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Improvement of alumina-based porous body fabricated by freeze casting route via alpha alumina/colloidal silica sol precursors

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Abstract

In this paper, alumina-based porous bodies were fabricated by the freeze casting method, and the effects of solid content and freezing conditions on mechanical properties, water permeability, and microstructure of samples were thoroughly investigated. Microstructural evaluation revealed highly porous microstructures with unidirectionally aligned porosities in the samples. SEM micrographs exhibited uniform pores with an average size of 5 μm. Additionally, EDS analysis and SEM mapping showed a comprehensive interconnected porous framework among alumina particles fabricated by amorphous colloidal silica during the freezing step. Mullite phase was observed in the XRD patterns of the samples after sintering at 1400 °C for 2 h. Maximum compressive strength reached 145 MPa, and this significant mechanical strength was owing to the particle densification caused by the mullitization reaction between alumina and silica during sintering. Physical properties measurements illustrated the minimum open porosity of 41 vol.% and the maximum bulk density of 2.1 g cm⁻³. Permeability assessment as an important factor to evaluate filtration efficiency showed at least 0.22 (g. cm⁻². s⁻¹. bar⁻¹) water flow rate, which was approximately twice greater than that of other recent works.

1. Introduction

In accordance with recent research and studies, it is found that porous ceramic bodies drew considerable attention in the past decade. This is owing to their application in various fields such as membrane and catalyst supports, fuel cells, energy devices, biomaterials scaffolds, exhausted diesel and industrial hot corrosive gas [1–3]. Additionally, porous ceramics have been increasingly used in filtration and catalysts, thermal insulation, implantable materials, and composites [4]. Filtration and catalyst applications are highly important due to the global concern over drinking water purification. Recently, fabrication of porous ceramic filters has gained more interest and came to light for various applications. Membranes, as a good example of them, have been used to separate a large majority of micron-sized and even nano-sized materials. Different porous bodies with different pore size can separate specific materials according to their molecular size. For instance, a porous body with the permeable pore size of approximately 0.1 to 10 μm is a suitable option for microfiltration [3]. Therefore, choosing suitable materials, along with utilizing an efficient fabrication method is an initial step to fabricate a desired porous body. Appropriate materials may have specific chemical and thermal stability, in addition to other favorable properties for target application.

Alumina, as an engineering ceramic, has received particular attention owing to its high mechanical strength, thermal shock resistance, and excellent thermal and chemical stability. These properties made alumina a remarkable candidate for several fields, such as high-temperature catalyst supports, refractories, thermal insulators, and molten metal filters [6, 7].

Having aligned and permeable porosity is another key factor of porous filter materials. Therefore, utilization of a suitable method to fabricate this kind of porosity is extremely important. Gel casting and freeze casting are two novel forming methods to fabricate this kind of porosity inside the microstructure of a porous body [8]. Gel casting is a promising modern ceramic forming technique to achieve desirable microstructures in porous
materials. However, it suffers from some restrictions such as expensive and toxic additive, which sometimes causes difficult polymerization reactions and hindered its applicability in various ceramic systems [9]. On the contrary, freeze casting has been recently introduced to fabricate advanced materials without such restrictions. It is an effective and versatile process to control the microstructure of porous bodies. It is also renowned as a low-cost simple forming route, which does not require any toxic chemical additive to work [10].

Basically, freeze casting is a simple wet forming method in which a slurry of ceramic powder and liquid vehicle (e.g. water or organic fluids) is frozen in a mold. After removing the frozen liquid phase by sublimation or drying, the porous green body can be achieved and finally sintered to obtain the maximum mechanical strength [11, 12]. According to Deville et al during the freezing process, ceramic particles were pushed over by growing lamellar ice crystals and trapped among them. Thermodynamic of the forming mechanism was precisely investigated in their work [13].

As freeze casting is a fairly new forming method, most of recent works have thoroughly investigated near-net-shaping or microstructure tailoring. Pekor et al [14, 15], and Sofie et al [9] described the effects of some additives on the microstructure, pore size and morphology of the freeze casted body. In addition, Donchev [14] determined the control of pore size and distribution. In another research, Mongkolkachit et al [15] investigated the effects of freezing rate on the microstructure of porous ceramic bodies. However, some interesting aspects can be possibly investigated in this field of study. Only few papers have focused on the mechanical properties or fluid permeability of alumina-based porous bodies. In this paper, we focused on fabricating porous alumina-based bodies by freeze casting to achieve permeable open porosities in microstructures with improved compressive strength for microfiltration application. Final porous bodies had fine lamellar and permeable porosity without any unfavorable deformation during the drying process with significant compressive strength improvement compared to other recent works.

