Desalination and Water Treatment
www.deswater.com

35 (2011) 33–38
November

doi: 10/5004/dwt.2011.3505

Processing of porous alumina substrate for multilayered ceramic filter

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Received 1 February 2011; Accepted 27 May 2011

ABSTRACT

The present paper reports results of an initial study related to the fabrication of multilayered ceramic filters with a gradient in porosity for efficient cleaning of liquid medium containing undesired particles/impurities. This study involves the fabrication of a porous ceramic substrate to support the intermediate and top layers. The choice of the support material and its properties in terms of porosity, pore distribution and structural quality are critical for effective performance of the multilayered filter. These properties need to be optimized to achieve proper integration of intermediate layer onto the support structure and to eliminate disturbances in the flow at the interface of the support and intermediate layer. Different ceramic materials including α-alumina, zirconia, and SiO_2 or a combination of these materials with a range of initial particle sizes are being studied for their suitability as support structures, although only results related to α-alumina are presented in this work. Disc shaped ceramic supports were fabricated by uni-axial compaction of powders followed by sintering in a tube furnace in air atmosphere. The effect of compacting pressure on the green density of the ceramic compacts was evaluated. After sintering at 1400°C for 2 h, the fabricated α-alumina ceramic support was characterized using X-ray diffraction, scanning electron microscopy and mercury porosimetry techniques to determine the nature of phases formed, crystallinity, morphology, pore size and pore size distribution. The structural integrity/strength of the substrate was measured using diametral compression test.

Keywords: Porous ceramic support; Alumina ceramic substrate; Multilayered ceramic filter; Powder compaction; Sintering; Porosimetry; Diametral compression

1. Introduction

Ceramic filters and membranes are of great interest in filtration applications because of their higher chemical, thermal, mechanical stability and control on the porosity and pore distribution as compared to their polymeric counterparts. Filters made of ceramic materials have been extensively used in purification of drinking water from germs, heavy metals and other contaminants; treatment of wastewater; treatment of sewage; pretreatment of seawater desalination and so on. The choice of ceramic materials for these filter applications is primarily due to the fact that they offer several advantages over their organic counterparts, such as superior thermal and chemical stability, better mechanical strength, resistance to the acid or base media, resistance to biodegradation, narrow pore size distribution, adjustable microstructure, low energy consumption under milder conditions and little pollution to the environment [1, 2]. In general, ceramic filters consist of a support substrate and subsequent layers with different pore sizes. The support provides the mechanical stability and the properties and

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specifications of the subsequent layers govern the filtration characteristics. Materials such as alumina, zirconia, silicon carbide and titania have been used to fabricate filters and membranes for a variety of applications [3–6]. Fabrication of the ceramic filters involves first fabrication of the support layer performed usually by powder metallurgy route (powder compaction and sintering). Sintering is done to strengthen the porous ceramic support and help the subsequently deposited layers adhere strongly to the porous support. The most common processes used for filter fabrication are extrusion, tape casting, dip and spin coating. Extrusion and tape casting are used to prepare the support system, tape casting and dip coating methods are used for depositing the microfiltration layers and dip coating and spin coating are used for nanofiltration applications. Studies have been undertaken to improve the filtering efficiency, mechanical stability and to increase the range of contaminants that can be filtered in terms of chemical nature, particle size and shape. For filtering gas and liquid media, to purify them from harmful microorganisms (bacteria, viruses, etc.), dust and other impurities including particles with nanometer sizes, it is necessary to use filters with a high filtration fineness as well as throughput and strength at the same time. One of the effective ways to produce filters with improved operating properties is to fabricate a sandwich-type structure consisting of layers with different granularity and, correspondingly, with different (macro-, micro- and nano-) porous structure thus possessing a gradient of pore sizes along the thickness of the filter [7]. The initial step in the development of multilayered ceramic filter is the fabrication of ceramic support. Fabrication of a suitable support is important for the development of a good quality filter. The main characteristics of the ceramic support include mechanical strength, pore size, pore size distribution, surface roughness, homogeneity, and purity of the surface [8].

This paper presents a study related to the fabrication of the ceramic support in the shape of a disc using sub-micron-size alpha-alumina (α-Al_2O_3) powder by compaction and sintering. The alumina discs were then characterized for their microstructure and structural integrity.

