Fabrication of Porous Alumina Ceramics by New Eco-Friendly Process

Takaaki NAGAOKA, Takahisa TSUGOSHI, Yuji HOTTA, Kimiyasu SATO and Koji WATARI
National Institute of Advanced Industrial Science and Technology (AIST),
2266-98, Anagahora, Shinoshidami, Moriymana-ku, Nagoya-shi, Aichi 463-8560

We have developed a new eco-friendly fabrication process for porous ceramics using hydraulic alumina (HA) and water. In the present study, we fabricated porous alumina ceramics using this new process. A boehmite gel 3-D network was formed by the hydration of HA in HA slurry. The HA slurry was hardened by the formation of this 3-D network. Even without the addition of an organic binder, green bodies containing the 3-D network demonstrated high compressive strength. Furthermore, the water acted as a fugitive material in the green bodies. Consequently, the open porosity of sintered alumina ceramics could be controlled over a wide range of 56.6–69.1% by addition of water (ratio of water to HA powder: 1.0 to 2.0 by weight) without the use of organic fugitive materials. The results of evolved gas analysis–mass spectrometry measurements showed that the emissions from the hardened green body mostly consisted of water. Consequently, the new fabrication process for porous alumina ceramics was confirmed to be eco-friendly.

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1. Introduction

Organic substances are important additives that are widely used in ceramic fabrication processes. For example, polyvinyl alcohol, latex, methylcellulose and starch are important additives that serve as organic binders in ceramic fabrication, because such ceramic powders do not harden when mixed with water.1–5 The role of a binder is to provide green strength so that a green body can be formed and will retain its desired shape before heating. Acrylic beads, carbon powder, and starch are widely used as fugitive materials for creating pores in porous ceramics.5,6 The pore size and porosity of porous ceramics can be adjusted by adjusting the sizes of the fugitive materials and the amounts added.

However, these organic binders and fugitive materials must be completely thermally decomposed so that they do not remain in the sintered body as carbon or ash. Moreover, large volumes of gases such as carbon dioxide and hydrocarbon species are emitted from the green body during heating. CO₂ is believed to be one of the greenhouse gases responsible for global warming, while emitted hydrocarbons can be malodorous as well as harmful. It is necessary to pyrolytically decompose the hydrocarbon species further to defuse them, which requires thermal energy, thus further increasing emissions of CO₂. Therefore, total volume of emitted CO₂ gas in the ceramic processing rises with increasing amounts of emitted hydrocarbon species. It is therefore important to develop an eco-friendly ceramic fabrication process employing inorganic substances that can reduce the amounts of organic substances used.

Hydraulic inorganic binders are promising materials for the consolidation of starting powders in green bodies with water by hydration and conversion into ceramics during heating.7,8 During this process, the emission of harmful gases is unlikely. Hydraulic alumina (HA) is an important mineral phase of hydraulic inorganic binders, and has been studied for use as a hydraulic inorganic binder in high-alumina castable refractory.9 The main phase of HA is α-Al₂O₃, an intermediate alumina. The hydration of α-Al₂O₃ forms bayerite and boehmite gel as follows9:

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\alpha-\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + \text{Al}_2\text{O}_3 \cdot 1-2\text{H}_2\text{O}. \\
(\text{Bayerite}) \quad (\text{Boehmite gel})
\]

This hydration process is not affected by a CO₂ atmosphere, with other hydraulic inorganic binders such as calcium monoaaluminate (CaAl₂O₄), calcium dialuminate (Ca₂Al₃O₇), and barium monoaaluminate (Ba₃Al₂O₆). Furthermore, hydrated HA is converted during heating into α-Al₂O₃, one of the main components of oxide ceramics. HA, therefore, has potential for use as a hydraulic inorganic binder in alumina-based ceramics processing. Another unique advantage of using HA is microstructure control of the green body by hydration of HA: it appears possible to control the mechanical properties of the green body, sinterability and microstructure of the sintered body by controlling the composition and morphology of the HA hydrates.

