Porous ceramics based on refractory double oxides are promising for the next-generation diesel particulate filter (DPF) materials. Similarly to aluminum titanate (Al₂TiO₅), MgTi₂O₅ has a pseudobrookite-type crystal structure with low thermal expansion coefficients among oxides. Since MgTi₂O₅ has higher stability of pseudobrookite phase than Al₂TiO₅, it is expected that MgTi₂O₅-based materials are suitable for the next-generation DPF materials. In this study, porous MgTi₂O₅/MgTiO₃ composites have been prepared by in situ processing (viz. reactive sintering) at 1000–1200°C. Porous MgTi₂O₅/MgTiO₃ composites with very narrow pore-size distribution at the diameter of ~1 µm were obtained by the pyrolytic reactive sintering at 1000–1100°C. Internal pore-structure was characterized by mercury intrusion–extraction porosimetry.

Key-words : MgTi₂O₅, Pseudobrookite, Karrooite, MgTiO₃, Geikielite, Pore-size distribution, Diesel particulate filter (DPF), In situ process

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Table 1. Lattice constants and linear thermal expansion coefficients of pseudobrookite-type compounds MgioO₅ by G. Bayer(4)

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice constants (Å)</th>
<th>Linear thermal expansion (×10⁻⁶/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a = 3.8755</td>
<td>βₐ = -2.9 ± 0.2</td>
</tr>
<tr>
<td>Al₂TiO₅</td>
<td>b = 9.4237</td>
<td>βₕ = 10.3 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>c = 9.6291</td>
<td>βₕ = 10.3 ± 0.6</td>
</tr>
<tr>
<td>MgTi₂O₅</td>
<td>a = 3.7442</td>
<td>βₐ = 2.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>b = 9.7363</td>
<td>βₕ = 8.1 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>c = 9.9870</td>
<td>βₕ = 13.2 ± 0.7</td>
</tr>
</tbody>
</table>

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processing and microstructure of uniformly porous MgTi2O5. Uniformly porous MgTi2O5 ceramics with very narrow pore size distribution have been synthesized by one-step pyrolytic reactive sintering (in situ processing), where decomposed CO2 gas from a carbonate source acts as an intrinsic pore forming agent.57-29

In order to control the pore-size distribution, to reduce the resource cost (i.e., using less TiO2 and more MgO), and to add some functions, MgTi2O5–MgTiO3 pseudobinary system seems to be attractive. In this paper, thus, porous MgTi2O5/MgTiO3 composites have been prepared by in situ processing at 1000–1200°C. Porous MgTi2O5/MgTiO3 composites with very narrow pore-size distribution at the diameter of ~1 μm were obtained by the pyrolytic reactive sintering at 1000–1100°C. Internal pore-structure was characterized by using mercury intrusion–extrusion porosimetry.

Similarly to previously reported UPC-3D51(6,25-29) (uniformly porous ceramic/composite with three dimension network structure), magnesium carbonate is used as a starting materials; decomposed CO2 gas, emitted during the one-step pyrolytic reacting sintering, forms very uniform open porous structure. Commercially available MgCO3 (basic) powder (approx. 3MgCO3–Mg(OH)2–3H2O in catalog, 99.9% purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan), TiO2 anatase powder (99.9% purity, Kojundo Chemical Laboratory Co. Ltd.), and LiF powder (99.9%, Wako Pure Chemical Ind., Ltd, Osaka, Japan) were used as the starting materials. X-ray diffraction analysis revealed that the commercial MgCO3 (basic) powder was composed of hydromagnesite phase (Mg5(CO3)4(OH)2·4H2O, ICDD-JCPDS PDF 25-0513). LiF acts as a mineralizer. Note that low-cost natural resources may be replaceable for magnesium carbonate and TiO2. It is an advantage of MgO–TiO2 system.

MgCO3 and TiO2 powders (Mg:Ti = 39:61 in mole fraction, corresponding to the eutectic composition of MgTi2O2–MgTiO3)18) with LiF (0.5 mass % for total starting powders) were wet-ball milled in ethanol for 2 h in a planetary ball-mill (acceleration: 4g). The mixed slurry was dried and then sieved through a 150-mesh screen.

The reaction behavior of the mixed powder was analyzed by high-temperature X-ray diffraction (HT-XRD) in an X-ray diffractometer (Multiflex, CuKα, 40 kV and 40 mA, XRD, RIGAKU, Japan) with a vertical-type goniometer, in the range between room temperature and 1200°C in air. Each XRD pattern was acquired after 5 min holding at each temperature.

To obtain bulk porous MgTi2O5/MgTiO3, the mixed powder was cold isostatically pressed at 200 MPa after mold-pressing. The green compacts with no binder, 15 mm in diameter and ~3 mm in thickness (cylinder), were sintered in air at 1000–1200°C for 2 h to obtain the porous MgTi2O5/MgTiO3. The constituent phases of the bulk materials were analyzed by XRD (Cu Kα, 40 kV and 40 mA). Before the measurement, bulk porous pellets were pulverized for the powder XRD measurement. The microstructure of porous MgTi2O5 was characterized using a scanning electron microscope (SEM, JSM-6500F, JEOL, Tokyo, Japan). The pore-size distribution was determined by mercury intrusion–extrusion porosimetry (PoreMaster-60-GT, Quantachrome/Systems, Kobe, Japan). Washburn equation was used to calculate the pore size, where mercury surface tension is 480 dyne/cm and mercury contact angle is 140°.30