2. Experimental procedure

Alpha-alumina (α-Al_2O_3, from Buehler Co.) powder with average particle size of ~0.3 μm was used to prepare the porous ceramic substrate/support.

2.1. Powder compaction

Alumina powder was uniaxially pressed using hydraulic press in a tool steel die using different compaction pressures to form the support ceramic green samples. Green samples in the form of cylindrical disks of diameters 12.7 mm and 25.4 mm with thickness 2–3 mm were compacted. Green densities were calculated by measuring the weight and the physical dimensions of the powder compacts.

2.2. Sintering

The green compacts were then sintered in a tube furnace (MTI, GSL-1700-60X) in air atmosphere at 1400°C for 2 h. The utilized ramp up rate was 4°C/min during heating and upon completion of the sintering cycle; the samples were furnace cooled to room temperature by simply switching off the furnace.

2.3. Porosimetry

To investigate the pore size and porosity of the sintered ceramic structures, mercury porosimetry measurements were performed using Micromeritics Autopore IV 9500 V1.09 Porosimeter. A pore size distribution representing a bulk value for the entire cross-section of the alumina substrate was obtained. The 25.4 mm ceramic disc was placed in the porosimeter pentrometer of volume 3.5 cm^3. Then, the sample container was placed in a pressure vessel to force the mercury into the pores of the substrate.

2.4. Diametral compression test

The structural integrity of ceramic filters was measured by the diametral compression test performed on the ceramic substrate. There is no standard strength test prescribed by ASTM for ceramic filters in general. Diametral compression test is frequently used to measure the strength of porous ceramics. It measures the tensile strength of the sample in the direction perpendicular to the loading direction. In this test, a circular disk or hollow ring is diametrally pressed between two flat plates. The diametral stress is then calculated as follows [11]:

$$\sigma = \frac{2P}{\pi D t}$$

where P is the load, D is the diameter and t is the thickness of the ceramic disc.

2.5. Characterization

The as-received alumina powder and the sintered samples were characterized using scanning electron microscopy (SEM) (JEOL, JSM-6460LV), X-ray diffraction (XRD) (BRUKER D8 Advance) and mercury porosimetry (Micromeritics Autopore IV 9500 V1.09).

3. Results and discussion

The results related to the characterization of the as-received alumina powder, influence of powder compaction on the green density of the compact and subsequent sintering of the compact are presented underneath.

3.1. Characterization of as-received α-alumina powder

Fig. 1 shows SEM images (15 kV, Secondary Electron Imaging) of as-received α-alumina powder. The alumina powder is non-agglomerated with an average particle size of 0.3 microns. The variation of particles size observed is very small which is essential to control the pore size of the ceramic support leading to a minimum variation throughout the support layer volume. Fig. 2 displays the XRD pattern of the as-received powder indicating that this powder is indeed α-alumina type and of high purity (the black pattern belongs to the analyzed powder sample and the red pattern is α-alumina reference taken from the database).

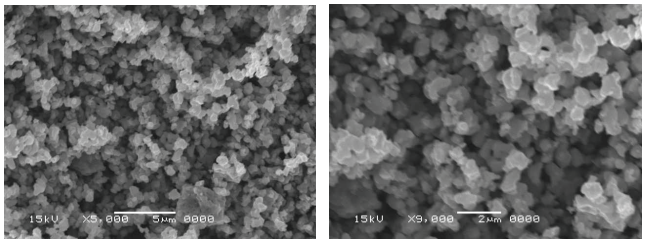

Fig. 1. SEM micrographs of as the received α-alumina powder taken at (a) low magnification, (b) higher magnification.

