Reactive synthesis of porous MgAl2O4 membranes on a macroporous Al2O3-based ceramic tube toward cross-flow ultrafiltration

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Porous ceramic filters made of MgAl2O4 spinel are promising due to their excellent thermal and chemical stability. In this study, toward future cross-flow ultrafiltration applications, reactive synthesis of porous MgAl2O4 membranes on a macroporous Al2O3-based ceramic tube has been examined. Fine (0.2 μm) and coarse (0.7 μm) α-Al2O3 powders and two types of MgO sources, i.e., MgO (2.8 μm) and MgCO3 (basic) [hydromagnesite Mg3(CO3)2(OH)2·4H2O (∼5.5 μm)] powders were used as starting materials for the reactive synthesis of porous MgAl2O4 membranes. For the intermediate layer, MgCO3 (basic) powder was favorable as a MgO source because it can clog up the large (15 μm) pores in the Al2O3-based tube. Meanwhile, for the top layer, MgO powder with finer particle size was favored to obtain homogeneous layer for ultrafiltration.

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Key-words: MgAl2O4 spinel, Dip-coating, Filter, Al2O3, Ultrafiltration

NOTE

Porous ceramics filters attract increasing interest because of their excellent characteristics such as high mechanical properties, high corrosion resistance and high thermal stability. Currently, they are widely applied to drinking water purification, waste liquid treatment, exhaust gas filtration, and so on. Thanks to their robust features, porous ceramic filters can be operated for longer time under severer conditions compared with organic membranes. Furthermore, they are reusable by the backwashing as well as by the regeneration via heat or chemical treatment.

Porous ceramic filters are generally categorized into 5 classes by their pore diameter d, i.e., (1) crude filtration (d > ∼10 μm), (2) microfiltration (∼100 nm < d < ∼10 μm), (3) ultrafiltration (∼10 nm < d < ∼100 nm), (4) nanofiltration (∼1 nm < d < ∼10 nm) and (5) reverse osmosis (d < 1 nm). A variety of porous ceramics made by partial sintering or made with pore-forming agent are widely available for the crude and microfiltrations. For the ultrafiltration, Al2O3, TiO2 or ZrO2 membranes on macroporous ceramics are commercialized (e.g., Celfilter® by NGK Corporation). For the nanofiltration and the reverse osmosis, membranes made of zeolite or polycrystalline TiO2 on macroporous ceramics are currently used.

Recently, our group has focused on porous ceramic filters made of MgAl2O4 spinel due to its excellent thermal and chemical stability. In the previous study, porous MgAl2O4 plates (thickness of ∼2–3 mm and diameter of ∼30 mm) was prepared by reactive sintering of MgCO3 (basic) [hydromagnesite (Mg3(CO3)2(OH)2·4H2O)] and 4-type of Al2O3 sources. Rod-like MgCO3 (basic) micrometer-sized particles thermally decompose into MgO nanoparticles at ∼500°C, which are chemically active for the double-oxide synthesis. Even with a simple dead-end type setting, the porous MgAl2O4 filter made from a fine boehmite source exhibited good microfiltration performance to remove submicron-sized colloidal particles (i.e., simulating bacteria) from a suspension. However, the filtration efficiency was very small due to their thick and dead-end type setting. In a practical point of view, a cross-flow type filter (like a tubular commercial product) is necessary to improve the filtration efficiency.

In this study, toward future cross-flow ultrafiltration applications, reactive synthesis of porous MgAl2O4 membranes on a macroporous Al2O3-based ceramic tube has been examined. Coarse and fine porous MgAl2O4 membranes were prepared by repeated dip-coating method.

Table 1 summarizes the starting materials for intermediate and top MgAl2O4 layers. For the Al2O3 source of MgAl2O4, two types of α-Al2O3 powders (AKP-50 and AKP-3000, Sumitomo Chemicals Co. Ltd., Japan) were used. For the MgO source of MgAl2O4, a MgO powder (99.9% purity, Kojundo Chemical Laboratory Co. Ltd., Japan) and a MgCO3 (basic) powder [Mg3(CO3)2(OH)2·4H2O, hydromagnesite, 99.9% purity, Kojundo Chemical Laboratory] were used. A commercial porous Al2O3-based tube (Hagi glass, A-#12, pore size: 14.7 μm) with cationic composition of Al2O3·2K2O·Na2O·CaO = 62.6:31.6:6.3:5.9:1.45:0.318:0.254 (in wt% by X-ray fluorescence) was used.