Added water is predicted to create numerous pores through the dewatering process during heating, acting as a fugitive material that does not produce any harmful gases, suggesting that a sintered body with high porosity is obtained if a large amount of water can be held in the green body. As mentioned above, the HA and water are expected to act as eco-friendly agents for consolidating the starting powders and creating pores.

This paper reports on the new eco-friendly fabrication process for porous alumina ceramics with a wide range of porosities using HA and water. The major gas species evolved during heating were also investigated by means of gas analysis.
2. Experimental procedure

2.1 Sample preparation

Hydraulic alumina (HA, BK-105, 99.7% purity, Sumitomo Chemical Co., Ltd.) with a mean particle size of 5 μm was used as a starting powder. A planetary ball mill with a pair of alumina pots containing alumina balls (diameter: 5 mm) was used to reduce the agglomerate and particle size of the HA powder. The HA powder was ground with methanol in the mill pot at 300 rpm for 1 h. The ground mixtures were dried at 60°C for 30 min in a vacuum, then screened through a #150-mesh sieve.

The HA powder was mixed with distilled water using a mini shaker at 2500 rpm for 1 min to make HA slurry. Degassing of the HA slurry was performed for 3 min in a vacuum. The HA slurry was cast into molds (inside diameter: 25 mm) for setting test and compressive strength measurements, after which the molds were kept tightly covered with laboratory film. The ratio of water to HA by weight (water ratio, hereinafter referred to as “WR”) ranged from 0.6 to 2.4. The HA slurry in the molds was cured at 25°C for 24 h in a container kept at over 90% relative humidity. The samples were taken out of the molds after 24 h. The hardened slurries (green bodies) were slowly dried at room temperature, and then sintered at 1400°C for 2 h in air. To protect the green bodies from cracking during dehydration, a slow heating rate (10°C/h) was applied at low temperatures.

2.2 Characterization of the HA slurry and sintered samples

The setting time of the HA slurry was measured at 25°C in 80% relative humidity using a Vicat needle apparatus. The initial set was determined as the moment when a needle under a load of 300 g stopped penetrating the 40 mm-high sample paste 1 mm from the bottom. The final set was determined as the moment at which the needle penetrated no more than 1 mm into the sample.

Green densities were calculated from the samples using simple volume and mass measurements. Compressive strength measurements of the green bodies were conducted using a crosshead speed of 0.5 mm/min at room temperature. X-ray diffraction (XRD) analysis was performed on the hydrated HA slurry to study the crystalline phase evolution as a function of curing time. The measurements were performed using an X-ray diffractometer (RAD-11 Powder diffractometer, Rigaku, Tokyo) with Cu Kα radiation (40 kV, 400 mA). The fracture surfaces of the samples were observed using a scanning electron microscope (SEM) (Model JSM-6340F, JEOL Japan). Samples for XRD analysis and SEM observation were immersed in methanol and acetone for 10 min each and dried to stop hydration. The bulk density and open porosity of the sintered samples were measured using Archimedes’ method. The pore size distributions of the sintered samples were measured using the mercury intrusion method. Mercury porosimetry (Model 9420, Shimadzu Corp.) provided pore-size distribution data for the sintered samples. The porosity values obtained by dimension-mass measurements and mercury porosimetry were in good agreement (within 5%).

The major gas species evolved by pyrolysis of the hydrated HA samples prepared by this new process and a conventional α-Al2O3 sample with an organic binder (commercially available polyvinyl alcohol) and fugitive material (acrylic beads) were investigated by means of evolved gas analysis-mass spectrometry (EGA-MS).10