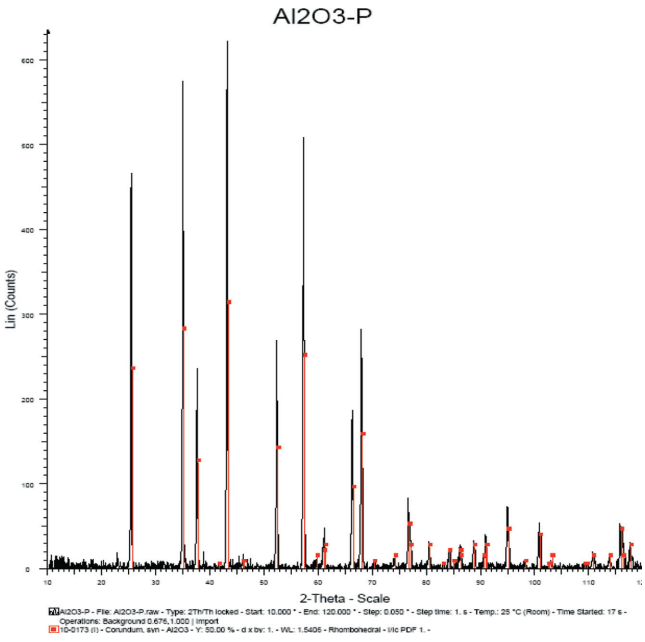

Fig. 2. XRD pattern of the as-received α-alumina powder.

Thus, the analysis of the powder as performed by both SEM and XRD techniques confirm that the as-received powder is of high quality and possesses a uniform particle size distribution.

3.2. Powder compaction

Figure 3 shows the green compact for the alumina powder compacted at a pressure of about 620 MPa. Compaction pressure was varied to achieve a green compact with sufficient strength to be able to perform dimensional measurements, weighing and handling of the green compact prior to sintering. Fig. 4 displays the variation of the green density with the compaction pressure. The green density increases linearly with increasing compacting pressure within the compaction range used in this study. The green density increased from 1.76 ± 0.01 g/cm^3 to 1.99 ± 0.01 g/cm^3 with the increase of compaction pressure from 232 MPa to 620 MPa, respectively. Green density gives an indication of the porosity level in the ceramic substrates, as the green density increases the amount of porosity and pore size generally tend to decrease.

Fig. 3. Green α-alumina compact pressed at 620 MPa.

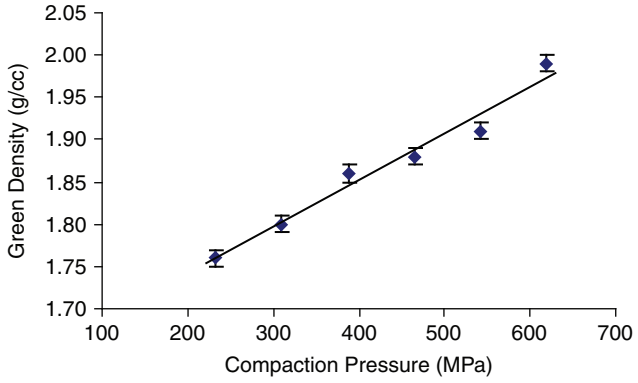

Fig. 4. Variation of green density with applied compaction pressure.

3.3. Sintering of the compact

The α-alumina supports were compacted at a pressure of 620 MPa and sintered at 1400°C for 2 h. Fig. 5 shows the alumina support before and after sintering. It can be observed that there was no distortion or cracking of the substrate during sintering. The sintered alumina support was further characterized using XRD and SEM. The XRD pattern of the sintered sample is shown in Fig. 6. By comparing the XRD patterns of the as-received alumina powder (Fig. 2) with that of the sintered sample (Fig. 6), it is confirmed that no new phase was formed during/after the sintering process. Fig. 7 shows the corresponding SEM micrographs of the sintered sample. The main objective of the sintering stage is inducing bonding and adherence of the alumina particles (densification via solid state sintering mechanism) by neck formation, which is crucial for achieving a crack-free filter support [9]. It can be observed from Fig. 7 that there

Fig. 5. α-alumina substrate before (green compact) and after sintering.