2. Experimental

In this research, $\alpha$-Al$_2$O$_3$ (with purity of 99.9%, $d_{50}$: 4.5 $\mu$m) and amorphous colloidal silica (40 wt.% of purity, $d_{50}$: 15 nm) were used as the main precursor and the non-organic gelation agent, respectively. Furthermore, liquid nitrogen was used as a freezing agent. To achieve a different amount of porosity in final microstructure, different powder ratios were used to prepare slurries. However, only two ratios were practically optimum for casting and fabrication processing that had improved mechanical strength and efficient permeability among others. Optimum sample 1 contained 43 vol.% alumina powder and 57 vol.% colloidal silica. Optimum sample 2 was a little less viscose, which had 41 vol.% alumina powder and 59 vol.% colloidal silica.

Figure 1 depicts the schematic of the freeze casting process. Based on figure 1, slurries were prepared by conventional ball milling precursors for 24 h to break agglomerates and increase the homogeneity of suspensions. Afterward, slurries were poured into cylindrical molds. To have unidirectional freezing in order to achieve unidirectional aligned porosity, the wall of mold was made of polystyrene, and its bottom was made of aluminum, aiming to force the anisotropic thermal gradient in molds. The casted molds were kept under a vacuumed desiccator to degas for 10 min. To freeze slurries, the bottom (metallic part) of mold was put into the liquid nitrogen bath, and slurries solidification took about 4 min. Finally, frozen slurries were demolded. The drying process has two steps; in the first step, green bodies were kept at room temperature for 24 h to reduce the drying rate and avoid distinct shrinkage or cracking of samples; in the second step, all samples were dried in a conventional drier oven at 120 °C for 2 h. Finally, dried bodies were sintered at 1400 °C for 2 h with a heating rate of 5 °C min$^{-1}$.

The Archimedes method was used to estimate the bulk density and open porosity of sintered bodies. Microstructures of sintered bodies were observed by scanning electron microscopy (SEM, TESCAN MUT VEGA3). X-ray diffraction (XRD, PANalytical X’Pert Pro MPD) with the monochromatic Cu-Kα radiation at 40 kV and 30 mA was equipped for phase characterizations of the samples. XRD patterns were compared to JCPDS cards to identify crystalline phases. Moreover, the compressive strength of cylindrical-shaped samples was measured with an automatic compression tester machine (CONTROLS PILOT3, max load 20 tons, loading rate of 2 Kg min$^{-1}$) under ASTM C133-97 standard. The permeability test was calculated based on a mathematical equation to measure the sample’s water flow rate and filtration efficiency. Water was used in this test as permeating fluid through fabricated porous samples with 3 ATM pressure.

3. Results and discussion

In this work, colloidal silica was used as gelation agent that could bind ceramic particles with each other during the freezing step. In other words, colloidal silica created gel binding during freezing and fixed particles in a gel framework even after the drying step. Therefore, it can avoid physical deformation such as unfavorable drying...
shrinkage and any catastrophic microstructural disorder during the drying process. According to the literature, aqueous colloidal sols are sensitive to temperature or pH changing. By changing each of them, irreversible gelation occurs in colloidal sols [16, 17]. Therefore, aqueous colloidal silica in slurries got started irreversible gelation by decreasing the temperature during freezing. Thus, colloidal silica acted as a gel binder during the freezing step, bound alumina particles together and created a comprehensive interconnected framework of ceramic walls among ice crystals. The mechanical strength of this gel binder framework was high enough to preserve the frozen sample’s shape even during the conventional drying process.

Owing to alumina and silica reactions during sintering, which caused particle densification, colloidal silica could also improve the mechanical strength of sintered samples.

Figure 2 illustrates the XRD patterns of sintered samples. According to the XRD results, the dominant phase was corundum accompanied by a perceptible amount of the mullite phase. The mullite phase was obviously formed by the reaction between alumina and silica during the sintering process.