Figure 1 shows HT-XRD patterns for the MgCO3 (basic) and TiO2 mixed powder (Mg:Ti = 39:61 in mole fraction) doped with LiF (0.5 mass % for total starting powders). From room temperature to ~300°C, only hydromagnesite (i.e., basic MgCO3) and TiO2 anatase phases were confirmed. Around 400–500°C, MgCO3 started to decompose into MgO fine particles (see a broad peak 2θ ~ 43°, corresponding to MgO(200)). At ~700°C, intermediate MgTiO3 phase began to form, and it was clearly observed at 700–900°C. At 900°C, un-reacted TiO2 anatase partially converted to TiO2 rutile phase. More than 1000°C, formation of MgTi2O5 phase became prominent. At 1000–1200°C, MgTi2O5 and MgTiO3 phases were observed. This HT-XRD study suggested that porous MgTi2O5/MgTiO3 composites can be obtained for sintering temperatures of 1000–1200°C.

Figure 2 shows XRD patterns for the porous MgTi2O5/MgTiO3 composites sintered at 1000–1200°C. All peaks were indexed as orthorhombic pseudobrookite-type structure.
(MgTi₂O₅ karrooite) and trigonal ilmenite-type structure (MgTiO₃, geikite). In situ processing in this study was effective to obtain porous MgTi₂O₅/MgTiO₃ composites.

**Figure 3** demonstrates SEM micrographs of the porous MgTi₂O₅/MgTiO₃ composites. Corresponding to the anisotropic crystal structure, elongated MgTi₂O₅ grains were formed during the *in situ* processing. At 1000°C, equiaxed fine MgTiO₃ particles formed colony-like structure, and they dispersed in the elongated MgTi₂O₅ grains matrix (Fig. 3(a)). At 1100°C, MgTiO₃ grew with the size of ~1 µm, and they dispersed more homogeneously in the MgTiO₃ matrix (Fig. 3(b)). When the sintering temperature was 1200°C, the microstructure became relatively dense (Fig. 3(c)). Probably due to the high sinterability of MgTiO₃ phase, structural change with temperature was more prominent for the porous MgTi₂O₅/MgTiO₃ composites, compared with monolithic porous MgTiO₃.⁵⁵

**Figure 4** shows pore-size distributions determined by mercury intrusion–extrusion porosimetry for the porous MgTi₂O₅/MgTiO₃ composites: (a) intrusion showing pore-channel size, and (b) extrusion showing internal pore-size.⁵⁶ In spite of the remarkable porosity change, the open pore-size for these composites remain ~1 µm (or more precisely 0.7–0.9 µm, Fig. 4(a)). The pore-size distributions calculated from the extrusion curves (Fig. 4(b)) nominally correspond to the internal pore-size. From these curves, we can estimate the pore-structure of the composites sintered at 1000–1100°C: pore-channel of ~1 µm and internal pore-size of ~4 µm. Relatively large internal pore-size can be explained by the irregular (or L-type) shape of MgTi₂O₅ matrix grains. At a higher sintering temperature (1200°C), the microstructure became denser, the grains became less anisotropic (see Fig. 3(c)), and the difference between pore-channel size and internal-pore size became smaller.

**Table 2** summarizes the pore structure of the porous MgTi₂O₅/MgTiO₃ composites. From these data, the porosity can be controlled (~10–50%) by changing the sintering temperature, with keeping the pore size close to 1 µm. Although the pore-size of 1.0 µm is rather small for ordinary DPF application (~10 µm), it can be further controlled e.g., by the addition of sacrificial pore-forming agent (like porous cordierite) or by the use of coarse grains (like porous SiC). Besides, the pore-size of 1.0 µm might be suitable for much severer filtration purposes (e.g., PM2.5 or smaller).

In this report, *in situ* processing and microstructure of porous MgTi₂O₅/MgTiO₃ composites were presented. Porous MgTi₂O₅/MgTiO₃ with narrow pore-size distribution at ~1 µm were successfully prepared by one-step reactive sintering. The porosity was controllable between ~10 and ~50% only by changing the sintering temperature with almost keeping the pore size.
Table 2. Pore structure of the porous MgTiO$_3$/MgTi$_2$O$_5$ composites prepared by the reactive sintering method

<table>
<thead>
<tr>
<th>Sintering temperature ($^\circ$C)</th>
<th>$V_p$ ($cm^3/g$)$^a$</th>
<th>$S_p$ ($m^2/g$)$^b$</th>
<th>$D_{hole}$ ($\mu m$)$^c$</th>
<th>$D_{average}$ ($\mu m$)$^d$</th>
<th>$P$ (%)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.329</td>
<td>1.76</td>
<td>0.82</td>
<td>0.75</td>
<td>53.3</td>
</tr>
<tr>
<td>1100</td>
<td>0.227</td>
<td>1.28</td>
<td>0.90</td>
<td>0.71</td>
<td>43.6</td>
</tr>
<tr>
<td>1200</td>
<td>0.078</td>
<td>0.45</td>
<td>0.73</td>
<td>0.69</td>
<td>11.7</td>
</tr>
</tbody>
</table>

a: Total pore volume.
b: Specific surface area, determined by mercury porosimetry.
c: Mode pore diameter.
d: Average pore diameter, calculated from $D_{ave} = 4V_p/S_p$.
e: Porosity, $P = 100V_p$/sample bulk volume/mass.

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