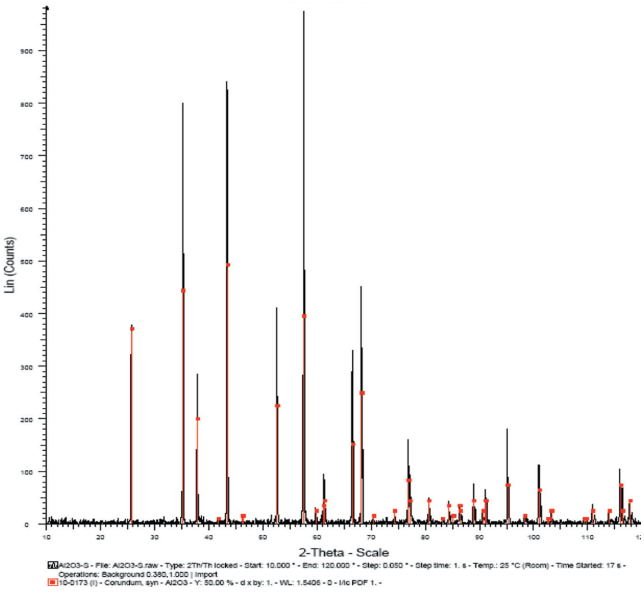

Fig. 6. XRD pattern of the as α-alumina substrate after sintering.

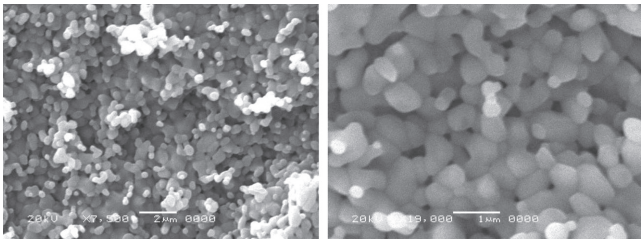

Fig. 7. SEM micrographs of the sintered α-alumina substrate at different magnifications.

is good bonding amongst the alumina particles thus providing a good mechanical strength for the ceramic porous support. The pore size, as estimated from the SEM images, ranges from 0.1 to 0.3 μm. In general, this pore size range is smaller than the desired pore size of 5–10 μm intended for the ceramic support of the multilayered ceramic filter. However, it is intended to put the layer processed in this study having an average pore size of 0.2 μm on top of the support structure with a larger pore size thus producing a gradient in porosity. One way to increase the average pore size for the ceramic support is to use larger alumina particles. On the other hand, it is worth mentioning that the microstructure/porosity of porous ceramics can be controlled not only by adjusting the particle size and shape of the initial powders, but also by controlling the compacting pressure as well as the sintering process parameters, mainly temperature and dwell time. This initial study has lead to the understanding of the relationship between compaction and sintering parameters for a given alumina powder. The authors intend to optimize the processing parameters of the ceramic support such as initial particle size, compaction pressure, sintering temperature and time as well as the type of sintering method (pressure-less sintering, spark plasma sintering, microwave sintering). The other ceramic layers will be deposited onto the support structure using a variety of techniques including sol-gel deposition, and dip coating for the fabrication of advanced bio-inert ceramic filters with graded macro/micro/nanoporous structure, this being investigated in the second stage of this study.

3.4. Porosimetry measurement

Alumina substrate was subjected to high pressure mercury intrusion, up to 60,000 psi. The relation between the minimum pore size diameter and the applied pressure is given by Washburn's equation [10]:

$$D = -4\gamma \cos\theta / P$$

where γ is the surface tension, D is the diameter of the pore and P is the applied pressure.

The above relationship indicates that the size of the pore into which mercury will intrude is inversely proportional to applied pressure. The size of the pore can be determined by substituting the pressure values in the equation, as the volume of the mercury that intrudes into the sample due to an increase in pressure from P_i to P_{i+1} is equal to the volume of the pores in the associated size range r_i to r_{i+1} [10]. The measurements of series of applied pressures and the volumes of the mercury intruded and extruded at each pressure give the results of the pore network. From the intrusion data results, the porosity was evaluated to be about 30% whereas the average pore size obtained was 0.2 µm, similar to that obtained from SEM images shown above. It is worth noting that the sintering temperature has a great effect on pore size and amount of porosity, because as the temperature increases the packing arrangement will be tighter leading to more extensive merging of neighboring particles thus producing smaller or closed pores. Therefore, by varying the sintering temperature and compacting pressure (green density), the porosity level and pore size can be controlled and tailored as required.

3.5. Compression test

Diametral compression test was performed on alumina discs. Samples used had dimensions of 25.4 mm diameter and 2–3mm thick (compacted at 375 MPs and sintered at 1400°C for 2 h). Samples were polished using SiC grinding paper to make the surfaces flat and parallel, then cleaned using ethanol and deionized water under ultrasonication and subsequently dried. Fig. 8 shows the polished samples. Instron universal testing machine was used for conducting the tests. Samples were diametrally pressed between flat platens with a crosshead speed of 0.5 mm/min.