3. Results and discussion

3.1 Characterization of the HA slurry

Although the setting test using the Vicat needle apparatus is not a universal quantitative method, it serves as a rough standard that indicates the progress of hardening of the slurry. It is thought that the work of casting can be performed until around the initial setting time, and that hardened slurry has sufficient strength after the final setting time. In this study, HA slurries with a wide range of water ratios (WR = 0.6–2.4) were prepared by mixing HA powder with distilled water. Among these slurries, those with low water ratios (WR = 0.6–0.8) had low flowability and could not be cast in the mold. On the other hand, bleeding was observed in the mold in the case of samples with high water ratios (WR > 2.2). HA slurries with water ratios of 1.0–2.0 were therefore selected for setting in molds after curing at 25°C for 24 h. Figure 1 shows the results of the setting test of the HA slurries at different water ratios from 1.0 to 2.0. Both the initial and final setting times of the HA slurries with low water ratios were short. For example, the initial and final setting times of the sample with WR = 1 were 3.5 h and 5 h, respectively. In contrast, the samples with higher water ratios had longer initial and final setting times. For example, the HA slurry with WR = 1.6 began to solidify after 4.5 h, and had completely hardened after 11 h. The samples with much higher water ratios among those selected (WR = 1.8 and 2.0) had not hardened completely even after 24 h, although they retained their shape when taken out of the mold. Thus, the degree of setting of the HA slurry was affected by the amount of water they contained. On the other hand, the setting time was also controlled by adjusting the curing temperature of the samples, without the addition of setting accelerators. For example, when the sample with WR = 2 was cured at 40°C, the initial setting time changed from 6 h to 1.5 h with the change in the curing temperature, as shown in Fig. 1. It was therefore confirmed that, irrespective of the water ratio, it is possible to secure an appropriate time for forming by adjusting the hydration conditions such as curing temperature.

Figure 2 shows the green density and compressive strength of the cured samples. The green density and average compressive strength decreased from 1.53 to 1.28 g/cm³ and from 7 to 0.2 MPa, respectively, as the water ratio increased (WR = 1.0–2.0). Although the compressive strength of the green bodies with high levels of water (WR = 1.6–2.0) was not high (< 0.6 MPa), these green bodies retained their original shapes.

Figure 3(a) shows the XRD patterns of the HA slurry with WR = 1 cured at 25°C for various times. Two broad peaks,
believed to be $\gamma$-Al$_2$O$_3$ and $\rho$-Al$_2$O$_3$, were observed in the sample before hydration. The XRD patterns of the sample cured for 1 and 2 h were almost the same as those of the HA powder before hydration. A small broad peak, believed to be that for boehmite gel, was observed in the sample cured for 4 h. As the curing time increased, the peak intensity of the boehmite gel increased. The formation of boehmite gel in the HA slurry corresponds to the initial setting time of the HA slurry, as shown in Fig. 1. A small peak representing bayerite was observed in the cured samples after hydration for 24 h. Figure 3 (b) shows XRD patterns of the HA slurry with WR = 2 cured at 25°C for various times. In the early stage of curing, the XRD patterns of the sample are almost the same as those of the sample with WR = 1. However, peaks of bayerite were observed in the sample cured for 12 h. The formation of boehmite gel and bayerite depended on the hydration conditions. For example, boehmite gel was observed in the sample cured at 40°C for 2 h, as shown in Fig. 3(c). This result, together with those of the setting test, indicates that the boehmite gel contributed to the hardening of the HA slurry.

Figure 4 shows SEM photographs of the fracture surfaces of the green bodies with WR = 1 and WR = 2 cured at 25°C for 8 h and 24 h. A three-dimensional (3-D) network is observed in the sample cured for 8 h, as shown in Fig. 4(a). The results of the XRD analysis show this 3-D network to be boehmite gel. With increasing curing time, the boehmite 3-D network in the green bodies became more densely packed, as shown in Fig. 4(b). These results, together with those of the setting test and compressive strength test, indicate that the boehmite gel 3-D network hardened the HA slurry. On the other hand, the microstructure of the green body with WR = 2 was a porous 3-D network structure, as shown in Fig. 4(c) and (d). Then the average compressive strength decreased as the water ratio increased, as shown in Fig. 2. We believe that the formation of the boehmite 3-D network facilitated hardening of the HA slurry and the holding of a large amount of water.