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Table 1

| Al2O3 source | MgO source |
|--------------|------------|
| AKP-50       | 99.9% purity Kojundo Chemical Laboratory Co. Ltd., Japan |
| AKP-3000     | MgCO3 (basic) [Mg3(CO3)2(OH)2·4H2O, hydromagnesite, 99.9% purity, Kojundo Chemical Laboratory] |

[Received November 24, 2018; Accepted February 4, 2019]
Dip coating was performed on the porous Al₂O₃ substrate. The particle size distribution of MgO and Al₂O₃ sources were measured by dynamic light scattering (DLS, FDLS3000, Otsuka Electronics Co.).

Figure 1 shows the sample preparation procedure. To prepare each slurry, 80 µL of acetylacetone as a dispersant was dropped into 8 mL of ethanol, and 1.00 g of raw material powder was dispersed. After putting the raw materials, ultrasonic agitation was carried out for 10 min. Thereafter, to prevent the sedimentation of the particles, and to increase the viscosity for better adhesion to the porous Al₂O₃ substrate, melted polyethylene glycol (PEG) was added and thoroughly stirred at 57°C for 10 min. Dip coating was performed on the porous Al₂O₃ substrate using the prepared slurry. When dip coating was carried out, a Teflon tape was wound around the upper and lower portions of the hollow porous tubes to prevent the slurry from entering the inside, and only the tube surface was coated. After dip coating, the samples were dried for 5 min and then sintered at 1200°C for 2 h. After the synthesis of the intermediate layer, second dip coating and sintering were carried out in the same flow to synthesize a top layer.

For the obtained samples, the constituent phases were identified by X-ray diffraction (XRD, Multiflex, Cu-Kα, 40 kV and 40 mA, Rigaku). The microstructures of the surface and cross section were observed by scanning electron microscopy (SEM, SU-70, Hitachi and JSM-5600LV, JEOL). The pore-size distribution of the whole sample (i.e., porous MgAl₂O₄ membranes on the macroporous Al₂O₃-based ceramic tube) was determined by mercury intrusion porosimetry (PoreMaster-60-GT, Quantachrome).

Figure 2 shows surface SEM images of the intermediate layers prepared from the three mixtures as given in Table 1. For the sample prepared with the MgO starting powder (IL-1), circular-like aggregates were observed. Such circular aggregates unevenly coated the porous Al₂O₃ substrate, and some uncovered part was also observed. With increasing the MgCO₃ (basic) (hydromagnesite) composition (IL-2 and 3), the surface of the intermediate layer became smoother, and the coverage of the intermediate layer became improved. The IL-3 sample was the best as an intermediate layer among the three sources.

In order to clarify the reason why the different microstructures were obtained, the particle size distributions of the MgO and Al₂O₃ sources were analyzed. Figure 3 shows particle-size distributions of the MgO and Al₂O₃ sources measured by DLS. As can be seen in Fig. 3(a), the mode diameters of MgO and MgCO₃ (basic) powders were ~2.8 and ~5.5 µm, respectively. In Fig. 3(b), the finer Al₂O₃ powder (AKP-50) exhibited nearly monodispersion, and thus its mode diameter was almost the same as the median value in Table 1. Meanwhile, the coarse Al₂O₃ powder (AKP-3000) exhibited nearly bimodal dispersion in this analysis.

During the dip coating, the slurry was drawn into the porous alumina substrate (with pore size of 15 µm) by the capillary force. For IL-3, the drainage of the particles into the 15 µm pores was prevented in the vicinity of the Al₂O₃ substrate due to the clogging of larger MgCO₃ (basic) particles. Similar phenomenon should partially exist for IL-2. On the other hand, for IL-1, finer MgO particles moved more easily and they tended to form denser aggregate-like ‘islands’. During the sintering, CO₂ and H₂O emissions resulted in the volume shrinkage of the intermediate layer, and then, circular aggregates formed for IL-1 (see Fig. 2).