In general, mullite formation is complex sets of high temperature (800–1400 °C) solid-state reactions between Al₂O₃ and SiO₂, which is based on the mutual diffusion of Al³⁺, Si⁴⁺, and O²⁻ ions among particles. As the glass transition temperature of silica is typically in the range of 900 °C–1100 °C, above this temperature, ultrafine amorphous silica viscous flow could behave as a sintering aid to achieve high particle densification and assist mullitization. In addition, in other studies, in the temperature range of 1300 to 1430 °C, ceramic particles obtained significant densification due to mullite generation reactions [18–20]. Therefore, in this work, to achieve the most particles densification and increase the mechanical strength of samples, the temperature of 1400 °C was chosen as the sintering temperature. However, weak mullite peaks in the XRD pattern suggested incomplete mullitization reaction. The reason might be the relatively low sintering time in this case. Moreover,
the XRD patterns revealed that by increasing silica content in sample 2, the mullite peaks did not noticeably increase, which could also prove insufficient sintering time.

It should be noted that, diffusion of cations was started on the interface of alumina and silica, and this reaction continued until mullite was formed. In other words, $\text{Al}^{3+}$ and $\text{O}^{2-}$ ions were separated from the surface of corundum particles and diffused into molten silica. Decrease of the $\text{Al}_2\text{O}_3$ free energy during diffusion was thermodynamical motivation for diffusion. However, due to the strong covalent bonding of $\text{Al}_2\text{O}_3$ and the strong lattice of corundum, the mullitization rate was slow [18]. Figure 6 reveals that the morphology of formed mullite in this research was not acicular. It appears that the reasons might be the types of precursors used or incompetent sintering conditions such as sintering temperature and even the lack of a common additive to assist mullitization.

Figures 3 and 4 display the SEM micrographs of the samples' microstructure. The unidirectional aligned porosity formation illustrated in all samples was due to anisotropic thermal gradient and unidirectional slurry freezing.

Figure 3 represents the vertical and cross-sections SEM images of sintered sample 1 in different magnifications. According to figures 3(A), (B), perpendicular porosity openings could be clearly observed on the surface of sample 1 cross-section. These open and permeable porosities were formed owing to unidirectional freezing direction. In other words, these porosities that can be seen in the vertical sections (C, D) presented in figure 3 were replicant of lamellar ice crystals grown from the bottom to the surface [21]. Based on the SEM images, the average pore size was measured around 5 μm.

Figure 4 depicts the SEM micrographs of sample 2 microstructure.

As figure 4 illustrates, like sample 1, the vertical and cross-sections of sample 2 also show unidirectional aligned porosities. However, as mentioned, this sample had lower solid content and consequently higher porosity compared to sample 1. Therefore, it was expected that sample 2 had higher porosity and slightly larger pore size than sample 1 had. The same results were reported in other researches [22, 23]. In fact, when slurry concentration was lower, ice crystals could deflect solid particles and grew more freely and easier compared to higher concentrated slurry.

Furthermore, comprehensive interconnectedness of ceramic walls was clearly seen among porosities in all represented microstructures. As a result, it seemed that (i) forming of this comprehensive interconnected porous framework of ceramic walls was made of freeze-gelation of colloidal silica and (ii) the particles densification caused by mullite generation reactions at 1400 °C during sintering was one of the two main reasons for the significant mechanical strength improvement of samples, while they were highly porous.

Figure 5 displays the EDS map analysis of a cross-section of sintered sample 1. It could be seen that colloidal silica was uniformly spread among alumina particles due to the efficient mixing process, the flawless freeze-gelation step, and the viscous flow behavior of amorphous colloidal silica during sintering.

Figure 6 represents the point EDS analysis of sintered sample 1’s microstructure.

The results in figure 6 also showed the presence of silica and its accumulation at different regions of microstructure, specifically in the ceramic wall bonding, this was important for the final mechanical properties of
Figure 3. SEM micrographs of cross section (A), (B) and vertical section (C), (D) of sintered sample 1 at 1400°C for 2 hours with 41 vol.% unidirectional porosity.

Figure 4. SEM micrographs of cross section (A), (B) and vertical section (C), (D) sintered sample 2 at 1400°C for 2 hours with 47 vol.% unidirectional porosity.
the bodies. Additionally, as mentioned earlier, figure 6 reveals that the formed mullite phase in the samples did not have acicular morphology.