3.2 Characterization of the sintered samples

XRD analysis revealed that $\alpha$-Al$_2$O$_3$ was the single-crystalline phase in the sintered samples (1400°C for 2 h), and no other aluminum hydroxide phase was detected. Figure 5 shows the bulk density and open porosity of the samples sintered at 1400°C for 2 h. The bulk densities of the sintered samples decreased slightly from 1.69 g/cm$^3$ to 1.19 g/cm$^3$ with increasing water ratio. The results of measurements by Archimedes’ method show that the pores in the sintered samples were almost all open pores. The open porosity increased from 56.6% to 69.1% linearly with increasing water ratio (WR = 1.0-2.0). Although the addition of a large amount of water was expected to create a large pore volume, the open porosity increased only by 56.6 vol% to 69.1 vol% due to shrinkage of the samples during heating. Nevertheless, the water acted as a fugitive material in the green bodies. The addition of water
also proved useful in controlling the wide range of open porosities seen in porous alumina ceramics.

Figures 6(a) and (b) show SEM photographs of the samples with WR = 1 and WR = 2 sintered at 1400°C for 2 h, respectively. A well-developed 3-D network structure was observed in each sintered sample. α-Al₂O₃ grains were connected to each other via thick necks. Figure 6(c) shows the pore size distributions of these porous alumina ceramics sintered at 1400°C. Median pore diameter of these samples with WR = 1 and WR = 2 were 0.24 µm and 0.48 µm, respectively. Porous alumina ceramics which sintered with WR = 1 had narrow pore size distribution. This result can be attributable to the green body having a densely packed 3-D network structure, as shown in Fig. 4(b). In the case of the green body with WR = 2, although the green body did not have a densely packed 3-D network structure, porous alumina ceramics which sintered with WR = 2 had a narrow pore size distribution. These results show that the added water was dispersed homogeneously in the HA powder and acted as a fugitive material of uniform size. In addition, since this porous alumina has a narrow pore size distribution, it has potential for use as a filtration material. Thus, porous alumina ceramics with a wide range of open porosity and a narrow pore size distribution can be produced by this new process using HA powder and water.

3.3 Analysis of gases evolved from the HA slurry

Figure 7(a) shows the EGA-MS spectrum obtained from the α-Al₂O₃ green body with 1.5 mass% polyvinyl alcohol as the organic binder and 16 mass% acrylic beads as the fugitive material at 356°C. The peak intensities of the larger fragmentated ions are high. These fragmentated ions, such as 15, 41, 69, 85 and 100 amu are thought to be hydrocarbon species, e.g., CH₃, C₂H₅, C₃H₇O, C₄H₉O₂ and C₅H₁₀O₂, respectively, originating as pyrolyzed species of the polyvinyl alcohol and acrylic beads. These emitted hydrocarbon species can be malodorous as well as harmful. On the other hand, in the case of the hardened HA green body prepared using this new process (WR = 1), although the peak intensity of 18 amu, identified as H₂O due to the dehydration of the hydrated HA, was high, larger fragment ions, considered to be hydrocarbons, were rare. Since the emitted hydrocarbons can be harmful, it is necessary to pyrolytically decompose these gases further to defuse them, which requires thermal energy, thus further increasing emissions of CO₂. In this new process, the peak intensities of hydrocarbon were low, with the peak intensity of CO₂ (2.78 × 10⁻¹⁰ A) being 69.3% of that (4.01 × 10⁻¹⁰ A) emitted when using the conventional method. Therefore, our approach using HA as a hydraulic inorganic binder and water as a fugitive material in the fabrication of porous alumina ceramics is confirmed to be an environmentally friendly technology.

4. Conclusion

Porous alumina ceramics were prepared using a new eco-friendly fabrication process employing hydraulic alumina (HA) and water. The HA slurry was hardened by the formation of a boehmite gel 3-D network. Even without the addition of an organic binder, hardened HA slurry (green bodies) had high compressive strength. The green bodies contained a large amount of water, which acted as a fugitive material. Consequently, the open porosity of the sintered alumina ceramics could be controlled by the addition of water without the use of organic fugitive materials. The results of evolved gas analysis – mass spectrometry measurements confirm that our approach, using HA as a hydraulic inorganic binder and water as a fugitive material in the fabrication of porous alumina ceramics, is
an environmentally friendly technology.

References