Figure 4 shows XRD patterns on the intermediate layers on the porous Al₂O₃ tubular substrate. Peaks of MgAl₂O₄ as well as those of Al₂O₃ and MgO (trace) were identified. The Al₂O₃ peaks are mainly attributed to the Al₂O₃ substrate, and trace MgO peaks are attributed to unreacted MgO. For the IL-1 sample, broad peaks at ~15° and ~22° were also observed, which implies that some of the constituent phases were identified by X-ray diffraction (XRD, Multiflex, Cu-Kα, 40 kV and 40 mA, Rigaku). The microstructures of the surface and cross section were observed by scanning electron microscopy (SEM, SU-70, Hitachi and JSM-5600LV, JEOL). The pore-size distribution of the whole sample (i.e., porous MgAl₂O₄ membranes on the macroporous Al₂O₃-based ceramic tube) was determined by mercury intrusion porosimetry (PoreMaster-60-GT, Quantachrome).

| Sample name | MgO source | Al₂O₃ source |
|-------------|------------|--------------|
| Intermediate layer | IL-1 | MgO | α-Al₂O₃ (0.7 µm*, AKP-3000) |
| IL-2 | 0.5MgO + 0.1[Mg₅(CO₃)₄(OH)₂·4H₂O] | α-Al₂O₃ (0.7 µm*, AKP-3000) |
| IL-3 | 0.2[Mg₅(CO₃)₄(OH)₂·4H₂O] | α-Al₂O₃ (0.7 µm*, AKP-3000) |
| Top layer | TL-1 | MgO | α-Al₂O₃ (0.2 µm*, AKP-50) |
| TL-3 | 0.2[Mg₅(CO₃)₄(OH)₂·4H₂O] | α-Al₂O₃ (0.2 µm*, AKP-50) |

*Median diameter (catalog value given by the supplier).
finer MgO particles were trapped in the large pores of the Al₂O₃ substrate, and they reacted with the SiO₂-K₂O-Na₂O additives in the substrate to form glassy phases.

Comparing the peak intensities of MgAl₂O₄, those from IL-3 [prepared from MgCO₃ (basic)] were the largest among three. In addition, the peak intensities of Al₂O₃, those from IL-3 were the smallest. These results well support above SEM observation (Fig. 2), i.e., the coverage of the intermediate layer IL-3 was the best in this study.

Using the IL-3 intermediate layers, two types of top layers (as filtration layer) were synthesized as shown in Figs. 3 and 4.

Fig. 2. SEM images of the surfaces of intermediate layers after sintering at 1200°C for 2 h.

Fig. 3. Particle size distributions of (a) MgO and (b) Al₂O₃ sources measured by DLS.

Fig. 4. XRD patterns of intermediate layers on porous (curved) Al₂O₃-based substrate. Note that due to the curvature and additives of the Al₂O₃ tubes, some peak shift may exist.
The thickness of intermediate and top layers was \( \sim 10 \) and \( \sim 100 \) \( \mu \text{m} \), respectively. By using the finer Al\(_2\)O\(_3\) source (0.2 \( \mu \text{m} \)), both TL-1 (using MgO) and TL-3 [using MgCO\(_3\) (basic)] were composed of fine MgAl\(_2\)O\(_4\) particles. From these SEM images, the TL-1 sample apparently contained less surface defects than the TL-3 sample, probably due to the size similarity of MgO and finer Al\(_2\)O\(_3\) sources, resulting the formation of finer and denser MgAl\(_2\)O\(_4\) particles.

Figure 6 shows XRD patterns of TL-1 and TL-3 top layers on the IL-3 intermediate layers covering porous (curved) Al\(_2\)O\(_3\)-based substrate. Note that due to the curvature and additives of the Al\(_2\)O\(_3\) tubes, some peak shift may exist.