Based on freezing thermodynamic, growing ice crystals needed a level of supercooling inside slurry. As the surface of particles was the potential site for ice crystal nucleation, smaller particles had a larger surface area or ice crystal nucleation sites. In this situation, the myriad ice crystal nuclei did not require high internal supercooling to grow. Therefore, ice crystals had more time to grow freely and become larger. As a result, the final pores obtained a larger size. This phenomenon is called ‘secondary ice crystal growth’.

Generally, the use of ultrafine particles in slurry could cause the secondary ice crystal growth phenomenon in freeze casting. On the contrary, if slurry particles had a larger size, internal supercooling would be increased due to overcoming the shortage of nucleation sites on the surface of particles. Thus, ice crystal or final pores became smaller.

Figure 5. SEM map analysis of a cross section of sintered sample at 1400°C for 2 hours.

Figure 6. EDS analysis of a cross section of sintered samples at 1400°C for 2 hours.
Secondary ice crystal growth was detrimental to the mechanical properties of ceramic body, so that it could make many microcracks in the final microstructure. Thus, making slurry using materials with a larger particle size is generally a good way to get rid of the secondary ice crystal growth defect to improve the mechanical strength \[11, 24\].

In this study, micron-sized alumina was used as the main precursor. Although nano-sized amorphous silica particles were used in slurry, final pores were uniformly small, which were apparently in contrast to freezing thermodynamic \[7, 25, 26\]. The reason might be the fast freezing rate of slurry due to use of liquid nitrogen coolant. In other words, liquid nitrogen forced external super cooling to slurry and kinetically overcame the effect of ultrafine particle size to prevent the secondary ice crystal growth defect during the freezing step. Thus, it led to achieving fine porosity in the final body. To illustrate this, some slurries were frozen at \(-20 \, ^\circ\text{C}\) to reduce the freezing kinetic and avoid the external super cooling effect on slurries.

Figure 7 presents the SEM images of the microstructure of sample 1 (A, B) and sample 2 (C, D) that were frozen at \(-20 \, ^\circ\text{C}\).

According to figure 7, samples frozen at \(-20 \, ^\circ\text{C}\) had significantly larger pores. The average pore size in these samples was at least 10 times larger than that the time they were frozen by liquid nitrogen. Therefore, mechanical strength of samples drastically dropped due to the presence of larger porosities and micro cracks made by the secondary ice crystal growth phenomenon. All samples had the same composition but different freezing conditions. As these microstructures had such large and non-uniform porosities, they were literally improper for the aim of this paper, which was filtration or membrane support application.

Figure 8 demonstrates the effect of solid content on the bulk density and open porosity of samples. It was expected that by increasing the solid content, the bulk density would be increased, while the amount of porosity would be decreased.

Physical properties measurements showed 41 vol.% and 47 vol.% open porosity for sample 1 and sample 2, respectively. The maximum bulk density of 2.1 g cm\(^{-3}\) was measured, which is depicted in figure 8.

Figure 9 shows the influence of solid content on cold crushing strength (CCS). As mentioned earlier, normally by increasing the solid content, the amount of water in the slurry decreases, and mechanical properties are generally improved, since water made porosity in the final body. Moreover, another reason for noticeable
mechanical strength improvement was bound and interconnected ceramics walls and mullitazation reaction during sintering, which were explained earlier.

As figure 9 shows, the maximum cold crushing strength of samples reached 145 MPa. It was a significant improvement compared to other recent works. As described earlier, researchers focus mostly on the microstructural evaluations of freeze casting. However, there are only few papers focusing on the mechanical properties or fluid permeability of alumina-based porous bodies. Different alumina porous bodies fabricated by freeze casting had approximately 25 to 45 MPa compressive strength, while they had 55% to 42% aligned porosity, respectively [16]. In another study, Guodong Shi et al formed an alumina porous body using freeze casting. They obtained the maximum compressive strength of 26 MPa and 60% open porosity [8]. Guofa Sui et al illustrated an alumina porous body with 49% open porosity and a plate-like microstructure. They achieved interlocked the ‘card house’ microstructure by freeze casting using TBA (tert-butyl alcohol) additive in the slurry. However, after sintering at 1500 °C, only 4 MPa compressive strength was observed in their sample [5].