A fractured sample is shown in Fig. 9. It can be observed that the sample fractured into two halves indicating that it underwent a tensile failure which is a necessary condition for considering the diametral compression test successful on ceramic structures [11]. Fig. 10 shows the output of the diametral compression test showing the variation of compressive stress versus compressive strain. The average strength of the sample tested up to a maximum compressive load of 1263N is 14.87 MPa.

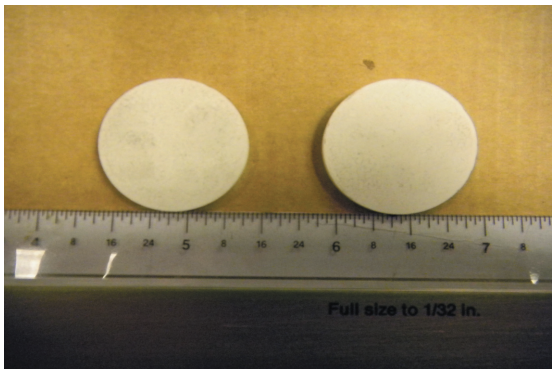

Fig. 8. α-alumina substrates used for diametral compression testing.

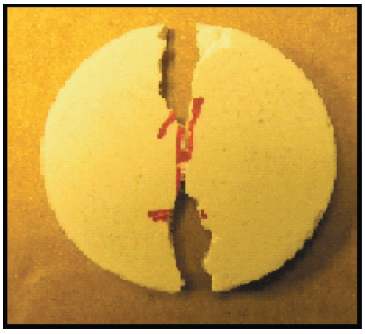

Fig. 9. Fractured sample after being subjected to diametral compression test.

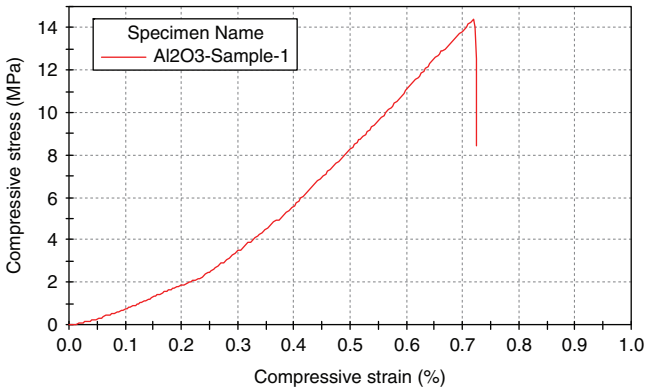

Fig. 10. Diametral compression test curve.

4. Conclusion

Porous alumina substrate, with controlled pore size and sufficient mechanical strength, was fabricated to act as a support for the multilayered ceramic filter to be utilized for efficient cleaning of liquid medium containing undesired particles/impurities. Alumina (α-Al_2O_3) powder with average particle size of 0.3 µm was compacted at different pressures (230 to 620 MPa), followed by sintering at 1400°C for 2 h. The results indicate that the fabricated α-alumina ceramic support has sufficient mechanical strength of 14.87 MPa which can still be increased by increasing the sintering temperature. The pore size range obtained in the sintered porous support compacted at 620 MPa, as estimated by SEM analysis

and proved from mercury porosimetry technique, is about 0.2 μm. Further work is underway to optimize the processing parameters such as the initial powder particle size, compaction pressure, sintering temperature and sintering method for the fabrication of a ceramic support possessing sufficient mechanical strength with the desired pore size range (1–10 μm) to remove relatively large particles of average size greater than 10 μm. This work is a part of a broad study, which involves fabrication of advanced bio-inert ceramic filter materials with graded macro/micro/nanoporous structure, using powder metallurgy route, sol-gel deposition, dip-coating and microwave-sintering process.

Acknowledgements

The authors would like to acknowledge the support provided by King Abdulaziz City for Science and Technology (KACST) through the Science & Technology Unit at King Fahd University of Petroleum & Minerals (KFUPM) for funding this work through Project 08-ADV70-4 as part of the National Science, Technology and Innovation Plan.

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