Figure 5 (also see Table 1). The thickness of intermediate and top layers was \( \sim 10 \) and \( \sim 100 \) \( \mu \text{m} \), respectively. By using the finer Al\(_2\)O\(_3\) source (0.2 \( \mu \text{m} \)), both TL-1 (using MgO) and TL-3 [using MgCO\(_3\) (basic)] were composed of fine MgAl\(_2\)O\(_4\) particles. From these SEM images, the TL-1 sample apparently contained less surface defects than the TL-3 sample, probably due to the size similarity of MgO and finer Al\(_2\)O\(_3\) sources, resulting the formation of finer and denser MgAl\(_2\)O\(_4\) particles.

Figure 6 shows XRD patterns of TL-1 and TL-3 top layers on the IL-3 intermediate layers covering porous (curved) Al\(_2\)O\(_3\)-based substrate. For the TL-3 sample (using larger MgCO\(_3\) (basic) as a MgO source), strong and sharp Al\(_2\)O\(_3\) reflections were observed at higher angles (2\( \theta \) = 65--68\(^\circ\)), although Al\(_2\)O\(_3\) reflections were somewhat weaker at middle angles (2\( \theta \) = 33--37\(^\circ\)). This result can probably be explained by the heterogeneous surface structure for the TL-3 on IL-3 sample (Fig. 5); X-ray can penetrate through its defect-like structure at higher angles, and XRD signals from Al\(_2\)O\(_3\) substrate become larger. These phenomena might be related to the second shrinkage of the intermediate layer IL-3 during the sintering step for the top layer. To further elucidate the microstructure development, pore-structure analysis was conducted in a following part.

Figure 7 shows pore-size distributions determined by mercury porosimetry. As can be seen from Fig. 7(a), all three samples contained 15 \( \mu \text{m} \)-sized large pores, corresponding to the porous Al\(_2\)O\(_3\) substrate. From Fig. 7(b), corresponding to the microfiltration range, pore volumes of coated samples clearly increased compared with the pristine porous Al\(_2\)O\(_3\) tube, which is mainly attributable to the intermediate layer (see Fig. 2, IL-3). From Fig. 7(c), corresponding to the nano-and ultrafiltration range, pore volumes much increased compared with the pristine porous Al\(_2\)O\(_3\) tube, in particular for the 10--100 nm range (right half of the figure). These results are in good agreement with the SEM observation (Fig. 5), and suggest that the porous MgAl\(_2\)O\(_4\) membranes on macroporous Al\(_2\)O\(_3\)-based ceramic tubes are promising for the ultrafiltration applications.

Throughout this study, for the intermediate layer, MgCO\(_3\) (basic) powder with larger particle size was favorable as a MgO source of MgAl\(_2\)O\(_4\) because it can clog up the large (15 \( \mu \text{m} \)) Al\(_2\)O\(_3\) pores. Meanwhile, for the top layer, MgO powder with finer particle size was somewhat favored to obtain homogeneous layer suitable for the ultrafiltration.

In this study, toward future cross-flow ultrafiltration applications, reactive synthesis of porous MgAl\(_2\)O\(_4\) membranes on a macroporous Al\(_2\)O\(_3\)-based ceramic tube has been examined. Coarse and fine porous MgAl\(_2\)O\(_4\) membranes were prepared by repeated dip-coating method.
Throughout this study, for the intermediate layer, MgCO₃ (basic) powder with larger particle size was favorable as a MgO source of MgAl₂O₄ because it can clog up the large (15 µm) Al₂O₃ pores. Meanwhile, for the top layer, MgO powder with finer particle size was somewhat favored to obtain a homogeneous layer suitable for the ultrafiltration. With some optimization, the hierarchical porous structure in this study will be applicable for cross-flow ultrafiltration applications.

**Acknowledgement** This work was supported by JSPS KAKENHI Grant Number JP16H04212 for Basic Research: Category B, and Sumitomo Chemical Co. We thank Dr. Kosuke Uoe and his colleagues at Sumitomo Chemical Co. Ltd. for kind measurements of the mercury porosimetry. We appreciate the Open Facility Network Office, Research Facility Center for Science and Technology, University of Tsukuba, for the DLS measurement.

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**Fig. 7.** Pore-size distributions determined by mercury porosimetry: (a) wide range, (b) enlargement for pore diameter d of 100 nm–10 µm (microfiltration range), and (c) enlargement for d of 1–100 nm (nano- and ultrafiltration range).