Permeability test is an important assessment to evaluate filtration efficiency for a porous body. In this test, a fluid such as water was permeated through a porous body, and the permeating rate was calculated to evaluate filtration efficiency. Some key factors in this test were fluid pressure, permeable porosity, and surface area of the porous body tested [27]. In this work, water was used as permeable fluid with the pressure of 3 ATM. The
permeability of water was calculated based on equation (1) [27].

\[ Q = \frac{m}{A.t.P} \]  \hspace{1cm} (1)

In equation (1), \(Q\) was the measured flow rate of permeated water through a porous body. Where \(m\) was the mass of permeated water, \(t\) was the test time, \(A\) was the surface area of the body tested, and \(P\) was the fluid pressure.

Table 1 shows the water flow rates of some fabricated porous bodies in different works and compares them to the results of this research. All sintering temperatures were around 1400 to 1500 °C. Samples had permeable porosity. However, their fabrication methods were different from freeze casting. Therefore, their porosity was not completely unidirectional and had a lower water flow rate.

As table 1 shows, the water flow rates of freeze cast samples in this study were noticeably higher than those in other works. Permeability assessment showed 0.22 and 0.30 (g. cm\(^{-2}\).s\(^{-1}\).bar\(^{-1}\)) water flow rates for samples with 41% and 47% porosity, respectively that were approximately twice greater than those of other samples fabricated by other methods [8, 28, 29]. Based on SEM images, it can be observed that the presence of open, permeable, and unidirectional aligned porosities in the microstructure of samples is the reason behind this high flow rate. In other words, these align and open porosities acted as open unidirectional micro canals letting water easily flow through them.

As the pore size of freeze cast samples was estimated to be approximately 5 \(\mu m\) by SEM images, and the water permeability of samples was high, these fabricated alumina-based bodies could be a good option for microfiltration or membrane supports. Freeze casting is an economic, simple, and nontoxic fabrication method that could keep production costs reasonably low. In addition, this eco-friendly forming method could fabricate a well-suited porous body for the filtration industry.

### 4. Conclusion

In this study, alumina-based porous bodies were fabricated by the freeze casting method. The effects of solid content and freezing conditions on the microstructure, mechanical strength, and water permeability of the samples were investigated. Micron sized alpha-alumina and amorphous colloidal silica were used as precursors to make slurries. Based on SEM results, the highly porous microstructure of alumina-based freeze cast body was achieved with unidirectional aligned porosities and an average pore size of 5 \(\mu m\). Furthermore, interconnected ceramic walls were comprehensively observed in the microstructure. Moreover, the EDS analysis revealed that amorphous colloidal silica acted as a gelation agent during the freezing step and bound and held particles together in a fixed gel framework after drying. It avoided physical deformation during the drying process and significantly improved the post-sintering mechanical strength of the samples.

The amounts of 41 vol.% and 47 vol.% open porosity were measured for optimum samples. By increasing the solid content, porosity and pore size were decreased, while the compressive strength was increased. Samples were sintered at 1400 °C for 2 h to achieve the maximum mechanical strength of 145 MPa due to the particle densification caused by the mullitization reaction between alumina and silica. The permeability assessment indicated at least 0.22 (g. cm\(^{-2}\).s\(^{-1}\).bar\(^{-1}\)) water flow rate, which was approximately twice greater than that in other recent works.

Freeze casting is an economic, simple, and nontoxic fabrication method that can maintain production costs reasonably low. Additionally, this eco-friendly forming method can fabricate a well-suited porous body for diverse industries such as refractories, composites, and catalyst or membrane supports.

| Composition | Porosity (vol.%) | Fluid pressure (Bar) | Fluid flow rate (g. cm\(^{-2}\).s\(^{-1}\).bar\(^{-1}\)) | Fabrication method |
|-------------|-----------------|----------------------|-------------------------------------------------|-------------------|
| *Alumina    | 41              | 3                    | 0.22                                            | Freeze casting    |
| **Alumina   | 47              | 3                    | 0.30                                            | Freeze casting    |
| Alumina     | 47              | 3                    | 0.11                                            | Extrusion         |
| Alumina     | 41              | 3                    | 0.08                                            | Cold press        |
| Alumina     | 47              | 3                    | 0.09                                            | Cold press        |
| Alumina     | 46              | 3                    | 0.10                                            | Extrusion         |

* / ** samples that were fabricated in this work.
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