and $p$ is the volume fraction porosity. This indicates that porosity is a factor that influences the mechanical properties of porous ceramics. The density and porosity of the MFPCs are 0.37 g/cm$^3$ and 85.4%, respectively. In the compressive stress–strain curve (Fig. 3), three distinct zones can be seen: (i) one elastic regime with a slope of 21.5 MPa (from O to A) and another elastic regime with a slope of 12.2 MPa (from A to B) where stress increases almost linearly with strain; (ii) a plastic regime (from B to C) where stress increases nonlinearly with strain; and (iii) a stress plateau regime (from C to D) exhibiting a trend of volatility over a large range of strain. The elastic modulus values of the MFPCs were taken from the linear slope of the compressive stress–strain curve, and the MFPCs therefore experienced two elastic regimes under compression with elastic moduli of 21.5 and 12.2 MPa, respectively.

The microstructures of fracture sections of the sample at different stages were investigated as shown in Fig. 4. It can be seen that, after the first elastic regime, some weakly bonded nodes were broken [Fig. 4(a)], but a large number of nodes remained securely by fibers, which enabled the samples to pass into the second elastic regime with a lower elastic modulus. In Fig. 4(b), it can be observed that some binder became unbound at the nodes after the second elastic stage, which inevitably damaged the fiber network. With load increases, fiber breakage and binder breakage at the nodes were aggravated, which greatly weakened the stability of the fiber network. We can see from Fig. 4(c) that the fiber network became densified due to an accumulation of fiber fragments and greater strain under increasing stress. Therefore, the overall structure of the MFPCs collapsed after the plastic stage [Fig. 4(c)].

### 3.2 Effects of freezing temperatures on the microstructures of MFPCs

Figure 5 shows the morphologies of the MFPCs that were freeze-dried at $-196, -80$ and $-20^\circ$C. The mullite fibers are oriented randomly in 3D space, thus making them isotropic in 3D directions. The mullite fibers are dispersed relatively uniformly, moreover, and are bonded at the fiber junctions by high-temperature binder, which was produced by sintering $\text{B}_4\text{C}$ and silica sol in air. The uniform distribution of mullite fibers in the MFPCs was attributed to the addition of PAM to the original slurry[19] and prevented aggregation between the fibers. It is noteworthy that there were some differences in the binder on the fiber
surfaces in MFPCs fabricated at different freezing temperatures. Thin borosilicate films covered the fibers of samples frozen by liquid nitrogen (−196°C) as shown in Fig. 5(a). The thin borosilicate films were transformed into borosilicate plates with stretching of the fibers, and the plates became larger with increases in the freezing temperature, as seen in Figs. 5(b) and 5(c). These features can most likely be attributed to the fact that relatively low freezing temperatures decrease the time required to freeze samples completely.

Figure 6 shows the variations in freezing times and binder plate sizes for MFPCs at different freezing temperatures. The freezing velocity was estimated by dividing the freezing distance (from the surface of a sample to the freezing position) by freezing time, which was obtained by recording the time from putting the wet samples into the cryopreservation box to the end of the freezing process. The freezing velocities at −20, −80 and −196°C was 44.2 ± 4.5, 6.5 ± 1.0 and 3.2 ± 0.2 mm/h. The freezing

![Fig. 4.](image)

Fig. 4. The fracture morphology of MFPCs (a) after the first elastic stage; (b) after the second elastic stage and (c) after the plastic stage.

![Fig. 5.](image)

Fig. 5. The morphology of MFPCs frozen at different temperatures: (a) −196°C; (b) −80°C and (c), (d) −20°C.

![Fig. 6.](image)

Fig. 6. Freezing times and plate sizes of MFPCs at different freezing temperatures.
time of the MFPCs increased from 0.1 to 3.2 h and the binder plate sizes increased from 1.5 to 21.2 μm as the freezing temperature increased from −196 to −20°C. The binder in the wet samples after vacuum filtration was frozen quickly at the fiber surfaces and the fiber nodes in the MFPC samples frozen at −196°C. For the samples frozen at −80 and −20°C, the binder collected along the fibers due to the flow characteristics before the samples were completely frozen and the collected binder increased with increases in freezing time. The binder plates at −20°C were therefore larger than those at −80°C. In the high-magnification image shown in Fig. 5(d), the binder plates were porous microstructures, which resulted from locally unidirectional freezing.21)–23) During the freezing process, temperature gradients between the fibers and the gas-phase, and the fibers became local cold sources. Therefore, the ice crystals in the collected binder grew directionally from the fibers, and the growth velocity increased with the decreases in the freezing temperature from −20 to −196°C. Binder particles were ejected by the upward moving ice fronts and accumulated between the growing ice crystals.21),22)

3.3 The effects of freezing temperature on the properties of MFPCs

The open porosities and densities of MFPCs frozen at different temperatures are presented in Fig. 7(a). As shown in Fig. 7(a), increasing the freezing temperature from −196 to −20°C resulted in a slight increase in density from 0.34 to 0.39 g/cm³ and a decrease in open porosity from 89.2 to 84.5%. Figure 7(b) shows variations in the room temperature thermal conductivity and compressive strength of MFPCs. The room temperature thermal conductivity of MFPCs increased from 0.055 to 0.103 W/(m·K) and the compressive strength decreased from 2.1 to 1.3 MPa as the freezing temperature increased from −196 to −20°C. Density and porosity both played important roles in determining the thermal and mechanical properties of porous ceramics. A slight change in porosity and density did not cause an almost twice as much change in thermal conductivity and compressive strength. The formation of binder plates should therefore be another influencing factor on the improvement of the properties. As shown in Fig. 6, increasing the freezing temperature leads to the formation and enlargement of binder plates. It can be concluded that the formation of binder plates on the fibers was the main factor affecting the thermal conductivity and mechanical properties of the MFPCs. The formation of binder plates decreased the amount of binder at the nodes leading to a decrease in the strength of the MFPCs, and expanding the joint faces of the fibers, which increased the thermal conductivity.

4. Conclusion

In this study, the microstructures and properties of mullite fibrous porous ceramics fabricated by vacuum filtration and freeze-drying were investigated. Furthermore, the effects of the freezing temperature on the microstructures and properties of MFPC samples were explored. The conclusions can be summarized as follows:

(1) The MFPCs exhibited a homogenous distribution of binder, which covered the fiber surfaces and bonded the fibers at the nodes. The three-dimensional random orientation and bonded node fiber network of the MFPCs had high structural stability and load-bearing capacity.

(2) Freezing temperatures affected the binder distribution in the MFPCs significantly. Lower freezing temperatures provided the benefit of achieving uniform bonded node fiber networks. When the freezing temperature was increased to −20°C, the binder formed plates on the fiber.

(3) The freezing temperature affected the properties of the MFPCs remarkably because of the formation of binder plates. The thermal conductivity and compressive strength of the MFPCs increased from 0.055 to 0.103 W/(m·K) and decreased from 2.1 to 1.3 MPa when the freezing temperature increased from −196 to −20°C, corresponding to density from 0.34 to 0.39 g/cm³ and porosity from 89.2 to 84.5%.

Rapid freeze-drying at an ultra-low temperature after vacuum filtration can therefore be considered an efficient...
method of preparing MFPCs with low thermal conductivity and enhanced mechanical properties.

Acknowledgment This work was supported by the National Natural Science Foundation of China (Project No. 51472176) and the Aeronautical Science Foundation (No. 2016ZF48006).

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